ANALYSIS OF IODINE AND CESIUM CHEMICAL FORMS EVOLVED FROM GRAPHITE SURFACES AT TEMPERATURES FROM 425 TO 1400°C
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OAK RIDGE NATIONAL LABORATORY

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ABSTRACT

Information has been obtained to aid in the identification of the chemical forms of fission product cesium and iodine which are evolved from graphite surfaces heated to temperatures up to 1400°C. Iodine and cesium were initially added to the graphite as adsorbed CsI; subsequently, more cesium was added as Cs₂O to allow variations of the initial cesium/iodine mol ratio from 1 to 10. The identifications were determined, in part, by inference from the locations of cesium and iodine deposits on a graphite thermal gradient tube, the measured mol ratios of the deposits, and the results of electron surface chemical analyses. Cesium iodide was the most abundant of the chemical forms found; however, significant quantities of cesium-rich oxygen-bearing deposits (probably cesium oxide) and of iodine-rich deposits (mostly molecular I₂) were also present. The iodine species, CsI and I₂, were found to move downstream with time and/or gas flow from the hotter to the colder regions of the system.

1. INTRODUCTION

The purpose of this investigation was to obtain information for use in identifying the chemical forms of cesium and iodine released from failed or defective high-temperature gas-reactor (HTGR) fuels to the graphite moderator and ultimately to the circulating coolant. Knowledge regarding the chemical forms of cesium and iodine, as well as other fission products released from the fuel material, is essential for the study of their subsequent rate of movement in the various environments in the pathway leading to the outside environment. The chemical form determines
the volatility (i.e., the location where it may condense), the rate of adsorption, the tendency for chemical combination with materials of construction, and the rate of diffusion in graphite. Although highly idealized thermodynamic estimates invariably show CsI to be the most stable iodine species in simple chemical environments with low oxygen levels,\(^1\) fission product transport test data taken in various HTGR environments usually indicate iodine to be in either an \(I_2\) or atomic iodine form. Release rate observations from both broken and intact particles indicate that the movement of iodine is similar to that of xenon (e.g., refs. 2 and 3). Further, in-pile loop data\(^4\) and reactor surveillance tests are usually analyzed with fair success, assuming that the predominant form of iodine in the primary circuit is gaseous \(I_2\) or deposits resulting from an \(I_2\) partial pressure.

The experiments described in this report were undertaken primarily to evaluate species identification procedures based on the use of a thermal gradient tube for HTGR conditions since future program directions may require such procedures. In addition, the performance of these exploratory and developmental tests using a cesium-iodine system under controlled oxygen potential conditions has provided some insight into the movement of iodine in graphite placed there initially as CsI.

2. EXPERIMENTAL METHOD

2.1 GENERAL APPROACH

The experiments described here were designed to evaluate the thermal gradient tube procedure for identifying the chemical forms of cesium and iodine that are vaporized from a graphite surface into helium gas containing low concentrations of carbon monoxide (CO) gas. For this purpose, H-451 graphite source pellets containing iodine as cesium iodide (CsI) and additional cesium, in most tests, as cesium carbonate (Cs\(_2\)CO\(_3\)) were heated at temperatures up to 1400°C. Vaporized material from the source pellets was picked up in the flow of cover gas and redeposited downstream on cooler surfaces of the graphite thermal gradient tube. Determination
of the chemical forms of cesium and iodine was made by: (1) inference from the mol ratio and the location of the condensed material in a thermal gradient tube held at temperatures ranging from 1000 to \( <100°C \), and (2) analyses of the surface deposits using electron surface chemical analysis (ESCA) techniques.

The chemical potential of oxygen is a variable reported to affect vapor pressures, diffusion rates, and chemical forms of fission products in other systems \(^5,^6\) and therefore is likely to be a significant factor in determining which chemical forms of cesium and iodine will be present in our system. Carbon monoxide was used in the cover gas in our tests to fix the oxygen potential so that it would not vary in an uncontrolled way. Carbon monoxide reacts in the system to form carbon and oxygen as follows:

\[
2\text{CO} \rightarrow 2\text{C} + \text{O}_2.
\]  

The oxygen chemical potentials listed in Table 1 were calculated using the following expression (based on data extracted from JANAF Thermochemical Tables \(^7\)):

\[
\mu_{\text{O}_2} = -55,202 - 40.84T + 2RT \ln \frac{P_{\text{CO}}}{760},
\]

where \( \mu_{\text{O}_2} \), \( T \), and \( P_{\text{CO}} \), respectively, denote the oxygen chemical potential, in cal/mol; absolute temperature; and the partial pressure of CO in the cover gas, in atm.

The present experimental conditions, of course, represent a large simplification of the actual chemical environment experienced by fission products in the reactor core. In our study, the graphite source pellets and deposition tube contained no fuel material, silicon carbide, or other fission products which would be an integral part of a realistic environment. In addition, the intense radiation field was absent. Therefore, it is important to note that fission product iodine and cesium in
Table 1. Summary of tests and conditions

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Duration (h)</th>
<th>Temperature (°C)</th>
<th>Source pellet or material</th>
<th>Cesium (µmol)</th>
<th>Iodine (µmol)</th>
<th>CO in gas (vol %)</th>
<th>Calculated oxygen chemical potential (kcal/mol)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120.00</td>
<td>1000</td>
<td></td>
<td>1.34</td>
<td>1.34</td>
<td>1.00</td>
<td>-130</td>
<td>Scoping test</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>1000</td>
<td></td>
<td>57.5</td>
<td>5.70</td>
<td>1.00</td>
<td>-130</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>24.00</td>
<td>1000</td>
<td></td>
<td>66.0</td>
<td>6.50</td>
<td>1.00</td>
<td>-130</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>1000</td>
<td></td>
<td>45.8</td>
<td>4.49</td>
<td>0.10</td>
<td>-142</td>
<td>Effect of CO on deposits</td>
</tr>
<tr>
<td>5</td>
<td>0.25</td>
<td>1000</td>
<td></td>
<td>45.6</td>
<td>4.80</td>
<td>0.01</td>
<td>-159</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.17</td>
<td>1400</td>
<td></td>
<td>32.8</td>
<td>3.58</td>
<td>0.10</td>
<td>-170</td>
<td>High-temperature test for vapor density determination</td>
</tr>
<tr>
<td>7</td>
<td>0.12</td>
<td>425</td>
<td></td>
<td>0.0</td>
<td>0.04</td>
<td>1.00</td>
<td>-96</td>
<td>Effect of time of I₂ adsorption</td>
</tr>
<tr>
<td>8</td>
<td>0.50</td>
<td>425</td>
<td></td>
<td>0.0</td>
<td>0.04</td>
<td>1.00</td>
<td>-96</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.75</td>
<td>425</td>
<td></td>
<td>0.0</td>
<td>0.04</td>
<td>1.00</td>
<td>-96</td>
<td></td>
</tr>
</tbody>
</table>
graphite, originating via failed microspheres, tramp fuel, or diffusion from intact particles, would be subject to conditions other than those taken into account in these tests.

2.2 PREPARATION OF SOURCE PELLETS

The H-451 graphite used in the preparation of the source pellets had a bulk density of 1.75 g/cm³, a BET surface area of 0.63 m²/g, and an open porosity of 17.2 vol %. Each pellet was 1.25 cm long and 0.8 cm in diameter. For Test 1 (Table 1), which was a scoping investigation, CsI was adsorbed on the surface of the pellet. The procedure involved soaking the pellet in 50 vol % ethanol-50 vol % water solution containing 0.3 M CsI for 24 h at ~23°C, drying the pellet in air for 24 h at 130°C, and then baking it under helium gas for ~1 h at 600°C. (A similar procedure was previously developed and used to adsorb uranium on H-451 graphite.8) The CsI was widely and evenly adsorbed on the surface of the graphite, as can be seen in the x-ray map in Fig. 1.

For Tests 2 through 6 (Table 1), a CsI-Cs₂CO₃ mixture was used as the source material in the pellets in order to obtain an approximate cesium/iodine mol ratio of 10/1. The source materials were packed into a 0.50-cm-diam, 0.55-cm-deep hole drilled into one end of the graphite source pellet; then the hole was capped with a graphite plug. Source pellets were not used in Tests 7, 8, and 9 (Table 1), where the source material, molecular iodine, was introduced as a gas without cesium in the helium flow. More details about these tests are reported in Sect. 3. Tests 1-5 and Test 6 were conducted with the source pellets heated at 1000 and 1400°C, respectively. In the remaining tests (7, 8, and 9), the maximum temperature of the thermal gradient tube was 425°C.

2.3 DEPOSITION TESTS

A diagram of the equipment used in the deposition tests is shown in Fig. 2. The source pellets in Tests 1-5 (Table 1) were placed in the center of the quartz tube in the horizontal tube furnace, where they were heated at 1000°C for periods ranging from 7.5 min to 5 d. A cover gas
Fig. 1. X-ray map of cesium iodide adsorbed on H-451 graphite. Magnification, 4000X.
Fig. 2. Quartz tubing used for vaporization of CsI adsorbed on graphite pellet surfaces.
composed of helium plus 0.01, 0.10, or 1.00 vol % CO was passed through the system at the rate of 25 to 50 cm$^3$/min during the heating period. A fraction of the CsI was vaporized from the pellet in each individual test (Tests 1 through 6) and then redeposited at a lower temperature on a thermal gradient tube downstream from the pellet.

The thermal gradient tube was composed of either five or six graphite tube segments. Each segment was 1.9 cm long with a 0.93-cm outside diameter and 0.63-cm inside diameter and weighed ~1.08 g. Temperature profiles for the thermal gradient were prepared by plotting the measured temperatures at five points on the gradient (designated as TC-1, TC-2, TC-3, TC-4, and TC-5 in Fig. 2) vs the distance of the designated points from the center of the furnace. The amounts of CsI in, or on, source pellets at the beginning and end of each test and the amounts deposited on the thermal gradient segments were determined by neutron activation analysis (NAA). In some tests, the amounts of CsI-Cs$_2$CO$_3$ initially loaded into the center of the pellets were determined by weight. In addition to the NAA, selected graphite thermal gradient segments were submitted for electron surface chemical analysis (ESCA) to determine the chemical form of the deposited cesium and iodine. Quantities of cesium and iodine found adsorbed on the quartz tube housing the graphite thermal gradient tube were added, for data analysis purposes, to the quantities found on corresponding graphite segments. The quantities found on the quartz were relatively small unless specifically noted otherwise. Test 6, in which the source pellet was heated to 1400°C, was conducted similarly to the first five tests (Table 1), except that an induction-heated furnace was used instead of a resistance-heated type. Data from Test 6 were used only to determine the average vapor-phase iodine density at 1400°C.

Tests 7, 8, and 9 (Table 1) were conducted using a gaseous I$_2$ source without cesium. In these tests, the I$_2$ was placed in a small porcelain boat in the furnace tube ~8 in. outside the furnace heating zone. After the furnace had been heated to 425°C with the thermal gradient tube (425 to 70°C) in place, the boat with the I$_2$ was moved by means of a wire hook and a magnet to the edge of the heating zone.
The iodine was quickly vaporized, although the gas flow (He + 1% CO) was continued for up to 45 min. These tests (7 through 9) were conducted in order to determine the extent to which iodine would adsorb on the thermal gradient tube in the absence of cesium.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 DEPOSITS FROM A SOURCE WITH A CESIUM/IODINE MOL RATIO OF 1.0 (TEST 1)

The first and most simple confirmation that cesium and iodine were, in part, deposited on the graphite thermal gradient tubes as species other than CsI can be found in the test results shown in Table 2. This test was a scoping investigation in which the pellet initially contained 346 µg (1.33 µmol) of surface-adsorbed CsI. The pellet was heated at 1000°C for 120 h in a helium-1.0 vol % CO gas stream. At the end of the heating period, analyses (Table 2) indicated that: the thermal gradient tube could be roughly divided into (1) a cesium-rich zone between 460 and 890°C, (2) an apparent cesium iodide (mol ratio = 1.0) intermediate-temperature zone at ~250°C, and (3) an iodine-rich zone at temperatures <100°C. The decrease in the cesium/iodine mol ratio with temperature decrease can be seen in Fig. 3. Approximately 89% of the deposited iodine was in the intermediate-temperature zone where the cesium/iodine mol ratio was ~1.0. Another 10% was deposited in the low-temperature, iodine-rich zone. The source pellet at the end of the test retained 1.8 µg of cesium and 3.8 µg of iodine. Subsequent tests showed residual quantities (1 to 4 µg) of cesium and iodine since these elements were difficult to vaporize from the graphite pellets under the conditions used here. This effect is thought to result from reactions with impurities in the graphite. Subsequent tests also showed that major fractions of the cesium and iodine could be vaporized from source pellets in less than 1 h at 1000°C. It is likely, therefore, that most of the cesium and iodine in Test 1 (120 h) were vaporized from the pellet in the first few hours of the test and that little or no vaporization occurred during the remainder of the test period.
Table 2. Deposits on graphite thermal gradient tube from source pellet with 1.33 \( \mu \)mol of adsorbed cesium iodide at 1000°C with 1% CO in cover gas (Test 1)

<table>
<thead>
<tr>
<th>Deposit temperature (^{a}) (^{0})C</th>
<th>Amount of element (nmol/g)</th>
<th>Cs/I mol ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cesium</td>
<td>Iodine</td>
</tr>
<tr>
<td>890</td>
<td>34.96</td>
<td>0.47</td>
</tr>
<tr>
<td>738</td>
<td>45.56</td>
<td>0.79</td>
</tr>
<tr>
<td>607</td>
<td>77.97</td>
<td>2.68</td>
</tr>
<tr>
<td>460</td>
<td>58.50</td>
<td>3.07</td>
</tr>
<tr>
<td>250</td>
<td>1049.62</td>
<td>1067.70</td>
</tr>
<tr>
<td>&lt;100</td>
<td>10.22</td>
<td>115.75</td>
</tr>
</tbody>
</table>

\(^{a}\)Temperature at midpoint of thermal gradient tube segment.

3.2 DEPOSITS FROM SOURCES WITH CESIUM/IODINE MOL RATIOS OF \(\sim\)10.0

3.2.1 Effect of Vaporization Time on Deposits in Tests 2 and 3

Data from two similar tests with different vaporization periods, 0.25 and 24 h, are shown in Tables 3 and 4, respectively. A cesium/iodine mol ratio of \(\sim\)10:1 (approximately the fission yield ratio) was used for the source pellet. The source temperature was set at 1000°C, and a 50-cm\(^3\)/min flow of helium-1 vol % CO gas was used. A chromatographic effect for iodine can be seen by comparing the plots of iodine concentration vs temperature for the 0.25- and 24-h tests in Fig. 4. In the 0.25-h test, relatively large amounts of iodine were adsorbed on the graphite thermal gradient tube at temperatures from 850 to 500°C, with lesser amounts being adsorbed at temperatures from 500 to 200°C. The major amount of iodine adsorbed in the 24-h test was shifted from the high-temperature zone to areas with temperatures \(<400°C\).

A similar mobility for cesium is shown in Fig. 5 except that, as noted, the cesium deposited in the high-temperature (>500°C) zone appeared to be relatively stable. In the 0.25-h test, relatively large amounts of cesium were adsorbed at temperatures >500°C; lesser amounts were found
Fig. 3. Cesium/iodine mol ratio in deposits on thermal gradient tube as a function of temperature. Initial cesium/iodine mol ratio = 1; carrier gas = helium-1% CO.
Table 3. Cesium and iodine deposition from source\textsuperscript{a, b} with cesium/iodine mol ratio of 10
(Test 2; test period = 0.25 h)

<table>
<thead>
<tr>
<th>Deposit temperature\textsuperscript{c} (°C)</th>
<th>Element inventory at end of test (nmol/g)</th>
<th>Cs/I mol ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 (source pellet)</td>
<td>18,370.0</td>
<td>70.7</td>
</tr>
<tr>
<td>1000</td>
<td>738.3</td>
<td>2.6</td>
</tr>
<tr>
<td>850</td>
<td>1,552.6</td>
<td>1.0</td>
</tr>
<tr>
<td>620</td>
<td>1,025.6</td>
<td>1.0</td>
</tr>
<tr>
<td>500</td>
<td>561.6</td>
<td>0.2</td>
</tr>
<tr>
<td>430</td>
<td>12.0</td>
<td>0.3</td>
</tr>
<tr>
<td>300</td>
<td>1.5</td>
<td>0.1</td>
</tr>
<tr>
<td>200</td>
<td>1.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Initial pellet contained 7647 \( \mu \)g of cesium and 730 \( \mu \)g of iodine sealed into a center hole.

\textsuperscript{b}Cover gas was helium-1\% CO.

\textsuperscript{c}Temperature at midpoint of graphite tube segments in the thermal gradient.

\textsuperscript{d}Charcoal trap, 1 g.

Table 4. Cesium and iodine deposition from source\textsuperscript{a, b} with cesium/iodine mol ratio of 10
(Test 3; test period = 24 h)

<table>
<thead>
<tr>
<th>Deposit temperature\textsuperscript{c} (°C)</th>
<th>Element inventory at end of test (nmol/g)</th>
<th>Cs/I mol ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 (source pellet)</td>
<td>65,600.0</td>
<td>87.5</td>
</tr>
<tr>
<td>950</td>
<td>2,903.8</td>
<td>1,814.4</td>
</tr>
<tr>
<td>819</td>
<td>1,392.5</td>
<td>588.2</td>
</tr>
<tr>
<td>633</td>
<td>416.5</td>
<td>88.6</td>
</tr>
<tr>
<td>526</td>
<td>278.2</td>
<td>27.3</td>
</tr>
<tr>
<td>384</td>
<td>4,075.2</td>
<td>1.1</td>
</tr>
<tr>
<td>&lt;100</td>
<td>533.8</td>
<td>0.6</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Initial pellet contained 8782 \( \mu \)g of cesium and 830 \( \mu \)g of iodine sealed into a center hole. Part of the cesium was present as \( \text{Cs}_2\text{CO}_3 \).

\textsuperscript{b}Cover gas was helium-1\% CO.

\textsuperscript{c}Temperature at midpoint of graphite tube segments in the thermal gradient.

\textsuperscript{d}Charcoal trap, 1 g.
Fig. 4. Adsorption of iodine from CsI-Cs₂CO₃ source (cesium/iodine mol ratio = 10) on graphite thermal gradient tubes. Cover gas = 1% CO.
Fig. 5. Adsorption of cesium from CsI-Cs$_2$CO$_3$ source (cesium/iodine mol ratio = 10) on graphite thermal gradient tubes. Cover gas = 1.0% CO.
at temperatures <500°C. In the 24-h test, the amounts adsorbed at temperatures >500°C remained about the same as in the 0.25-h test, but the amounts adsorbed at temperatures <500°C were significantly increased. Chromatographic effects, if any, of the cesium adsorption may have been partially hidden by the large amounts of cesium which were vaporized and redeposited.

Again, the data in Tables 2 and 3 show that the cesium/iodine mol ratios decreased as the temperature of the deposits decreased. For example, the ratio decreased from 2.6 to 0.3 as the deposit temperature decreased from 1000 to 200°C in the 0.25-h test (Table 2) and from ~1800 to 0.6 as the temperature decreased from 950 to <100°C in the 24-h test (Table 3). Approximately 80% of the deposited iodine was in the intermediate-temperature zone, 500 to 850°C, with a cesium/iodine mol ratio of ~1.0 in the 0.25-h test. The intermediate-temperature zone was shifted down to ~380°C in the 24-h test, but the fraction of the deposited iodine recovered in this zone with a cesium/iodine mol ratio of ~1.0 remained large, ~82%. The amount of iodine in the iodine-rich zone increased from 3% in the 0.25-h test to 18% in the 24-h test.

Dissociation of CsI on the graphite surfaces, particularly at the higher temperatures, may account for the formation of several of the species evident on the deposition surfaces. The cesium species (Cs and CsOx) that are formed from such a dissociation would bond strongly with the graphite and remain relatively stationary, while the more volatile molecular iodine is more weakly bound to graphite and thus would move downstream toward cooler adsorption sites, becoming essentially stationary at temperatures <200°C.

3.2.2 Effects of Diminishing Oxygen Potential, Tests 4 and 5

Tests 4 and 5 (Table 1) were conducted in an attempt to ascertain the effect of diminishing oxygen potential in the cover gas. Data from 0.25-h tests using 0.1 vol % CO and 0.01 vol % CO are shown in Table 5. A large fraction of the cesium and iodine deposition in the
Table 5. Effect of oxygen potential on cesium/iodine mol ratio in deposit and degree of deposition\(^a\)
(Tests 4 and 5)

<table>
<thead>
<tr>
<th>Carbon monoxide in gas (%)</th>
<th>Temperature (°C)</th>
<th>Deposit(^b)</th>
<th>Cs/I mol ratio in deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cesium (μmol/g)</td>
<td>Iodine (μmol/g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>1000 (source pellet)</td>
<td>21.88</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>5.08</td>
<td>2.68</td>
</tr>
<tr>
<td></td>
<td>527</td>
<td>0.13</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>170</td>
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</tr>
<tr>
<td></td>
<td>130(^d)</td>
<td>&lt;0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>0.01</td>
<td>1000 (source pellet)</td>
<td>16.39</td>
<td>1.24</td>
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<tr>
<td></td>
<td>1000</td>
<td>5.52(^c)</td>
<td>2.05(^c)</td>
</tr>
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<td>434</td>
<td>0.51</td>
<td>0.37</td>
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<td>&lt;0.01</td>
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<td>135</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>70(^d)</td>
<td>0.01</td>
<td>0.02</td>
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\(^a\)Tests conducted at 1000°C for 0.25 h.
\(^b\)Source pellets contained ~4760 μg of cesium and ~570 μg of iodine.
\(^c\)Deposits largely on quartz tubing instead of graphite thermal gradient tube.
\(^d\)Charcoal trap, 1 g.

0.01 vol % CO test occurred at ~1000°C on the quartz tubing in and around the source pellet, while the deposition pattern from the 0.1 vol % CO test appeared to be similar to that obtained from the 1.0 vol % CO tests (Table 3).

A comparison of the results from Tests 2, 4, and 5 shows no major impact of oxygen potential reduction from -130 kcal/mol in Test 2 to -159 kcal/mole in Test 5. There was some indication of enhanced iodine retention at the highest temperature for the lowest oxygen potential run (Test 5), probably due to enhanced CsI stability. In
addition, there was evidence of increased cesium and iodine reaction with quartz tubing at the ~1000°C section in the test performed with the lowest oxygen potential.

3.3 DEPOSITS FROM MOLECULAR IODINE SOURCES IN TESTS 7, 8, AND 9

These tests were conducted similar to Tests 1-6 except that molecular iodine, I₂, was used as a source and the range of thermal gradient tube temperatures was less, ~100 to 425°C. Experimental details for the tests are provided in Sect. 2.3 and in Table 1. Results of the tests show that iodine was adsorbed in smaller amounts on the thermal gradient tube than was the case with cesium present. Plots of the amounts adsorbed in 7.5, 30, and 45 min as a function of temperature are shown in Fig. 6. The adsorption pattern varies with time in that the amount adsorbed between 300 and 400°C decreases from a maximum of ~40 µg/g in 7.5 min to ~3 to 5 µg/g in 45 min. At the same time, the amount adsorbed increases from ~10 to >100 µg/g in the 150 to 250°C temperature range. Iodine material balances of 85 to 90% were obtained, with most of the iodine passed through the system being caught in the charcoal cold trap (Fig. 2).

These results substantiate results reported in Sect. 3.2 indicating that (1) molecular iodine can be adsorbed by graphite over a wide temperature range and (2) the adsorbed iodine moves downstream with time and/or gas flow to cooler graphite adsorption sites.

3.4 ELECTRON SURFACE CHEMICAL ANALYSES

Electron surface chemical analysis (ESCA) was used to identify cesium species in deposits with large cesium/iodine mol ratios on the surfaces of individual sections of graphite thermal gradient tubes. The Cs(3d) spectrum for the gradient section shown in Fig. 7 is representative of the results obtained from several samples. The peak at ~738.2 eV, which is slightly higher than that reported for cesium in CsI (727.7 eV) and for cesium in CsOH (724.0 eV), is probably CsO₂.
Fig. 6. Adsorption of iodine on thermal gradient tubes from molecular iodine source.
Fig. 7. Electron surface chemical analysis for Cs(3d, 5/2, 3/2) electrons in an adsorbed deposit on a graphite thermal gradient tube.
Individual gradient sections with Cs/I mol ratios of ~1:1 were also analyzed for iodine by ESCA. A typical I(3d, 5/2, 3/2) spectrum is shown in Fig. 8. Its binding energy is consistent with that reported for iodine in CsI.

4. SUMMARY AND CONCLUSIONS

4.1 SUMMARY

The results obtained in this study can be summarized as follows:

1. In a series of nine tests (Table 1), the relative movements of cesium and iodine were observed in a system consisting of a quartz tube containing H-451 graphite and flowing helium with a controlled oxygen potential. A range of source cesium/iodine mol ratios, annealing times, and oxygen potentials was investigated.

2. A scoping test (Test 1) was conducted using a CsI source in a graphite pellet held at 1000°C for 120 h. At the end of this time, the bulk of the observed cesium and iodine (~85%) was observed to be at the 250°C location in the thermal gradient with a mol ratio of ~1. This material, therefore, appeared to be largely condensed CsI. The balance of the cesium (~15%), however, was distributed in higher-temperature zones, whereas the balance of the iodine (~15%) was located in the downstream trap.

3. A comparison of Tests 2 and 3 illustrates the movement of the cesium/iodine = 1 zone (presumably CsI) from the 500 to 850°C zone in the shorter test to a lower-temperature location (~389°C) at the longer annealing time. The longer test also showed that a far larger portion of the iodine which moved was located in the downstream trap (~0.1% vs ~20% in the
Fig. 8. Electron surface chemical analysis for I(3d, 5/2, 3/2) electrons in an adsorbed deposit on a graphite thermal gradient tube.
longer test). In comparison, ~0.04% of the cesium that moved was in the downstream trap at the end of the short test as compared with 6% at the end of the longer test.

4. A comparison of the results of Tests 2, 4, and 5 shows no major impact caused by the reduction of the oxygen potential from -130 to -159 kcal/mol at the inlet on the cesium and iodine transport behavior. There was enhanced iodine retention at high temperature for the lowest oxygen potential run, perhaps due to enhanced CsI stability. In addition, an increase in cesium and iodine interaction with the quartz wave was seen at the lowest oxygen potential.

5. Electron surface chemical analysis indicated the presence of adsorbed cesium oxides and iodide (I⁻) ions on the graphite surfaces.

6. Once adsorbed on the graphite surfaces of the source pellet, small residual amounts of cesium and iodine (1 to 4 µg/g of each), were not vaporized under any of the test conditions. This effect is thought to result from the reaction of impurities in the graphite with the cesium and iodine.

4.2 CONCLUSIONS

Based on the data obtained in these tests, we can draw the following conclusions:

1. Our scoping tests with cesium and iodine compounds illustrate the potential utility of the thermal gradient tube concept in HTGR fission product transport test systems. Use of this device may provide a low-cost approach to the identification of fission product species in transport experiments by inference from deposition location and measured elemental ratios, or more directly by use of ESCA or other techniques.
2. Iodine was added to the source pellet as CsI for most of the tests, even though experience indicates that the dominant iodine species in the primary system is I₂. Nevertheless, it is seen that while iodine is initially present as CsI, some processes exist which tend to partially dissociate this compound in graphite. Under the conditions used in our experiments, up to perhaps 10% of the iodine transported was evidently not in its original chemical form at the end of each test.

5. REFERENCES


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