Release Process of Fission Xenon Produced by β-Decay of Precursor Iodine in Natural Graphite at 1,000°C

Takeshi FUKUDA, Shunzo OMORI and Shigeru YAMAGISHI

Division of Nuclear Fuel Research, Tokai Research Establishment, Japan Atomic Energy Research Institute*

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In order to study the release process of fission xenon produced by decay of the precursor iodine in natural graphite powder, post-irradiation experiments were carried out at 1,000°C soon after 20 min irradiation with UO₂ powder. In an experiment with interruption (2 hr heating—10 day cooling—10 hr heating), it was found that the decay of ¹³³I to ¹³³Xe caused a fraction of the ¹³³Xe produced to be released rapidly, while the remaining fraction was released gradually. This was followed by a continuous heating experiment, during which the release rates of ¹³³Xe, ¹³⁵Xe and ¹³⁵ᵐXe were measured, and in which production and release of xenon occurred simultaneously in a manner similar to conditions prevailing under actual irradiation experiments. The rates of nuclide release were explained by assuming the same release probability for each xenon nuclide as that for ¹³³Xe in the first experiment. The origin of the initial rapid release by decay of iodine to xenon was considered mainly to be the change of chemical interaction between the defects and the atoms trapped therein. The release behavior of xenon after its production was explained by assuming that the activation energies for the release from the defects were lowered by about 10 kcal/mol by the decay.

KEYWORDS: beta decay, iodine ¹³³, fissile materials, high temperature, xenon ¹³³, xenon ¹³⁵, xenon ¹³⁵ᵐ, heating, irradiation experiment, chemical interaction, defects, xenon behavior, activation energy, natural graphite powder

I. INTRODUCTION

Kamemoto & his coworkers, including the present authors(1)–(3), studying the release behavior of fission gas from natural graphite under irradiation and just after irradiation, proposed a hypothesis which they called ‘β-decay controlled process’ for fission gas release from graphite under irradiation. According to this theory, when fission halogens trapped in defects that are not annealed at the irradiation temperature decay to fission gases, a certain fraction thereof is released rapidly out of the sample by recoil energy of the β-decay and by the change in nature of the defects, while the residual fraction remains trapped in the defects. These fractions should be nearly constant at a constant temperature, and the release rate of fission gas in an isothermal experiment should be proportional to the amount of precursor halogen in the sample.

In order to study in detail the release behavior of xenon after its production by decay of the precursor iodine and to ascertain the reality of the above hypothesis, we made post-irradiation experiments which were started either 40 min or 2 hr after 20 min irradiation of the samples. This procedure produced favorable experimental conditions for the study of the contribution of the precursor iodine to xenon release, there being present at the outset of the experiment a far larger quantity of iodine than of xenon in the sample.

II. EXPERIMENTAL

1. Preparation of Graphite Samples

The procedure adopted for sample preparation followed that of Yajima et al.(4) A mixture of 500 mg of natural graphite powder and 50 mg of...
UO₂ powder (particle size of both powders about 1 μ) was degassed for 10 hr at 1,100°C, sealed into a small quartz tube in vacuo and irradiated in the Japan Research Reactor-2 (JRR-2, 7 × 10¹⁴ n/cm²-sec thermal neutron flux) for 20 min. One end of the quartz tube wall was made thin so that it could be easily fractured by a breaker. The irradiated mixture was used as graphite sample from which fission gas was to be released. By this arrangement, most of fission products produced in the UO₂ powder (about 90%⁵) are recoiled into the surrounding graphite during irradiation and the fractional release of the fission gas from the natural graphite in post-irradiation annealing experiments below 1,000°C is at least one order of magnitude higher than that from UO₂.

2. Apparatus and Experimental Procedure

The irradiated sample was set in the apparatus shown in Fig. 1. The quartz tube (8) containing the sample was fractured by hitting it with the breaker (9) moved by means of a magnet outside the column; the furnace (6), heated beforehand, was lowered down to the position of the sample. The sample temperature was controlled by a PID-controller within ±1°C from the set temperature. Helium gas from the cylinder (1), purified in the device (5) by Cu-net at 300°C and by Ti-foil at 800°C, was used to carry the fission iodine and xenon released from the sample (flow rate, about 150 ml/min). A capillary was placed above the sample to prevent back diffusion of iodine and xenon released from the sample. To trap iodine and xenon in the carrier gas, a special silver-foil trap (6) heated at 300°C (10) and an activated charcoal trap (12) cooled with dry-ice-alcohol (13) were used, respectively. Both traps were replaced at pre-set intervals. The silver-foil traps were changed frequently to prevent contamination of the xenon released from the sample by xenon produced in the silver-foil by β-decay of the trapped iodine. The activities of iodine and xenon in the traps were measured by a multi-channel γ-ray spectrometer. To measure the residual amounts of iodine and xenon in the sample, it was ignited in O₂ gas stream at 1,000°C, which was passed instead of the He gas stream. An alkali trap (11) was placed between the silver-foil trap and the activated charcoal trap to remove the CO₂ gas resulting from the ignition, which would decrease the capacity of the activated charcoal to trap xenon.

III. RESULTS

First, a preliminary experiment was made to obtain quantitative data on xenon and iodine releases independently, and subsequently 4 main experiments were made.

1. Preliminary Experiment

The isothermal release rates of ¹³¹I and ¹³³Xe from the irradiated sample, cooled for 10 days
after irradiation, were measured at 1,000°C. The results are shown in Fig. 2. As reported by many workers, the release curves obtained do not show the time behavior predicted by simple diffusion model: an initially rapid and subsequently slow release was observed for both \(^{131}\text{I}\) and \(^{133}\text{Xe}\). The fraction released at 1,000°C, was greater for \(^{133}\text{Xe}\) than for \(^{131}\text{I}\), which is consistent with the result by Yajima et al. About 31% of \(^{131}\text{I}\) and 48% of \(^{133}\text{Xe}\) were released during the first 2 hr and only 4% of \(^{131}\text{I}\) and 3% of \(^{133}\text{Xe}\) in the ensuing 2 hr. The remaining fraction of \(^{131}\text{I}\), \(F(t)\), is expressed approximately by the following experimental equation applicable to the period between 1 and 10 hr:

\[
F(t) = 0.71 \exp(-3.1 \times 10^{-4} t),
\]

where \(t\): Time (min)
The difference between the observed data and the calculated values by Eq. (1) is less than 2%.

2. Experiment 1

An irradiated sample cooled for 2 hr after irradiation was heated at 1,000°C for 2 hr and cooled again for 10 days at room temperature. After this, an isothermal experiment was made on \(^{133}\text{Xe}\) release at 1,000°C. The release rate \(\phi(t)\) thus obtained is shown in Fig. 3, together with the cumulative release fraction. The meaning of this experiment will be explained in Sec. IV-1.

3. Experiment 2

Isothermal release rates of \(^{133}\text{Xe}\), \(^{135}\text{Xe}\) and \(^{135m}\text{Xe}\) from the irradiated sample, cooled for 40 min after irradiation, were measured for 9.4 hr

Fig. 2: Isothermal release of \(^{131}\text{I}\) and \(^{133}\text{Xe}\) at 1,000°C from sample cooled for 10 days

Fig. 3: Isothermal release of \(^{133}\text{Xe}\) at 1,000°C from sample previously heated for 2 hr at 1,000°C 2 hr after irradiation and cooled for 10 days

Fig. 4: Isothermal release rate of xenon at 1,000°C from sample cooled for 40 min
at 1,000°C. The respective fission yields of the three xenon nuclides by thermal neutrons is negligible compared with the cumulative fission yields of the precursor iodines $^{133}$I and $^{135}$I, which have half-lives of 20.8 and 6.7 hr., respectively. At the beginning of the experiment, therefore, there was a far larger quantity of precursor iodine than of xenon in the sample. During the experiment, xenon was released from the sample while it was produced within the sample. The progress of the reaction is represented by the solid lines in Fig. 4. The release rates of $^{135}$Xe and $^{135m}$Xe is seen to have decreased exponentially except in the initial stage of the experiment. The slopes of the curves in the region of exponential decrease were nearly the same as the decay constant of the precursor $^{135}$I. In the release curve of $^{133}$Xe, the release rate dropped sharply at first, then increased gradually and decreased again slowly.

4. Experiment 3

This experiment was similar to Experiment 2 except that the heating was suspended three times for 15 min. The results are shown in Fig. 5. Heating bursts were observed when the temperature was raised again to 1,000°C after the interruptions. About 1 hr after each burst, the release rates regained their previous trend curves. A similar phenomenon has been reported previously(11)-(13).

5. Experiment 4

Two irradiated samples cooled for 2 hr were heated for 2 hr at 800°C and 400°C, respectively. The fractions of release of $^{133}$I during the 2 hr heating were found to be 20.0 and 6.7%, respectively. The samples were further cooled for 10 days, after which, tempering experiments were made, in which the release rates of $^{133}$Xe were measured. The results are shown in Fig. 6 (curves A and B). For comparison, the result with a sample not heated previously but cooled for 10 days is also shown (curve C) in the figure.

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Fig. 5 Release rate of xenon in isothermal heating interrupted three times by interludes at room temperature

Fig. 6 Release rate of $^{133}$Xe in tempering, from samples previously heated for 2 hr at various temperatures 2 hr after irradiation and cooled for 10 days. (The precursor iodine released during the preliminary 2 hr heating was also taken into account as released fraction.)
IV. DISCUSSION

1. Rapid Release of Xenon Produced by Decay of Iodine

In Experiment 1, about 31% of the $^{131}$I must have been released during the preliminary 2 hr heating, this percentage being derived from the results of Preliminary Experiment. The $^{131}$I remaining in the sample after the preliminary heating changed to $^{133}$Xe during the second cooling period (10 days). (The amount of $^{131}$I which decayed to $^{133}$Xe during the preliminary 2 hr heating was less than 10%.) The results of Experiment 1 are again plotted in Fig. 7, where the solid line indicates the release of $^{133}$Xe in the second heating, and the two dotted lines reproduce the curves of Fig. 2 representing the release of $^{131}$I and $^{133}$Xe during the preliminary heating alone. In Fig. 7, it can be seen that the decay of $^{131}$I to $^{133}$Xe caused a rapid release of a certain fraction of the $^{133}$Xe within about 1 hr after commencement of the second heating. This can be taken to indicate that the reaction was a 'β-decay controlled process'.

Strictly speaking, however, there is a lapse in logic here, since in Experiment 1, the production of xenon occurred at room temperature while the release occurred at 1,000°C, whereas in conditions under irradiation the two reactions occur simultaneously at the same temperature. It may thus be inferred that it was the difference between the production temperature and the release temperature that had caused the rapid release in Experiment 1. In order to clear this doubt, in Experiment 2, the production and the release were made to occur simultaneously in a manner similar to conditions prevailing under actual irradiation. If the fractional release rate $\rho(t)$ in Experiment 1, which should represent the probability for $^{133}$Xe to be released expressed as a function of time elapsed after production, can be applied to $^{133}$Xe, $^{135}$Xe and $^{135m}$Xe releases in Experiment 2, and moreover, if $\rho(t)$ can be assumed not to change appreciably with the duration of the preliminary heating, the release rate of each xenon nuclide in Experiment 2 may be calculated with the equation

$$R(t) = \int_0^t \lambda_i N_i(t)\rho(t)\exp(-\lambda_x(t-t))dt,$$

where $R(t)$: Release rate of xenon at time $t_1$ (atoms/min)
$\lambda_i$: Decay constant of iodine (min$^{-1}$)
$\lambda_x$: Decay constant of xenon (min$^{-1}$)
$t_1$: Heating time (min)
$\rho(t)$: Probability that a xenon atom produced by β-decay of iodine trapped in a defect is released out in unit time from sample at time $t$ after production (fraction/min)
$N_i(t)$: Number of iodine atoms in sample at time $t$, expressed by
$$N_i(t) = N_i(0)F_i(t)\exp(-\lambda_it)$$

where $N_i(0)$: Initial number of iodine atoms in sample
$F_i(t)$: Residual fraction of iodine at time $t$.

Assuming the release behavior of $^{135}$I and $^{133}$I to be the same as that of $^{131}$I, $F_i(t)$ will be given by Eq. (1) for each iodine nuclide. The remaining amounts of $^{133}$I and $^{135}$I in the sample, $N_i(t=9.4\text{ hr})$, were directly determined from Experiment 2 by the method already described. Then, $N_i(0)$ and $N_i(t)$ were calculated by Eq. (3) for each iodine. (The effect of the precursors of iodine was neglected.) The release rates calculated by Eq. (2) are shown by the dotted lines in Fig. 4. They are in good agreement with the observed values except in the early stage of the experiment. (In this stage, the release of xenon produced during the 40 min cooling period occupied a significant part of the total release, in addition to the error due to the time limits in $F_i(t)$.)

All considered, $\rho(t)$ can be said to represent adequately the probability for xenon to be released.
from the sample after production through the decay of iodine in Experiment 2, so that in this case too, it may be considered to be in principle a ‘β-decay controlled process’.

In what was termed ‘β-decay controlled process’ in previous papers(10)–(13), however, it was postulated that the “rapidly released fraction”, which meant the fraction released within a few hours after production, occupied a major part of the total fraction released. Consequently, the ratio between the release and the production rates of xenon (the latter is proportional to the amount of precursor iodine) should always be nearly constant. There is however a weakness in this postulation. As shown in Fig. 3, p(t) was not negligible even at t = 10 hr and the cumulative fraction released was still increasing at this time. The ratio between release and production rates in Experiment 2, therefore, must gradually increase with lapse of time in the case of a xenon nuclide of long life such as 133Xe and 135Xe ($t_{1/2} = 20.8$ and 9.13 hr), while the ratio should be constant in the case of 135mXe ($t_{1/2} = 15.3$ min) because of its short life.

This estimation was directly verified from the result of Experiment 3 (Fig. 5). Each heating burst observed was obviously due to the xenon produced in the preceding interruption, and the peak-heights of these heating bursts, which should represent the “rapidly released fraction” after production, decreased slightly as the experiment advanced in the cases of 133Xe and 135Xe, while they were always constant in the case of 135mXe.

The release behavior observed in the isothermal experiment immediately after irradiation using an in-pile loop(2) had nearly the same characteristics as that observed in Experiment 2. Hence, in the in-pile isothermal experiment, the probability for xenon to be released after production by the β-decay of iodine should behave similarly in time as $p(t)$ observed in Experiment 1 although the absolute quantities need not necessarily be the same.

2. Origin of Rapid Release of Xenon

In previous papers(10)–(13), two possible origins of the rapid release of xenon were proposed: (1) the recoil energy imparted to the xenon atom by β-decay of the precursor iodine and (2) the change in nature of defects by changes brought to the trapped atom.

The recoil energy imparted to $^{133}$Xe by the β-decay of $^{131}$I (origin (1)) ranges from 0 to 12 eV (277 kcal/mol). Yajima et al.(10) calculated the activation energy of xenon release near 1,000°C from natural graphite to be less than 80 kcal/mol. It may thus be probable that a fraction of the xenon produced by β-decay of the precursor iodine trapped in the defects is released.

In Experiment 3, however, no release was detected at room temperature during the 10 days of the second cooling period although xenon can move through interlaminar space at room temperature(11). From this observation, it is considered that the xenon receiving the recoil energy cannot be released into interlaminar space: the xenon may possibly be displaced from its original lattice site by the recoil energy (the recoil energy is insufficient to make a displacement of carbon atom in lattice site because the displacement energy of graphite is about 25 eV(12)), but not to the extent of leaving the defect.

A part of the recoil energy will be used to displace the xenon and the residual energy (all of the recoil energy when the xenon is not displaced) will be dissipated into the surrounding lattice. Consequently, a limited region around the xenon may be subjected to rapid heating, which would bring about some annealing of the defect, and the activation energy for the release of xenon from the defect would be lowered. But we have found from application of Brinkman’s calculation(13) that the recoil energy is too small to anneal the defect.

The displacement of a trapped atom in the defect by the recoil energy may cause degradation of the defect, which would produce a change in the activation energy for the release of the trapped atom. While there are no available data on the recoil energy imparted to each xenon nuclide in Experiment 2, the recoil energy would differ according to the nuclide. Hence the probability of xenon atom displacement by the recoil energy, which should eventually correspond to the released fractions, would differ from nuclide to nuclide in Experiment 2. As already mentioned, the same value of $p(t)$, however, has been found applicable for the calculation of the release rate of the different xenon nuclides in Experiment 2. This indicates that the xenon release behavior could not be explained wholly from considerations of recoil energy alone, proposed as origin (1).

Hence, while we cannot yet affirm positively,
the principal cause of the rapid release of xenon might more plausibly be attributed to the change in the chemical nature of the trapped atom (origin (2))—namely by the change from halogen to inert gas, which should alter the interaction between the trapped atom and defect, and in turn modify the activation energy required for its release.

3. Determination of the Activation Energy Change by Decay of Iodine to Xenon

The very low activation energy of xenon diffusion through interlamellar space in graphite (11), the low defect concentration and the small particle size of natural graphite powder used in the present experiment will allow us to regard the release curve during tempering (e.g. Fig. 6) as a rough representation of the distribution of the activation energy required for the release of xenon atoms trapped in the defects (see Ref. (14)). In Experiment 4 (Fig. 6), it is seen that a higher preliminary heating temperature is conducive to a smaller fraction of release in the lower temperature region, and some release is seen to have taken place below the preliminary heating temperature. This phenomenon can be considered to suggest that a defect requiring a relatively high activation energy for iodine release will similarly require a relatively high activation energy also for the release of xenon, although to a somewhat lower extent. This means that the change in activation energy accompanying the decay of iodine to xenon will not be random but rather a fixed value.

Iwamoto et al. (11) analyzed the release behavior of fission gas from nuclear fuel during and after irradiation using Primak's model (16), which is a mathematical model representing the annealing rate of defects distributed continuously in terms of activation energy required for the annealing, on the assumption that the fission gas is released from the defect by the annealing, and released straight out of the fuel without any retrapping by another defect, and that the activation energy is the same for both iodine and xenon. Neglecting this second assumption but utilizing the same model, we shall determine the amount of the change in the activation energy: we take an equivalent rectangular spectrum between $e_1$ and $e_2$ as the initial distribution of the activation energy required for the release of trapped atoms. During isothermal heating, an atom trapped in a defect corresponding to an activation energy lower than $e$, given by the following Eq. (4), is assumed to be released. We here neglect the effect of diffusion:

$$e = RT \ln (\beta_0 t),$$

(4)

where $R$ is the gas constant, $T$ the absolute temperature and $\beta_0$ a constant having the dimension of frequency. The fraction $F(t)$ remaining trapped is expressed by

$$F(t) = \frac{e_2 - e}{e_2 - e_1},$$

or

$$F(t) = -\frac{2.303 RT}{e_2 - e} \log_{10} t$$

$$+ \frac{e_1 - 2.303 RT \log_{10} \beta_0}{e_2 - e_1}.$$  

(5)

As indicated by Eq. (6), $F(t)$ is a linear function of the logarithm of heating time. The fractions remaining trapped in Preliminary Experiment and in Experiment 1 are plotted in Fig. 8 against the logarithm of heating time to determine $e_1$ and $e_2$ in each experiment. We choose the value of $6 \times 10^4 \text{min}^{-1}$ for $\beta_0$, as derived by Iwamoto (16), for both iodine and xenon.

![Fig. 8 Determination of ranges of energy spectra](image)

For iodine in Preliminary Experiment, the activation energies of 50.8 and 109.1 kcal/mol for $e_1$ and $e_2$ give the best results. In Experiment 1, during the preliminary 2 hr heating at 1,000°C, iodine of activation energy below 69.1 kcal/mol, calculated by Eq. (4), would be released. Accordingly, after the preliminary 2 hr heating, iodine in the activation energy range from 69.1 to 109.1 kcal/mol must remain in the sample. On the other hand, for xenon in Experiment 1, the activation energies of 58.9 and 101.1 kcal/mol are
found to be the best suited for $\varepsilon_1$ and $\varepsilon_2$. Consequently, it will be reasonable to expect that the activation energy for release would be lowered by about 9 kcal/mol by the decay of iodine to xenon. This value is supported by the result shown in Fig. 8 for xenon release in Preliminary Experiment, in which the activation energies of 40.0 and 98.3 kcal/mol were obtained for $\varepsilon_1$ and $\varepsilon_2$. These values were both about 11 kcal/mol lower than the corresponding values for iodine in Preliminary Experiment. Thus, the release behavior of xenon in Experiments 1 and 2 can be satisfactorily explained by assuming that the activation energy would be lowered by roughly 10 kcal/mol through the decay of iodine to xenon.

V. Conclusion

Several post-irradiation experiments were performed on the release of fission xenon from natural graphite powder at 1,000°C soon after irradiation with UO$_2$ powder. It was found that decay of precursor iodine to xenon induced the rapid release of a certain fraction of the xenon produced, while the remaining fraction was released gradually. The rapid release is considered to be due mainly to change in the chemical interaction between the defects and the atoms trapped therein (iodine or xenon).

Taking an equivalent rectangular spectra of activation energies required for the release of atoms trapped in the defects, the release behavior of xenon can be explained by assuming that the activation energy is lowered by about 10 kcal/mol by the decay of iodine to xenon.

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References