The Behavior of Fission Products Captured in Graphite by Nuclear Recoil. II. The Diffusion of Xenon-135 in Graphite at a High Temperature

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In the previous study[1], it was shown that, when a mixture of uranium dioxide and graphite in a weight ratio of 1 : 30 was irradiated with JRR-1 (Japan Research Reactor-1) neutrons, about 95% of the fission products recoiled out of uranium oxide powder into graphite. The orbital electrons of the recoiled fission fragments are partially stripped, and the initial velocities of fission fragments are about 10^9 cm./sec. It has also been shown that they are highly ionized, bearing ionic charges of 20 or more. Because of this high velocity and the charge, the fission fragments interact readily with matter.

One of the practical problems connected with the operation of a reactor that employs a dispersion type fuel is the determination of the extent of diffusion of radioactive fission products from the fuel pellet when the mixture of graphite and uranium dioxide is pressed to give a density of about 1.8. Since the release of gaseous fission products from the fuel pellet will cause the destruction of the pellet and the radioactive contamination of the coolant and other establishments, it is important to study the behavior of gaseous fission products captured in graphite particles. Likewise the build-up of xenon-135 in a pellet is of some importance because of its abnormally large absorption cross section. In this case continuous elimination of xenon-135 from the pellet through some adequate process should be favorable in relation to the neutron economy of a reactor. Because of these reasons the firm retention and the continuous elimination of gaseous fission products would be of the greatest importance for the dispersion type fuel. Investigators of the North American Aviation Laboratory studied the diffusion of xenon-133 from graphite[2]. When discs of graphite, 0.84 cm. in diameter and 0.064~0.5 cm. in thickness, impregnated with uranium carbide to a concentration of about 520 mg./cc., were heated to 900~1500°C, the leakage rate of xenon varied from approximately 2% per 3 hr. of heating at 900°C to approximately 50% per 3 hr. at 1500°C.

However, an investigation of the state of

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

[2] G. A. Cowan and C. J. Orth, *A/CONF.*, 15/p/613 (1958).

TABLE I. ANALYTICAL DATA OF IMPURITIES IN GRAPHITE

Impurity	Natural graphite-1 (N.G.-1)	Natural graphite-2 (N.G.-2)	Natural graphite-3 (N.G.-3)	Artificial graphite (A.G.)	Amorphous carbon (A.C.)
Particle size, micron	1	50	50	30	20
Ash (total)	0.3%	0.6%	0.8%	0.07%	0.1%
SiO_2	220 p.p.m.	2600 p.p.m.	3700 p.p.m.	250 p.p.m.	350 p.p.m.
Al_2O_3	60 〃	2300 〃	3500 〃	210 〃	100 〃
Fe_2O_3	24 〃	250 〃	300 〃	130 〃	250 〃
MgO	24 〃	80 〃	100 〃	15 〃	10 〃
CaO	36 〃	290 〃	300 〃	70 〃	150 〃
V_2O_5	0.12〃	5.5〃	0.5〃	— 〃	50 〃
MnO	— 〃	— 〃	— 〃	— 〃	— 〃
Na_2O	12 〃	15 〃	25 〃	20 〃	35 〃
K_2O	12 〃	17 〃	20 〃	15 〃	30 〃
NiO	0.06〃	— 〃	— 〃	— 〃	— 〃
ThO_2	2.4 〃	— 〃	— 〃	— 〃	— 〃
CuO	— 〃	— 〃	— 〃	— 〃	— 〃
B_2O_5	0.02〃	0.3〃	0.5〃	0.1〃	3 〃

gaseous fission products diffusing from the graphite particles is thought to be worth while. Consequently, the present work has been carried out to study the diffusion, at 400, 800 and 1200°C, of xenon-135 captured in several kinds of graphite powder.

Experimental

Preparation of Samples.—The mixture of 1 g. of graphite and 50 mg. of uranium dioxide was irradiated with thermal neutrons for about one hr. in an experimental hole (thermal neutron flux, about 5×10^{11} neutrons/cm^2 sec.), JRR-1. After irradiation, the mixture was washed with a hot 4 N nitric acid solution in order to dissolve uranium and neptunium, and dried at 70°C. The fission products captured in graphite particles were not leached with a 4 N nitric acid solution within the short time procedure1). The fission products in graphite were cooled for twenty hours after irradiation and used for the diffusion experiment. During such a cooling time iodine-135, which is the precursor of xenon-135, decayed sufficiently and the xenon-135 was predominantly built up. The graphite samples used in this experiment are tabulated in Table I.

Determination of the Diffusion of Xenon-135.—For the escape rate of xenon-135 from graphite powder to be determined at a high temperature, graphite samples into which fission products recoiled were heated in a stream of argon. The furnace, in which the heating in argon took place, consisted of a silicon carbide heater and a silica tube. The temperature of the furnace was measured with a platinum, platinum-rhodium thermocouple and controlled with a regulator. In the range 400 to 1200°C, the temperature of the furnace was found to remain constant within 10°C throughout the experiment. Argon gas was purified through sponge titanium at about 700°C and through phosphorous pentoxide to prevent the oxidation of the graphite surface. The flow rate of argon gas was checked with a glass capillary flow meter and maintained at a constant rate. The xenon released from graphite was trapped in a charcoal trap cooled with a dry ice-benzene mixture. At appropriate intervals the trap was replaced by a new one. Xenon-135 activity in the charcoal trap was determined with a gamma ray spectrometer. In this experiment an RCL 256 channel gamma ray scintillation spectrometer with a well-type sodium iodide scintillator (2 in.×1.75 in. diameter) was used.

The gross gamma ray spectrum of fission products in graphite after twenty hours cooling, of the trapped xenon and of the fission products which remained in graphite after the diffusion run are shown in Fig. 1. The amount of the diffused xenon was determined by comparing the heights of

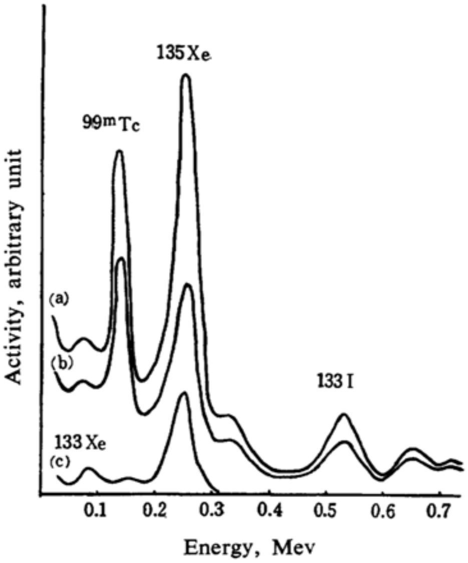

Fig. 1. Gamma-ray spectrum of the fission products in graphite.
(a) Fission products before diffusion.
(b) Fission products remained after diffusion.
(c) Trapped xenon.

the photoelectric peak of xenon-135 of the charcoal trap and of a standard graphite sample of a known weight which was not heat-treated.

Results

As already mentioned, the results were obtained from gamma ray spectra at appropriate time intervals. The photoelectric peak of gamma ray spectra is proportional to the amount of xenon that escaped from graphite. On the other hand, the initial amount of xenon in graphite was obtained from the gross gamma ray spectrum of the standard graphite sample. Therefore, the fraction of xenon which escaped can be calculated as a function of time. The diffusion rates of xenon-135 from the several kinds of graphite at 400, 800 and 1200°C are shown in Figs. 2—4, respectively.

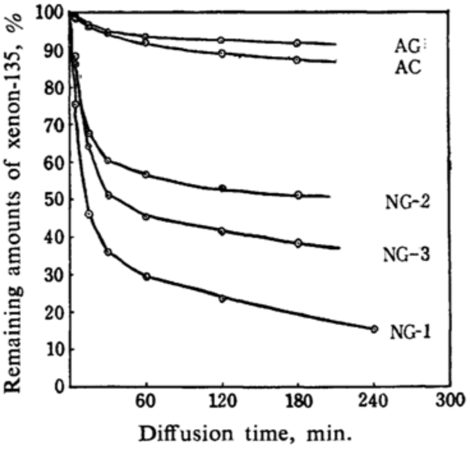

Fig. 4. Diffusion rates of xenon-135 at 1200°C.

To analyze these diffusion curves the relation between the logarithmic values of the remaining amounts of xenon-135 and the time intervals at 400, 800 and 1200°C was obtained and shown in Figs. 5—7, respectively.

From these figures it is seen that the curves consist of two fractions which are a steep slope

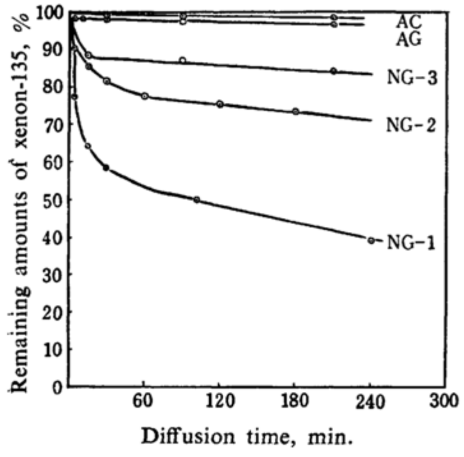

Fig. 2. Diffusion rates of xenon-135 at 400°C.

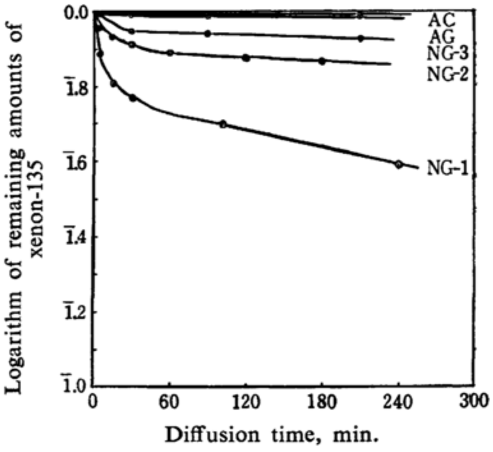

Fig. 5. Results at 400°C.

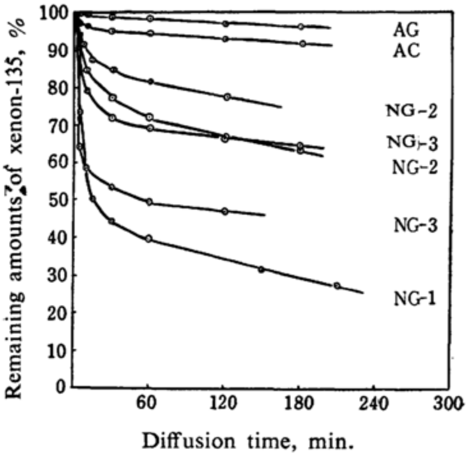

Fig. 3. Diffusion rates of xenon-135 at 800°C.

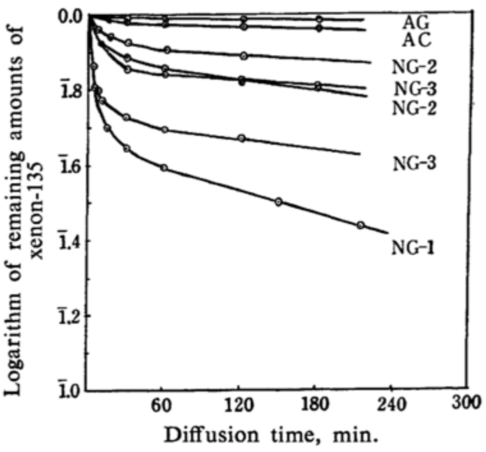

Fig. 6. Results at 800°C.

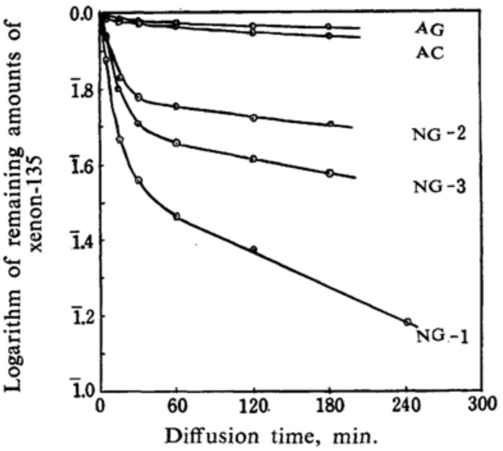

Fig. 7. Results at 1200°C.

curve for one hour and a slow inclination line after one hour. The results show that there are two mechanisms for diffusion in a graphite grain; they are a rapid and a slow diffusion.

The amounts of diffusion of xenon-135 for rapid diffusion are appreciably greater than those for slow diffusion and the amounts vary with the temperature and the kinds of sample. The amounts of diffusion from the natural graphite samples are appreciably greater than those from the artificial graphite or the amorphous carbon samples. The dependency of diffusion amounts on the kinds of sample will be discussed later.

The diffusion rate of a straight line fraction may be used to evaluate a diffusion constant of xenon-135 as shown in the following. In Figs. 5—7 the apparent inclination of a straight line fraction depends on the diffusion constant of xenon-135. Further, from the slope of the linear line for each sample, a diffusion constant is obtained, and they are summarized in Table II. Eq. 1 shows the relation between the diffusion constant and the activation energy, and from this equation the activation energy can be obtained as the inclination of the values of the logarithm of diffusion constants against the reciprocal of the absolute temperatures.

$$D = D_0 \exp\left(-\frac{\Delta H}{\boldsymbol{R}T}\right) \qquad (1)$$

TABLE II. THE ACTIVATION ENERGY OF XENON-135

Sample	Inclination	Activation energy cal./mol.
Natural graphite-1	0.50×10^3	2.3×10^3
Natural graphite-2	0.50×10^3	2.3×10^3
Natural graphite-3	0.58×10^3	2.7×10^3
Artificial graphite	0.51×10^3	2.3×10^3
Amorphous carbon	1.06×10^3	4.9×10^3

where D: diffusion constant, D_0: diffusion constant at 0 of absolute temperature degree, $\boldsymbol{R}$: gas constant, T: absolute temperature degree and H: activation energy.

The apparent activation energy of diffusion calculation from the slow inclination of these straight lines is shown in Table II.

Discussion

If one assumes that xenon diffuses along the interlaminar spaces in a perfect graphite crystal, the activation energy of diffusion can be calculated theoretically. An elementary process of xenon diffusion in graphite is the migration of xenon from position 1 to position 3 through position 2 in Fig. 8. As the activation energy is represented to be the energy difference between position 1 and position 2, the activation energy can be obtained by use of the strain energy of each position. The strain energy is calculated by the interatomic force evaluated from an elastic constant as a specific heat at a low temperature. According to Suzuki3), the activation energy calculated is about 2000 cal./mol. and is of the same order as the values obtained in this experiment. On the other hand, the calculated activation energy of diffusion across carbon layers is also about 200000 cal./mol. From this high value, the assumption that the diffusion occurs entirely along the interlaminar spaces is justified.

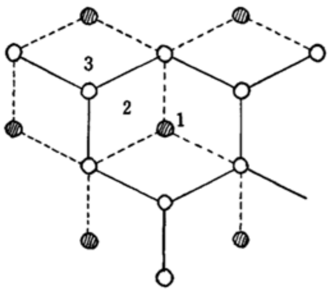

Fig. 8. A pertect graphite crystal.

It is well known that graphite, in general, has a small mosaic, particularly in artificial graphite. Dislocation density in graphite is high along the boundary of mosaic structure. Xenon is trapped in trapping centers around a dislocation line rather than a interstitial site in a crystal at room temperature, because it is evident in the present experiment that the activation energy of xenon is fairly small. Therefore, the actual process of diffusion must be discussed with reference to the chemical potential of the trapping centers including the

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3) H. Suzuki, private communication.

effect of a stress field as well as the concentration gradient in a sample.

The mosaic size of the graphite samples was determined by the X-ray diffraction method and the electron diffraction method. As a result, the mosaic size of the natural graphite is appreciably larger than those of the artificial graphite and of the amorphous carbon. It is evident that the dislocation density in the region of the mosaic boundary of the natural graphite is appreciably smaller than those of artificial graphite and of amorphous carbon. Therefore, in the case of the natural graphite, xenon-135 which was not captured by the trapping center, diffuses with a high concentration gradient. After that, xenon-135, which was captured by the center is successively released and slowly diffuses along the interlaminar space of a crystal. In this case, because the concentration gradient of xenon-135 in the sample is very small, it is very likely that the gradient is constant, and this warrants the calculation of activation energy.

Since the number of the trapping center of artificial graphite and of amorphous carbon and the amount of xenon-135 which was trapped in the trapping center are greater than those in the case of the natural graphite, the diffusion amounts of a rapid diffusion fraction of the amorphous carbon and the artificial graphite are relatively small.

The diffusion of gaseous fission products of dispersion type fuel will be related to the mosaic size of graphite material. It may be pointed out that, on the basis of the above discussion, the problem of xenon poisoning will be solved.

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