The Behavior of Fission Products Captured in Graphite Powder by Nuclear Recoil. I. The Stability of the Fission Products toward Nitric Acid Solution

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(Received September 22, 1959)

In his pioneering study McMillan[1] placed a thin film of uranium oxide powder between filters or cigarette papers and irradiated it with cyclotron neutrons. He found that most of the fission products recoiled out of the film and were captured in the paper. This separation made it possible to identify the strong activity of neptunium-239 with a half life of 2.3 days that had been left behind.

If a fission reaction is caused to proceed in particles of uranium oxide with maximum dimensions smaller than the minimum range* of the fission products, these products will probably recoil out of the uranium oxide. On the other hand, heavier nuclei formed by neutron capture and beta decay will have a much shorter range and remain within the original particles. This means that in a suitable heterogeneous system the fission products will be completely separated from the actinide elements without complicated chemical treatment. Since McMillan's work appeared in a journal, several investigators studied the separation of the fission products and the actinide by nuclear recoil using several kinds of heterogeneous systems.

The authors have been investigating the possibility of the utility of the dispersion-type nuclear fuel element which consists of a mixture of graphite and uranium dioxide. In such a fuel, the behavior of fission products is most characteristic compared with the other solid-type nuclear fuels. If the dimensions of uranium oxide powder are smaller than the minimum range of fission products and the weight ratio of graphite powder to uranium oxide powder is great enough to prevent the penetration of the fission fragments into the neighboring uranium oxide particles and if uranium oxide particles are uniformly dispersed in graphite powder, the fission products produced in uranium oxide powder will be thoroughly recoiled out of them and captured by graphite powder. In the previous paper[2], it was made obvious that when the weight ratio of graphite (particle size is about 50 microns) to uranium dioxide (particle size is about 0.1 microns) was 10, approximately 70% of the overall fission product activity remained in graphite powder and that when the ratio was 30, approximately 95% was captured. Mixtures of graphite and uranium dioxide were irradiated with JRR-1 neutrons (Japan Research Reactor-1, a water boiler type) and after the addition of saturated zinc bromide solution (hydrochloric acid was slightly added), these mixtures were centrifuged. The graphite powder of these mixtures gathered on the upper layer and the uranium oxide powder settled at the bottom. The distribution of the fission products in these fractions was determined using gamma ray spectrometry. From the results, the possibility of a brief reprocessing of the dispersion-type spent fuel was suggested.

The present study was undertaken to investigate the variation of the gross gamma ray spectra of the fission products captured in graphite powder at various cooling times after irradiation, and the stability of the fission products captured in graphite toward nitric acid of several different concentrations at varying durations of immersion at a constant temperature.

Experimental

The Gross Gamma Ray Spectra of the Fission Products Captured in Graphite Powder. — *Procedure 1.*—Twenty milligrams of uranium dioxide (particle size, about 0.1 microns) was mixed with 600 mg. of natural graphite prepared by the Nippon Carbon Co., (particle size, about 50 microns), and the mixture was irradiated in the No. 16 experimental hole of JRR-1 under a thermal neutron flux of about 5×10^{11} neutrons/cm^2 sec. for about three minutes. The irradiated mixture was transferred to a centrifuging tube with 70 ml. of a saturated zinc bromide solution which contained a small amount of hydrochloric acid. After centrifugal separation, the graphite powder fraction which was collected on the upper side was transferred into a polyethylene tube (1.5 cm. in diameter and 7 cm. in length) and was gamma-assayed by the RCL

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[1] E. McMillan, *Phys. Rev.*, 55, 510 (1939).

* The minimum range of the fission products in uranium dioxide is 8 microns.

[2] T. Nakai and S. Yajima, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 79, 1267 (1958).

256-channel gamma ray scintillation spectrometer with a welll-type sodium iodide crystal (2 in. ×1.75 in. diameter) as scintillator. The separation procedure was commenced after 20 min. cooling, and finished within 30 min. after irradiation. Gamma ray spectra were measured at appropriate intervals for two days.

Procedure 2.—Instead of the centrifugal separation, the irradiated mixture was treated for 5 min. with 50 ml. of 4 N hot nitric acid solution in order to dissolve uranium dioxide and neptunium formed by neutron capture and beta decay. The residual graphite powder was filtered and washed twice with 20 ml. of 0.1 N nitric acid solution, and then the graphite sample was gamma-assayed by the same method as above mentioned. In this case, the separation procedure was commenced after 20 min. cooling, and finished within 15 min.

Procedure 3.—The abundance of the fission nuclides contained in graphite powder varied with the cooling time, and also the state of each nuclide which was captured in a graphite crystal might vary. In this experiment, the irradiated mixtures were cooled for one day after irradiation and then submitted to the centrifugal separation or the nitric acid treatment. The obtained gamma ray spectra were compared with the spectra of the samples which were treated after 20 min. cooling and then cooled for 23 hr. Comparison of gamma ray spectra of the above mentioned treatments gave a good agreement.

Several gamma ray spectra of the gross fission products obtained by procedure 2 are shown in Fig. 1. The short lived nuclides in the fission products identified by these spectrodiagrams give a good agreement with those deduced from Peirson's experiment[3)].

The respective abundance and the cross sections of uranium-238 and of uranium-235 are such that the irradiation of natural uranium by thermal neutrons leads to a temporary obliteration of the low energy portion of the fission products spectra by more intense X-rays and gamma rays emitted from neptunium-239 (half life 2.3 days). If a chemical treatment was used to eliminate the interfering neptunium-239, gaseous fission products such as xenon-135 would escape, and the complete spectrum of the gross fission products could not be obtained. For this reason, in Peirson's experiment[3)] the gross gamma ray spectrum was measured by using a uranium, fifty times enriched in uranium-235. However, in this experiment the measurement of the gross gamma ray spectrum can be performed satisfactorily by using nautral uranium**.

The gamma ray spectrum of the fission products obtained by procedure 1 was similar to those obtained by procedures 2 and 3. From these results, it is evident that the centrifugal separation or the nitric acid treatment for such a short period can not affect the state of fission products captured in a graphite crystal. The effect of long time nitric acid treatment will be described in the next section.

Leaching of Fission Products out of Graphite by Nitric Acid Solution.—*Procedure.*—The graphite samples used in this experiment are artificial graphite

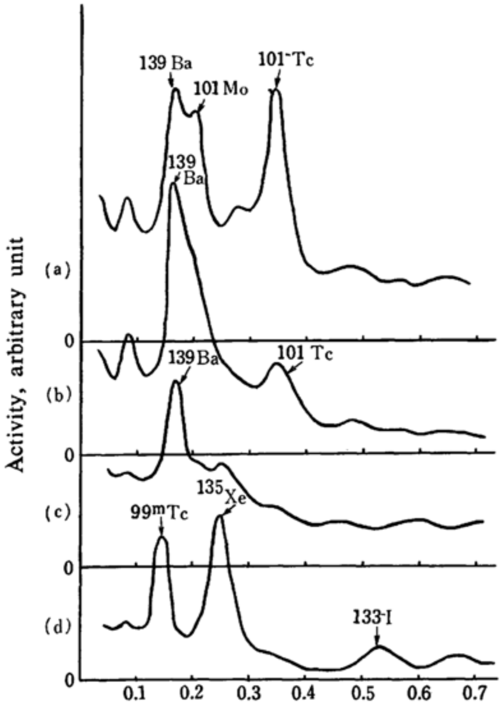

Fig. 1. Gamma ray spectrum of the fission products in graphite (a) at 26 min., (b) at 60 min., (c) at 160 min. and (d) at 20 hr. after irradiation.

TABLE I. PARTICLE SIZE OF GRAPHITE

Sample	Particle size, micron
Artificial graphite (A. G.)	30
Natural graphite (N. G.—1)	1
Natural graphite (N. G.—2)	50

TABLE II. ANALYTICAL DATA OF IMPURITIES IN GRAPHITE

Impurity	A.G.	N.G.-1	N.G.-2
Ash (total)	0.07%	0.3%	0.8%
SiO_2	250 p.p.m	220 p.p.m	3700 p.p.m
Al_2O_3	210 〃	60 〃	3500 〃
Fe_2O_3	130 〃	24 〃	300 〃
MgO	15 〃	24 〃	100 〃
CaO	70 〃	36 〃	300 〃
V_2O_5	— 〃	0.12〃	0.5〃
MnO	— 〃	— 〃	— 〃
Na_2O	20 〃	12 〃	25 〃
K_2O	15 〃	12 〃	20 〃
NiO	— 〃	0.06〃	— 〃
ThO_2	— 〃	2.4〃	— 〃
CuO	— 〃	— 〃	— 〃
B_2O_5	0.1〃	0.02〃	0.5〃

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3) D. H. Peirson, *Brit. J. Appl. Phys.*, 6, 444 (1955).

** It has been confirmed that the gaseous fission products captured in a graphite crystal did not diffuse at room temperature, and the results will be reported in the next article. The activity of fission products can not be recognized in the zinc bromide solution which has been used for the centrifugal separation.

TABLE III. LEACHING OF FISSION PRODUCTS

Conc. of HNO_3 (normality)	Digestion time hr.	120∼160 keV. photo peak main nuclide Tc-99m leaching, %	490∼580 keV. photo peak main nuclide I-133, La-140 leaching, %	630∼720 keV. photo peak main nuclide I-132, Nb-97 leaching, %
	Sample A.G. (not heated)			
0	1	0.37		
	2	0.37	0.25	
	4	0.38	0.27	0.31
1	1	0.51	0.44	0.44
	2	0.49	0.51	0.71
	4	0.68	0.51	0.85
5	1	0.79	0.36	0.78
	2	0.85	0.36	0.75
	4	0.97	0.36	0.54
10	1	0.81		0.76
	2	1.33		0.89
	4	1.57	0.36	0.73
	Sample N.G.-1 (not heated)			
0	1	0.64		
	2			
	4	0.69		
1	1	0.90		
	2	1.01		
	4	0.88	0.76	
5	1	1.26	0.86	
	2	1.28	0.86	1.71
		1.26	1.15	1.71
10	1	1.37	0.96	1.54
	2	1.37	1.96	2.05
	4	1.39	2.29	2.05
	Sample N.G.-2 (not heated)			
0	1	2.03	0.52	0.74
	2	1.90	1.03	
	4	1.90	1.03	
1	1	2.33	1.03	
	2			
	4			
5	1			
	2			
	4	3.71	1.55	1.97
10	1	3.88	1.81	
	2	3.79	1.55	3.94
	4			
	Sample N.G.-1 (heated)			
0	1	2.19	10.29	1.13
	2	2.18	8.82	1.35
	4	3.06	6.40	1.58
1	1	3.10	11.76	1.35
	2	3.26	11.76	1.35
	4	3.93	12.94	2.70
5	1	3.50	10.59	6.31
	2	6.70	10.59	6.31
	4	6.53	14.12	8.11
10	1	7.16	11.76	9.91
	2	8.20	11.76	9.91
	4	8.71	9.41	9.01
	Sample N.G.-2 (heated)			
0	1	5.99	3.80	2.83
	2	5.65	3.80	2.54
	4	5.54	5.06	2.83
1	1	5.04	5.06	2.12
	2	5.60	6.33	1.41
	4	4.05	3.80	7.76
5	1	5.16	7.60	1.70
	2	7.15	7.60	9.89
	4	8.09	5.06	9.89
10	1	8.20	5.06	11.31
	2	8.65	5.06	11.31
	4	8.87	5.06	14.13

made from petroleum coke, and two kinds of natural graphite. Grain sizes of the samples are shown in Table I and impurities contained in the samples in Table II.

A mixture of 5 g. of graphite and 0.5 g. of uranium dioxide was irradiated for one hour under the same condition mentioned above. The irradiated mixture was transferred into a centrifuging tube with a saturated zinc bromide solution which contained a small amount of hydrochloric acid. After a centrifugal separation, the graphite was washed rapidly with a diluted hydrochloric acid solution. After being dried at 70°C or heated at 1000°C for four hours in an argon gas stream, it was divided into portions of 100 mg. each. They were immersed in 30 ml. nitric acid solution of 0∼10 N concentration at 80°C for a period of 1∼4 hr. After the immersion, the solution were filtered the filtrates were evaporated to 3 ml.; this volume was suitable for gamma ray spectrometry. The gamma ray spectrum of fission products in filtrates and precipitates was measured by the RCL 256 channel gamma ray spectrometer with a well-type sodium iodide crystal (2 in. × 1.75 in. diameter) as scintillator. By comparing the gamma ray spectra of the filtrates with their total spectra (filtrate + precipitate), the leaching of fission products in nitric acid solution was made clear.

Results

Experimental data are summarized in Table III. Based on these data the following results are elucidated.

1) Fission products captured in graphite are leached with difficulty in a nitric acid solution under various conditions of immersion; however, the leaching of all the nuclides is slightly increased with the nitric acid concentration.

2) There is no difference due to varying graphite samples.

3) When the samples were heated at a high temperature, the leaching of fission products increased with acid concentration. For example, 10% of the fission products was leached by 10 N nitric acid solution.

4) However, the fraction of the fission products leached is almost constant regardless of immersion time.

From the results, it is considered that fission products in graphite are very stable toward nitric acid and such stabilities are attributed to a hindrance effect because most fission products are captured in a graphite crystal. It is not yet clearly demonstrated that the leaching is increased with acid concentration when samples are heated at a high temperature.

The authors wish to thank Dr. Kenjiro Kimura for his encouragement.

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