The Behavior of Fission Products Captured in Graphite Powder by Nuclear Recoil. VI. The Chemical State of Iodine-131 Diffused out from Graphite, Uranium Dioxide and Thorium Dioxide

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(Received June 22, 1962)

A large portion of the enormous energy of nuclear fission is converted into the kinetic energy of nuclear fission fragments. This energy forces the fission fragments to move in the material, in which the kinetic energy is finally absorbed in the form of heat. The range of the fission products is about 5 μ in uranium dioxide and about 12 μ in graphite. Within this short distance, about 0.8 MeV. of the fission fragment energy is imparted to the material, violently disturbing the arrangement of atoms in the material; the fringes of a fragment track are instantly heated to an extremely high temperature. Such a track is called a thermal spike. The chemical behavior of the fission products in the thermal spike belongs to the field of hot atom chemistry. The authors have studied the diffusion of krypton, xenon, tellurium, and iodine trapped in graphite by fission recoil, thus clarifying the following facts. The diffusion rates of the above elements in natural graphite were much larger than in artificial graphite[1]. The diffusion of xenon in graphite was found as not governed by a simple diffusion mechanism, but to depend on the state of imperfection in the graphite crystal[2]. The distribution of the activation energy of xenon diffusion in natural graphite was determined by making a heating curve of xenon-133 or -135 in natural graphite. The distribution of the activation energy shifted to a higher temperature with an increase in the fission product concentration in the graphite[3].

These studies were carried out in connection with the development of a semi-homogeneous fuel in which uranium dioxide or uranium carbide is dispersed in graphite. In the present investigation, the chemical states of the fission fragment iodine-131 diffusing out of uranium dioxide and thorium dioxide and diffusing after being caught by fission recoil in graphite, were studied by means of thermochromatography. The primary fission yield of iodine-131 from uranium-235 (n, f reaction) and thorium-232 (γ, f reaction) is so small that it has little chance to react with the material surrounding the recoiled iodine-131 track in the hot atom state, but it is still of interest to study the diffusion behavior of the iodine-131 generated by its precursor, on account of the high chemical affinity of the iodine-131 and the thermal spike. The results obtained show that the chemical state of the iodine-131 diffusing out of uranium dioxide and graphite was not that of an elementary iodine (I^0) but of iodide (I^-), and that, irrespective of the diffusing matrix concerned, the iodide species were fairly stable at high temperature and deposited on the graphite powder heated to 500~600°C in an argon atmosphere. These facts should be useful in developing an internal trap for the semi-homogeneous fuel element whose features are high burn-up and high temperature.

Experimental Method and Results

Preparation of Samples.—*Sample No. 1 (Uranium Dioxide Powder Containing Fission Products).*—Uranium dioxide powder of a particle size of less than 1 μ was reduced with hydrogen for 5 hr. at 1000°C to obtain a stoichiometric uranium dioxide. About 100 mg. of this uranium dioxide was sealed in a polyethylene bag placed in a glove box filled with nitrogen gas. Then it was neutron-irradiated in the reactor JRR-1 (water-boiler type, thermal neutron flux: about 5×10^{11}n/cm^2·sec.) for 15 hr.

TABLE I. ANALYTICAL DATA OF IMPURITIES IN URANIUM DIOXIDE AND THORIUM DIOXIDE

	Sample	
	Uranium dioxide	Thorium dioxide
Content	99.85%	99.91%
Alkalies and alkaline earths	0.13%	—*
Heavy metals (Pb)	0.005%	—*
Fe_2O_3	0.013%	0.008%
Cl^-	0.004%	0.004%
NO_3^-	Trace	—*
SO_4^{2-}	0.002%	0.07%

* Not analyzed

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[1] T. Nakai, S. Yajima, K. Shiba, J. Osugi and D. Shinoda, This Bulletin, 33, 497 (1960).

[2] S. Yajima, S. Ichiba, Y. Kamemoto, K. Shiba and M. Kori, ibid., 34, 697 (1961).

[3] S. Yajima, S. Ichiba, K. Iwamoto and K. Shiba, ibid., 35, 1263 (1962).

After irradiation, the sample was cooled for 5 days to cause the other short-lived isotopes of iodine, as well as the precursor of iodine-131, to decay out. The impurities contained in the uranium dioxide are shown in Table I.

Sample No. 2 (Mixture of Natural Graphite Powder and Uranium Dioxide Containing Fission Products).—Natural graphite powder previously degassed (in vacuum, 1000°C, 24 hr.) was mixed with the stoichiometric uranium dioxide powder in a weight ratio of 2 : 1 in a glove box filled with nitrogen gas. Three handred milligrams of the mixture was sealed in a polyethylene bag, neutron-irradiated and cooled in a way similar to that for sample No. 1. The impurities contained in the graphite are shown in Table II.

TABLE II. ANALYTICAL DATA OF IMPURITIES IN GRAPHITE

Impurities	
Ash	0.8%
SiO_2	3700 p.p.m.
Al_2O_3	3500 p.p.m.
Fe_2O_3	300 p.p.m.
MgO	100 p.p.m.
CaO	300 p.p.m.
V_2O_5	0.5 p.p.m.
Na_2O	25 p.p.m.
K_2O	20 p.p.m.
B_2O_3	0.5 p.p.m.

Sample No. 3 (Natural Graphite Powder Containing Fission Products). — Formbar was dissolved in dioxane, and stoichiometric uranium dioxide powder was suspended in this solution. The suspended solution was then spilled out on a glass plate, and the dioxane was evaporated. The formbar film was removed from the glass plate and cut into chips (500 mg. of chips containing 300 mg. of uranium dioxide). Five hundred milligrams of the formbar chips was mixed with 500 mg. of natural graphite powder, and the mixture was sealed in a polyethylene bag placed in a glove box. The sample was neutron-irradiated and cooled in a way similar to that for samples Nos. 1 and 2. After cooling, the formbar chips were removed from the sample by screening them through a brass sieve. The graphite powder was found to contain sufficient fission products for the experiment.

Sample No. 4 (Natural Graphite Powder Containing Fission Products).—Three hundred milligrams of the same mixture as sample No. 2 was irradiated in JRR-1 and cooled. The mixture was then treated with a nitric acid solution to eliminate uranium dioxide, washed with water, and dried. Most of the fission products were found to be captured in this treated graphite.

Sample No. 5 (Thorium Dioxide Containing Fission Products).—Thorium dioxide powder wrapped in aluminum foil was gamma-irradiated in a linear accelerator for 5 hr. (maximum gamma-energy, 20 MeV.). Fission products were generated in the thorium dioxide by the (γ, f) nuclear reaction, and then the sample was cooled for 5 days. The impurities contained in the thorium dioxide are shown in Table I.

Sample No. 6 (Mixture of Natural Graphite Powder and Thorium Dioxide Containing Fission Products).—Degassed natural graphite powder was mixed with thorium dioxide powder to a weight ratio of 1 : 2. Three hundred milligrams of the mixture was wrapped in aluminum foil, gamma-irradiated, and cooled in a way similar to that for sample No. 5. Most of the fission products were found to have recoiled out of the thorium dioxide powder and to have been captured in the graphite powder.

Sample No. 7 (Elementary Iodine (I_2) Labeled with Iodine-131).—Five hundred milligrams of uranium dioxide powder was irradiated in JRR-1 for 15 hr. and cooled for 5 days. The irradiated uranium dioxide was dissolved in 10 ml. of a 7 M nitric acid solution, to which was added successively 1 ml. of a 0.05 M potassium iodide solution as a carrier and 1 ml. of a 0.1 M sodium nitrite solution as an oxidizing reagent. Iodine-131 was extracted, together with the carrier, with carbon tetrachloride and back-extracted with a mixed solution of sodium hydrogen sulfite and sodium hydroxide. When this procedure was repeated three times, iodine-131 was completely separated from the other fission products, uranium and neptunium.

The Apparatus.—The apparatus used is shown schematically in Fig. 1. The quartz tube seen in the figure (0.6 cm. in inner diameter, 100 cm. long) was packed, in some experiments, with natural graphite powder, and in others with α-alumina powder or copper powder. The sample was placed on the powder. The graphite and α-alumina were degassed (in vacuum, 1000°C, 24 hr.) before use. The atmosphere in the tube was replaced by purified argon after packing. Then the tube was heated with external resistance wires so as to produce a

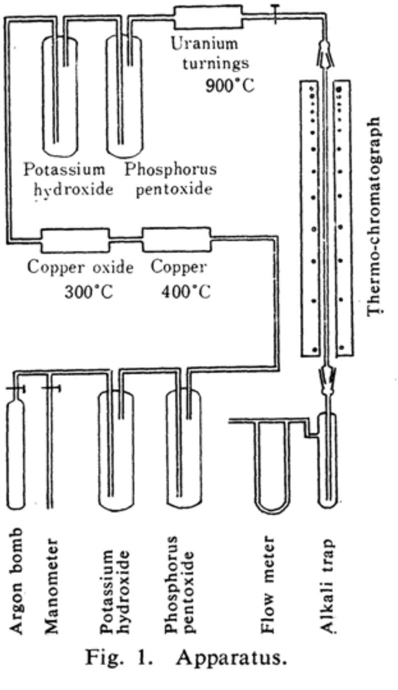

Fig. 1. Apparatus.

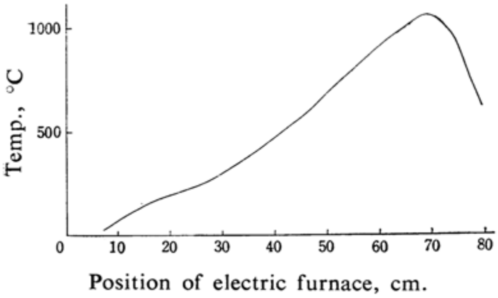

Fig. 2. Condition of the electric furnace when an equilibrium was attained.

linear temperature gradient of about 14°C/cm. ranging from 1000°C to room temperature. This condition, which is shown in Fig. 2, was maintained for 2 hr. after attaining an equilibrium. Then the sample was cooled in a stream of purified argon. After cooling, the specimen tube was surveyed along its whole length in order to locate the iodine-131 activity. An RCL 256 channel gamma-ray scintillation spectrometer connected with a sodium iodide crystal with a lead slit 1 cm. wide was used.

Purification of Argon Gas.—Commercial grade argon was dried over phosphorus pentoxide, and all the carbon dioxide was removed with potassium hydroxide. All the oxygen was removed through a copper net at 300°C. Traces of hydrogen and carbon monoxide were oxidized with copper oxide at 400°C to carbon dioxide and water. After then passing through potassium hydroxide and phosphorus pentoxide tubes, all the gases except argon were removed by passage over uranium turnings at 900°C.

Packing Materials for Quartz Tubes. — *Natural Graphite Powder*.—The natural graphite powder shown in Table II was degassed by heating it in a vacuum at 1000°C for 24 hr. The treated graphite was kept in a helium gas atmosphere until used for the experiment.

α-Alumina Powder. — γ-Alumina commercially available for gas chromatography was heated and kept at 1100°C for 5 hr. By this treatment, the γ-modification was converted into the α-modification, the alumina being degassed.

Copper Powder.—Commercial, triangularly-shaped copper powder was used.

Determination of the Chemical State of Iodine-131.—Iodide (I^-), iodine (I^0), iodate (IO_3^-) and periodate (IO_4^-) states were taken into consideration for the iodine-131 diffusing out of the samples and depositing on the graphite powder. The portion of graphite powder in the quartz tube containing the deposited iodine-131 was removed by cutting the tube, and the graphite powder thus obtained was treated with carbon tetrachloride to determine whether or not iodine-131 (I^0) existed in the graphite powder. The carbon tetrachloride solution was filtered to separate the graphite powder, and the filtrate was assayed with a gamma-ray spectrometer. The separated graphite powder was transferred into an aqueous solution containing 3 mg. of potassium iodide and 8 mg. of potassium iodate and left for 1 hr. to bring about a complete homogeneous mixing of the iodine-131 and its carriers. After 1 hr., the graphite powder was separated by filtration and its radioactivity was measured with a gamma-ray spectrometer. To acidify the filtered solution, small amounts of nitric acid were added. By this treatment the iodide ion (I^-) in the solution was completely

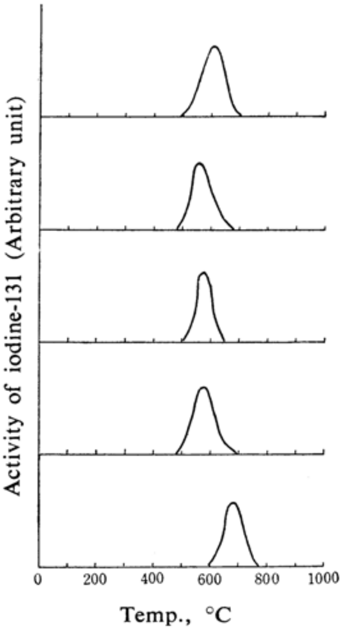

Fig. 3. Sample No. 1
Packing; Natural graphite powder
Time; 2 hr.

Fig. 4. Sample No. 2
Packing; Natural graphite powder
Time; 2 hr.

Fig. 5. Sample No. 3
Packing; Natural graphite powder
Time; 2 hr.

Fig. 6. Sample No. 4
Packing; Natural graphite powder
Time; 2 hr.

Fig. 7. Sample No. 2
Packing; Natural graphite powder
Time; 0.5 hr.

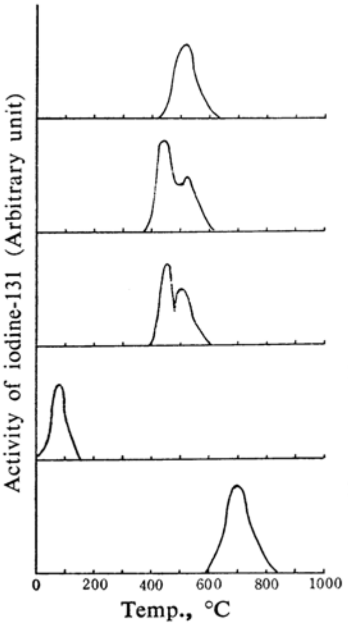

Fig. 8. Sample No. 2
Packing; Natural graphite powder
Time; 6 hr.

Fig. 9. Sample No. 5
Packing; Natural graphite powder
Time; 2 hr.

Fig. 10. Sample No. 6
Packing; Natural graphite powder
Time; 2 hr.

Fig. 11. Sample No. 7
Packing; Natural graphite powder
Time; 2 hr.

Fig. 12. Sample No. 2
Packing; Copper powder
Time; 2 hr.

TABLE III. CHEMICAL FORMS OF FISSION IODINE-131 DEPOSITED ON THE GRAPHITE POWDER

Chemical form and residue	Iodide (I^-)	Iodine (I^0)	Iodate or periodate (IO_3^-, IO_4^-)	Residue in graphite
Iodine-131 from uranium	62.5	2.0	2.3	33.2
Iodine-131 from thorium deposited at a lower temperature portion	59.8	0	0	40.2
Iodine-131 from thorium deposited at a higher temperature portion	54.2	20.7	12.6	12.6

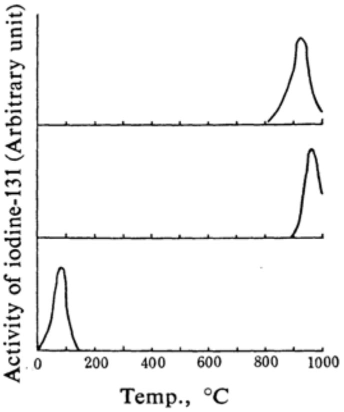

Fig. 13. Sample No. 7
Packing; Copper powder
Time; 2 hr.

Fig. 14. Sample No. 2
Packing; α-Alumina powder
Time; 2 hr.

Fig. 15. Sample No. 7
Packing; α-Alumina powder
Time; 2 hr.

converted into iodine (I^0) The reaction occurring in the solution is as follows:

$$5I^- + IO_3^- + 6H^+ = 6I^0 + 3H_2O$$

The produced iodine (I^0) was extracted and measured with a gamma-ray spectrometer*. The iodate ions (IO_3^-) remaining in the solution was converted into iodine (I^0) by the addition of excess iodide ions (I^-), and the remaining, superfluous iodide ion (I^-) was oxidized into iodine (I^0) by sodium nitrite. The iodine (I^0) thus produced was extracted by carbon tetrachloride, and the radioactivity was measured with a gamma-ray spectrometer**.

As is shown in Figs. 3 to 10, iodine-131 from uranium deposited in only one position, whereas iodine-131 from thorium deposited in two positions on the graphite powder. Experiments were carried out for each portion of the graphite containing the deposited iodine-131. The results obtained are shown in Table III.

The activities of the iodine-131 from uranium and from thorium, which deposited on the lower temperature portion of the graphite powder, were all found to be in iodide fractions. Consequently, the chemical state of the iodine-131 which diffused out of the sample and deposited on the graphite powder should be iodide (I^-). The iodine-131 deposited on the higher temperature portion was in various chemical states. This may be due to the oxygen sensitivity of iodine-131, i.e., the iodide under these conditions may have been decomposed when it was moved into the air from the tube filled with argon. The presence of a considerably large amount of iodine-131 in the graphite may have been caused by the absorption of iodine-131 in the graphite powder or by the intercalation of iodine-131 with graphite.

Thermo-chromatograms.—The results obtained with graphite powder as the packing material are shown in Figs. 3 to 11. A carrier gas of purified argon was made to flow at a rate of 0.5 ml./min., and the sample was heated for 2 hr. at 1000°C. The fission iodine-131 diffusing out was carried by the argon stream and deposited on graphite powder in the tube. The thermo-chromatograms obtained under these conditions with samples of uranium dioxide (sample No. 1), a mixture of uranium dioxide and graphite (sample No. 2), and graphite (sample Nos. 3 and 4) are shown in Figs. 3, 4, 5 and 6 respectively. In each case, the iodide deposisted at the same position of the graphite; the temperature of the position was 580°C. Figures 7 and 8 show the results obtained when the experiments lasted 0.5 and 6.0 hr. respectively; the iodine deposited at 670°C and at 520°C respectively. All the

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* It has been shown by W. H. Burgus and T. H. Davies[4] that the exchange reaction between iodide ions (I^-) and iodine (I^0) in an aqueous solution is rapid, but that the reaction between other chemical states is hardly appreciable. The exchange reaction occurs according to the chemical equation:

$$2I^0 + H_2O = HIO + H^+ + I^-$$

In a carbon tetrachloride solution, however, such a reaction cannot occur. In an acid solution, five chemical equivalents of iodide ions (I^-) react with one equivalent of iodate ions (IO_3^-). In the present experiment, the chemical equivalent ratio of iodide ions (I^-) to iodate ions (IO_3^-) was about 13:18, so that if the iodine-131 existed in the iodate state when it diffused out of the sample, about one-seventh of the iodine-131 would be converted into iodine (I^0).

** The iodine (I^0) extracted by the reduction assay of the iodate ions (IO_3^-) contained six-seventh of the indine-131 which had diffused out of the sample as the iodate (IO_3^-). The activity of the iodate fraction was small, so that the fraction of the reduced iodate ions (IO_3^-) did not contribute much to the activty of the iodide fraction. Similarly, no further separation of periodate ions (IO_4^-) from the iodate ions (IO_3^-) was made, because the periodate ions (IO_4^-) behaves in a way very similar to that for the iodate ions (IO_3^-) in the above reactions and, as is shown in Table III, the activity of the iodate fraction was small.

4) W. H. Burgus and T. H. Davies, "National Nuclear Energy Series: Radiochemical Studies: The Fission Products", Book I, Mcgraw-Hill Book Co., Inc., New York (1951), pp. 209—219.

experimental conditions except the time were the same as in the case of Fig. 6. As compared with the results given in Fig. 6, the location of the fission iodine-131 deposited moved toward a lower temperature as the duration of the experiment increased. The experiment which was repeated three times showed that the reproducibility of the deposition temperature was within ±20°C in each case.

The thermo-chromatograms obtained from the thorium dioxide (sample No. 5) and from the mixture of thorium dioxide and graphite (sample No. 6) are shown in Figs. 9 and 10 respectively. It was found that two peaks appeared in both thermo-chromatograms; the corresponding temperatures were 520°C and 430°C in both cases. Figure 11 gives the thermo-chromatogram of the elementary iodine (sample No. 7) obtained under the same conditions as in Figs. 3, 4, etc. The location of radioactivity when using copper powder as the packing material is shown in Figs. 12 and 13. The fission iodine-131 (sample No. 2) was located at 700°C, and the elementary iodine (sample No. 7), at 920°C. When α-alumina was used as the packing material under the same experimental conditions as above, the fission iodine-131 (sample No. 2) deposited at a temperature higher than 950°C, while elementary iodine (sample No. 7) deposited at 80°C.

Conclusion

The data obtained may be summarized as follows:

1) The thermo-chromatograms of the fission iodine-131 were extremely different from that of elementary iodine, whichever packing material was used, i. e., graphite, α-alumina or copper powder.

2) The fission iodine which deposited on graphite at a temperature of 580°C was iodide in terms of its chemical state.

3) Elementary iodine deposited on graphite at 80°C as elementary iodine itself under these experimental conditions. That is, the elementary iodine was not reduced by either graphite, impurities in the graphite, or carrier gas. These results [1), 2) and 3)] indicate that the fission iodine-131 was not diffused out as elementary iodine but as iodide.

4) The displacement of the iodine-131 peak toward a lower temperature, as shown in Figs. 6, 7 and 8, was not the result of the oxidation of iodide to iodine by impurities in the carrier gas. It must be related to the vapor pressure of the fission iodide, since the velocity of the movement tends to decrease sharply with an increase in the diffusion time.

5) The data obtained from samples Nos. 1, 2, 3 and 4, using graphite as the packing material, coincided well with each other. The most reasonable conclusion to be drawn under these circumstances is that the fission iodine-131 exists in the same chemical state and species in all the samples.

6) Since the fission iodine-131 exists as iodide, it should be thought that the fission iodine combines with other fission products, with impurities in uranium dioxide, thorium dioxide, etc., or with the fissionable material, i. e., uranium or thorium.

7) As shown in Figs. 3 and 9, the locations of the fission iodine-131 obtained from uranium on the graphite were different from that of thorium. This eliminates the possibility that the fission iodine-131 combines with the other fission products, even if the fission product-yield curve of uranium is different from that of thorium.

8) The combination of the fission iodine-131 with impurities in uranium dioxide, etc., is not supported by the coincidence of the thermo-chromatograms obtained from samples Nos. 1 and 3, whose impurities are different.

9) Lastly, the combination of fission iodine-131 with fissionable materials, in the present instance, uranium and thorium, may be considered. The fact that the thermo-chromatogram of the fission iodine-131 originating in uranium differs from that of thorium and the results discussed in 7) and 8) lead to the conclusion that the iodine-131 combines with fissionable materials, uranium or thorium. Also, it has been observed by Ershler and Lapteva[5] that, when a foil of uranium metal is neutron-irradiated in high vacuum, a large number of uranium atoms are vaporized from the foil. The present authors cannot help thinking, on the basis of the foregoing data, that a considerable number of uranium or thorium atoms are brought into the graphite crystal by primary fission fragments. The fission iodine-131 would center in the imperfection composed of unstable atoms of uranium or thorium caused by fission, born uranium or thorium iodide, and would diffuse out of the samples.

10) The fission iodine-131 diffusing out of the sample reacts with α-alumina at temperatures higher than 950°C. This finding indicates that α-alumina is a suitable material for use as an internal trap in a semi-homogeneous fuel reactor characterized by high temperature and high burn-up.

11) To determine precisely the chemical species of the iodide, thermo-chromatograms or uranium iodide and thorium iodide must

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[5] B. V. Ershler and F. S. Lapteva, *J. Nuclear Energy*, II 4, 471 (1957).

be studied, and the presence of uranium or thorium in thermal spikes must be confirmed.

The authors wish to express their thanks to Dr. Eizaburo Nishibori, director of the institute, for his valuable advice and discussions, and also to Dr. Toshio Nakai, chief of the division of chemistry, for his encouragement in this work.

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