The Behavior of Fission Products Captured in Graphite Powder by Nuclear Recoil. VIII. Further Studies of Iodine-131 Diffused out of Graphite

By Seishi Yajima, Koreyuki Shiba and Muneo Handa

In the sixth and seventh papers of this series,[1-2] the chemical state of fission iodine-131 diffusing out of various kinds of ceramic fuels was studied by using a thermochromatograph, and the following experimental results were reported:

1) The fission iodine-131 diffusing out of uranium dioxide, thorium dioxide, and a mixture of graphite and uranium dioxide, all containing fission products, was not an elementary iodine but was composed of iodine compounds.

2) The iodine compounds were fairly stable at high temperatures in a helium atmosphere; i. e., the compound diffusing out of uranium dioxide and the mixture of graphite and uranium dioxide was able to exist as a solid at 580°C; the compound from thorium dioxide was of two kinds of states, one in a solid at 530°C and the other at 430°C.

3) From the behavior of iodine compounds in solvent extraction, it was found that the chemical state of the compounds was iodide.

4) As iodide is a chemical form, it should be thought that iodine combined with other fission products, with impurities in uranium dioxide, thorium dioxide, graphite, etc., or with the fissionable material, i. e., uranium or thorium. Of the above possibilities, that that the fission iodine-131 combined with impurities was eliminated, because the fission iodine-131 diffusing out of the uranium dioxide and that diffusing out of the mixture of graphite and uranium dioxide, the impurities in the two differing from one other, were stable at 580°C in a solid form. The theory that the fission iodine-131 combined with other fission products was weakened by the fact that there was a difference between the fission iodine-131 from uranium dioxide and that from thorium dioxide at the temperature where the iodide existed as solid, even if the fission products yield curves of uranium were different from that of thorium.

On the basis of the above facts, it was assumed that the fission iodine-131 combined with the fissionable material, uranium or thorium. To prove directly the chemical forms of these iodine compounds by the chemical or physical methods was, however, very difficult. This was because the amount of fission iodine-131 in the irradiated sample was extremely small ($\mu\mu$g. level) and, further, because, if the fission iodine-131 existed as a uranium iodide or thorium iodide, these compounds were considerably unstable in the atmosphere.

The present paper will describe further studies made to prove the combining of the fission iodine-131 with fissionable material. A uranium tetraiodide was prepared by the reaction of uranium metal powder with iodine labeled with iodine-131. The behavior of uranium tetraiodide was compared with that of the fission iodine-131 by using a thermochromatograph. The uranium tetraiodide deposited on the same place in a thermochromato-tube as the fission iodine-131, in an inert gas atmosphere. Further, the chemical behavior of the uranium tetraiodide toward the oxygen contained in a small amount in the helium stream was compared with that of the fission iodine-131 diffused out of the graphite. The behavior of the uranium tetraiodide toward the oxygen was the same as that of the fission iodine-131. On the basis of above results, it seemed reasonable to assume that the fission iodine-131 diffused out from the graphite as uranium tetraiodide. As for the chemical behavior of the uranium tetraiodide toward the oxygen, it was clarified that the uranium tetraiodide was oxidized to triuranium octoxide and iodine through three intermediates, which deposited on the silica powders heated at temperatures of about 400°C, 300°C and 200°C respectively.

Experimental and Results

The Preparation of Samples. — *Sample No. 1 (A mixture of natural graphite powder and uranium dioxide containing fission products).*—Natural graphite powder degassed (in a vacuum, 1000°C, 24 hr.) was mixed with a stoichiometric uranium dioxide powder in the weight ratio of 2 : 1, in a glove box filled with purified helium gas. About 100 mg. of

1) S. Yajima, K. Shiba and M. Handa, This Bulletin, **36**, 253 (1963).
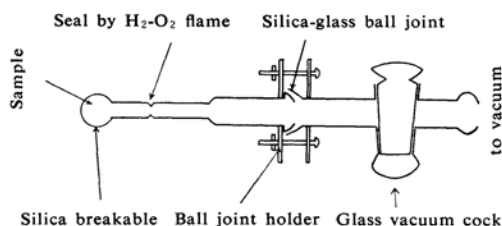2) S. Yajima, K. Shiba and M. Handa, ibid., **36**, 258 (1963).

Fig. 1. Assembly to prepare the sample packed in a silica breakable.

the mixture was packed in a silica breakable equipped with a ball joint, a joint which is shown in Fig. 1. Then a cock was attached to the breakable with a ball-joint holder, and the whole assembly was taken out of the glove box. The helium gas in the breakable was evacuated, and the part containing the sample was sealed by an oxygen-hydrogen flame. Then the mixture of graphite and uranium dioxide sealed in the silica breakable was neutron-irradiated in the JRR-1 (a water boiler-type reactor with a thermal neutron flux of about 5×10^{11} n/cm²·sec.) for 15 hr. After irradiation, the mixture was cooled for 5 days to allow the other short-lived isotopes of iodine, as well as the mostly precursor of iodine-131, to decay out. The fission iodine-131 diffusing out of this sample mixture when it was heated was determined to be the iodine-131 contained in the graphite, because about 70% of the fission iodine-131 was captured in the graphite by nuclear recoil[3] and the diffusion coefficient of the fission iodine-131 in the graphite was far larger than in the uranium dioxide.

Sample No. 2 (Uranium tetraiodide labeled with iodine-131).—Potassium iodide was added to a commercial aqueous solution of iodine-131, and the potassium iodide was oxidized to an elementary iodine with nitric acid. The iodine labeled with iodine-131 was washed with water to eliminte a potassium nitrate and was dried in a desiccator containing an anhydrous calcium chloride.

By the use of this elementary iodine, uranium tetraiodide labeled with iodine-131 was prepared by the method reported by Gregory.[4] About 100 mg. of the uranium tetraiodide was packed in a silica breakable in a way similar to that used for sample No. 1.

Packing Material for the Thermochromato-tube. —Natural graphite powder, with particle sizes less than one micron, or silica powder, twenty-to-thirty mesh, was degassed by heating it in a vacueum at 1000°C for 24 hr. The treated graphite or silica was kept in a helium gas atmosphere before being used in the experiment.

Apparatus. — The apparatus used is shown schematically in Fig. 2. The automatic Toepler pump was attached to the thermochromatograph reported on earlier.[1] The apparatus was modified in order to circulate the carrier gas through the apparatus. A trap for the mercury, cooled with a mixture of alcohol and dry-ice, was installed at the entrance and exit of the thermochromato-tube; the mercury

3) T. Nakai, S. Yajima, K. Shiba, J. Osugi and D. Shinoda, This Bulletin, 33, 494 (1960).
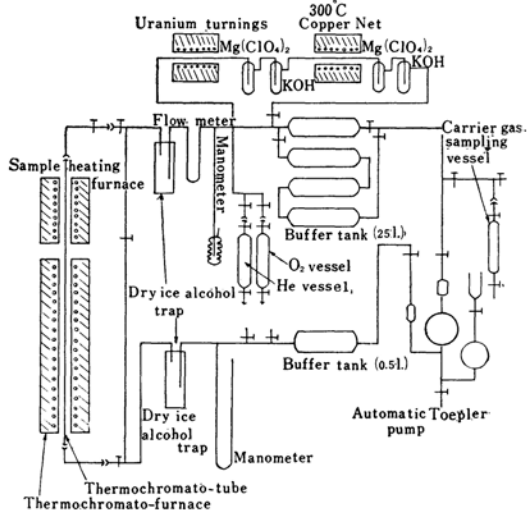4) N. W. Gregory, UCRL, RL-4, 6, 272 (1944).

Fig. 2. Thermochromatograph.

was used in the automatic Toepler pump. A buffer tank was set at the entrance and exit of the automatic Toepler pump in order to stabilize the flow rate of the carrier gas; the volumes of the buffer tanks were 0.5 l. and 25 l. respectively. The apparatus had a bypass gas-purification system and made possible the experiments with purified helium carrier gas. The thermochromato-tube was externally heated by a nichrome wire to produce the linear temperature gradient of 600°C to room temperature; the temperature gradient is shown in Fig. 3. The gradient was obtained by changing the
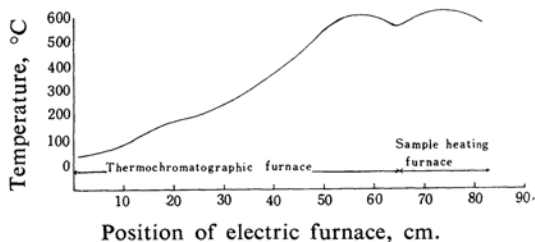

Fig. 3. Condition of two electric furnace (thermochromato-furnace and sample heating furnace) when an equilibrium was attained.

number of windings for each part of the furnace. The thermochromato-tube used was the same as in the previous study, with a transparent silica tube (0.6 cm. in inner diameter and 100 cm. long). Twenty-to-thirty mesh silica powder or fine natural graphite powder was used as the packing material in the thermochromato-tube. The sample-heating furnace was divided in two halves at the center of the furnace, so that the breakable in the thermochromato-tube could be broken from outside with a magnet.

Procedure.—Silica powder or graphite powder was packed into the thermochromato-tube. The sample in the silica breakable and its breaker (an iron bar sealed in a silica tube) were located in the center

of the sample-heating furnace on the packing material in the thermochromato-tube. Then the whole apparatus was evacuated by a rotary pump, and the thermochromato-furnace was heated for 2 hr. to remove the impurity gases adsorbed on the packing powders. Arbitrary volumes of helium and oxygen were introduced into the apparatus to a one-tenth atmosphere; these were then completely mixed by circulating them 5 hr. through the apparatus with the automatic Toepler pump. On the other hand, when the experiment was carried out in an inert atmosphere, only helium was introduced into the apparatus; it was purified by circulating 5 hr. through the gas purification system with the automatic Toepler pump. In both cases, the heating of the sample-heating furnace was then started. After the temperature of the sample-heating furnace reached 600°C, the circulation of the carrier gas was continued for a further 2 hr. The thermochromato-tube was cooled and surveyed along the whole length in order to locate the iodine-131 activities. An RCL-256 channel gamma-ray spectrometer connected with an NaI(Tl) crystal (a lead slit 1 cm. wide was set) was used for measuring the iodine-131 activity.

Thermochromatograms. — The thermochromatograms of the fission iodine-131 diffused out of the mixture of graphite and uranium dioxide, and that
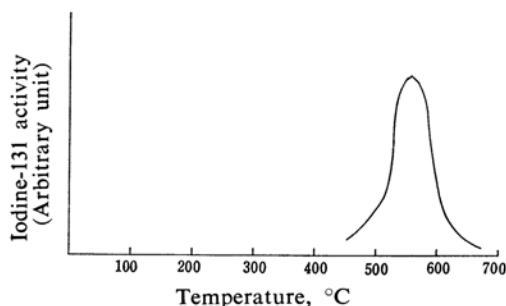
Fig. 4. Thermochromatograms.
   Sample: No. 1 (Mixture of graphite and uranium dioxide)
   Packing: Natural graphite powder
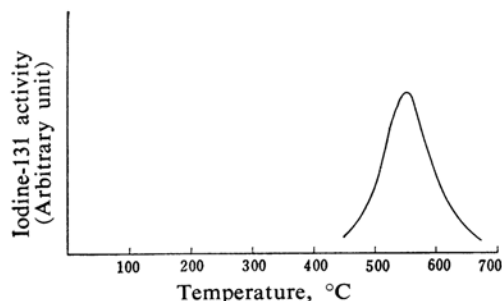   Time: 2 hr.
   Carrier: Pure helium

Fig. 5.
   Sample: No. 2 (Uranium tetraiodide)
   Packing: Natural graphite powder
   Time: 2 hr.
   Carrier: Pure helium

diffused out of the uranium tetraiodide prepared in a laboratory, for the pure helium carrier gas, are shown in Figs. 4 and 5 respectively. The results obtained for the two samples under various oxygen partial pressures are shown in Figs. 6 and 7 respectively. In the thermochromatograms in
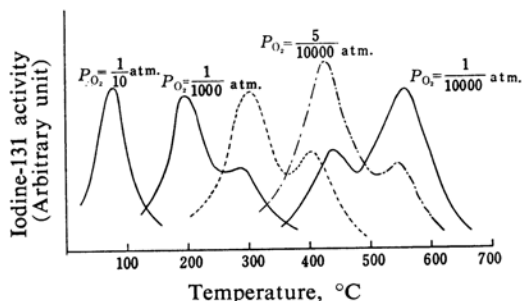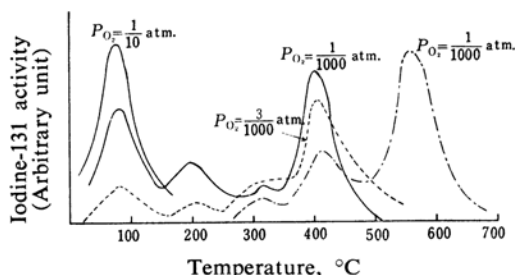
Fig. 6.

Fig. 7.
   Sample: No. 2 (Uranium tetraiodide)
   Packing: Silica powder
   Time: 2 hr.
   Carrier: O_2-He mixture

Figs. 4 to 7, the axis of the abscissa is shown by the temperature. These thermochromatograms were obtained by replacing each position of the thermochromato-tube with the temperature of the thermochromato furnace, according to Fig. 3.

Discussion

As is shown in Fig. 4, when thoroughly purified helium was used as the carrier gas (the partial pressure of oxygen was less than 10^{-5} atmosphere), the fission iodine-131 deposited on the graphite powder heated at 550°C,*

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* In a previous report,[1] it was reported that the fission iodine-131 deposited on the graphite powder heated at 580°C. The deposition temperature of the fission iodine-131 in the thermochromato-tube was mainly influenced by two factors, i.e., the flow rate of the carrier gas in the thermochromato-tube and the temperature gradient of the thermochromato-furnace. In the present experiment the thermochromatograph was modified considerably compared with the previous one, and so the location of the deposition of the fission iodine-131 shifted to a low temperature; it was deposited on graphite powder heated at 550°C. However, when the same thermochromatograph was used for the experiment, the deposition temperature of the fission iodine-131 was reproducible within ±20°C at the same experimental conditions.

temperature near the melting point of the uranium tetraiodide (the melting point of uranium tetraiodide reported in the literature is 506—518°C[5,6]). On the other hand, the uranium tetraiodide prepared in a laboratory deposited on the graphite powder heated at 550°C under the same experimental conditions as that of the fission iodine-131. The data shown in Fig. 6 indicate that, at a constant temperature, the reaction between the fission iodine-131 and oxygen is governed by the partial pressure of the oxygen in the carrier gas. The position of the fission pressure of the oxygen in the carrier gas increased.

When the partial pressure of oxygen was one-tenth atmosphere, the fission iodine-131 was oxidized to an elementary iodine and deposited at the position of 100°C (the melting point of iodine is 113.6°C). The results for the reaction of uranium tetraiodide with oxygen under the same experimental conditions, which are shown in Fig. 7, were the same as those obtained with the thermo-chromatograms for the fission iodine-131. From the above results, it must be considered that the fission iodine-131 diffusing out of the neutron-irradiated mixture of graphite and uranium dioxide is not an elementary iodine but is in the chemical form of uranium tetraiodide.

To prove the above facts directly, uranium must be detected at the position of the deposition of the fission iodine-131 by neutron activation analysis. These experiments are now planned in the author's laboratory. The intermediates which deposited at 400°C, 300°C and 200°C are thought to be either compounds of uranium and iodine (for example, UI_6 and UI_5) or compounds of uranium, iodine, and oxygen (for example, UO_2I_2 and UOI_2), but the existence of these compounds in the solid state is not reported in any literature. The mechanism of the formation of these compounds is thought to be the oxidation, decomposition or disproportionation of uranium tetraiodide or their combinations; the chemical forms and the types of crystallization are now being investigated.

Recently, Hudswell[7] confirmed that the fission iodine diffusing out of uranium-carbide fuel dopsited on the surface of graphite heated at the temperature of 350°C in a helium gas atmosphere. It is thought that Hudswell found one of the intermediates confirmed by the authors. The phenomenon that the fission iodine diffuses out in the chemical form of uranium tetraiodide from ceramic fuels, such as uranium dioxide or a mixture of uranium carbide and graphite, is important in connection with uranium migration in nuclear ceramic fuels; therfore, the mechanism of the formation of uranium tetraiodide in the fuels must be studied further.

The Research Institute for Iron,
Steel and Other Metals
Tohoku University
Katahira-cho, Sendai (S. Y.)

Division of Nuclear Engineering
Reactor Fuel Laboratory
Japan Atomic Energy Research Institute
Tokai, Ibaraki (K. S. & M.H.)

5) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium; The Element, Its Binary and Related Compounds," Dover Publications, New York (1951), p. 536.
6) M. M. Popov and M. D. Senin, *Zhur. Neorganichskoi Khimii*, 2, 1479 (1957).

7) F. H. Hudswell, Unpublished work.