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PAGE 1 OF 27

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ATOMIC ENERGY RESEARCH DEPARTMENT
NORTH AMERICAN AVIATION, INC.
P. O. BOX 309 DOWNEY, CALIFORNIA

SUBMITTED: MARCH 25, 1953

ISSUE DATE

JUNE 17, 1953

CONTRACT AT 11-1-GEN-8

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2033

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NAA-SR-232
Page 3

ACKNOWLEDGEMENT

We are indebted to the Los Alamos Scientific Laboratory, especially to Drs. David and Jane Hall and Dr. L. D. P. King, for providing the neutron irradiations which made these experiments possible.

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TABLE OF CONTENTS

	Page No.
Abstract	5
I. Introduction	6
II. Experimental Details	7
III. Experimental Results	10
IV. Discussion	12
V. Conclusions	14
References	27

LIST OF FIGURES

1. Per cent of Total Activity Lost During Heating	15
2. Per cent of Barium Lost During Heating	16
3. Per cent of Strontium Lost During Heating.	17
4. Furnace Assembly.	18
5. Flow Chart of Procedure Used for Obtaining Data at 1880°, 2000°, 2100° and 2200° C	19
6. Cross Section of Mounted, Total Activity Sample.	20
7. Per cent of Total Activity Lost During Heating at 2000° C	21
8. Per cent of Zirconium Lost During Heating at 2200° C.	22
9. Semilogarithmic Plot of the Time for Diffusion of a Fixed Fraction of Activity <u>vs</u> $1/T$, for Barium	23
10. Semilogarithmic Plot of the Time for Diffusion of a Fixed Fraction of Activity <u>vs</u> $1/T$, for Strontium	24
11. Final Slopes of Diffusion Curves from Figure 1 Referred to a Common Origin	25
12. Semilogarithmic Plot of the Time for Diffusion of a Fixed Fraction of Activity <u>vs</u> $1/T$, for Total Activity	26

ABSTRACT

The diffusion of total fission product activity and separated Ba, Sr and Zr activities, from uranium-impregnated graphite which had been exposed in the Los Alamos Fast Reactor, was investigated at temperatures from 1880° to 2200° C. Experimental equipment and procedures used were improvements of those reported in NAA-SR-72.

At 1880° C, more than 99 ⁷⁰per cent of the Ba and Sr activities diffused out of the graphite within 20 ^{minutes} of heating; at 2100° C, more than 99 ⁷⁰per cent diffused within 5 minutes. Only 2 ⁷⁰per cent of the Zr activity diffused out of the graphite after 4 ^{hr} hours at 2200° C. The differences in diffusion rates between ^{Zr}zirconium and the other two elements are in accord with known volatilities of their carbides. Approximately 85 ⁷⁰per cent of the total fission product activity diffused out after 4 ^{hr} hours at 2200° C, compared with 60 ⁷⁰per cent after the same time at 1880° C. These findings may be considered indicative, in a qualitative way, of the extent of decontamination by diffusion in homogeneous graphite fuel pellets of the size of the present samples, operating at high temperatures.

Desirable extensions of the investigation to include observations on other separated activities, and on the effects of varying experimental conditions, are briefly discussed. (auth)

This report is based on studies conducted for the Atomic Energy Commission under Contract AT-11-1-GEN-8.

I. INTRODUCTION

The study of the diffusion of fission fragments from uranium-impregnated graphite, which was reported in NAA-SR-72,¹ has been extended to the temperature range 1800 to 2300° C. The results of a preliminary series of experiments at these temperatures are presented in the present report.

Interest in the diffusion of gross fission products arose in the course of a design study of a high temperature reactor using uranium-impregnated graphite fuel blocks. Such diffusion into the coolant stream would present problems of decontamination either for discard or recirculation of the coolant. Fission fragments which act as reactor poisons might be removed some extent, which would have a bearing on reactor control. Likewise, recovery of the fuel for re-use might be facilitated if there is considerable diffusion of gross activity.

Experimental results for diffusion at 1560°, 1660° and 1760° C were reported in Ref. 1. A brief summary of these data will be presented at this point in order to provide a background for the work presented later in this report.

A. Pore Diffusion

Gaseous diffusion of fission fragments through the pores of graphite at high temperature was found to be extremely rapid compared to diffusion through a solid lattice or along grain boundaries.

B. Diffusion of Total Activity from Uranium-Impregnated Graphite

Samples of irradiated uranium-impregnated graphite were heated at 1560°, 1660° and 1760° C for various lengths of time. The percentages of the total activity lost as a function of heating time were plotted. (These are compared with the percentage lost at high temperatures as covered in this report in Fig. 1). The data were describable by an equation of the form

$$te^{-E/kT} = \text{a constant}$$

where

E = Activation energy
k = Boltzmann constant
T = Absolute temperature
t = Time at temperature

Sufficient data were available to compute the activation energy for diffusion of total fission activity from the graphite. This activation energy was found to be 20,700 cal/mole.

C. Diffusion of Ba¹⁴⁰ and Sr⁸⁹

Radiochemical separations of barium and strontium activities were made for all the samples and the percentages of activity diffusing were plotted as a function of heating time. (These are compared with diffusion data at high temperature in Figs. 2 and 3). Activation energies of 68,300 cal/mole for barium and 26,400 cal/mole for strontium were found.

D. Fraction of the Activity in the Graphite as a Function of Density of Impregnation

It was found that approximately 65 per cent of the fission activity was in the graphite crystal structure. This was determined by leaching the uranium from the graphite with HNO₃ (99.5+ per cent efficiency), burning the graphite at 800° C in O₂, dissolving the residue in HNO₃, and counting aliquots of leach solution and graphite solution. Densities of impregnation ranged from 3.5 to 350 milligrams of U/cc of AGOT-KC and 0.8 to 65.4 milligrams of U/cc of EBP. The percentage of activity in the graphite crystals was found to be independent of the density of impregnation.

II. EXPERIMENTAL DETAILS

A. Sample Irradiation

For the higher temperature diffusion studies, a block of graphite impregnated with normal uranium converted to the oxide,² was cut into cylinders 3/8 inch in diameter and subsequently into wafers 1/16 inch thick. The graphite had been impregnated with approximately 100 milligrams of U/cc of graphite, thus yielding about 11 to 11.5 milligrams of uranium per wafer. The wafers

were prepared before irradiation in order to avoid the necessity of cutting radioactive material. (In the previous work, wafers were cut from cylinders after irradiation.) The wafers were numbered and weighed. They were then sent to Los Alamos where they were irradiated in the thermal column of the Fast Reactor for a total of 1670 kilowatt hours. About 1.5×10^{12} fission/cc of graphite occurred during the irradiation, producing sufficient fission activity in each wafer for convenient analysis.

The activity of each wafer a week after irradiation was about eight microcuries and after 43 days, the longest period of decay before a heating cycle, the activity had dropped to less than 0.1 microcurie.

B. Heating Procedures

After 3 weeks of radioactive decay, several wafers were heated in a special vacuum furnace at a controlled temperature, a wafer being removed after each predetermined temperature interval of 10 minutes, 30 minutes, 1 hour, etc.

The vacuum furnace (Fig. 4) consists of a helical graphite heating element surrounded by tantalum shields. A detailed description is given in Ref. 3. An improvement for handling samples was added to the furnace assembly (Fig. 4) where after raising a small platform on which the wafers rest in the zone of definite temperature, the top wafer can be knocked to one side of the furnace by a tantalum vane which also serves as a radiation shield, using a magnet to control the movement. This removal procedure takes only a few seconds. The stack of wafers is then returned into the zone of definite temperature and heating continued. All this can be done without change of temperature, vacuum conditions, etc.

Since each wafer was numbered, reference was made to the heating time. This quick removal from the heated zone results in more accurate timing and permits heating intervals as short as 5 minutes with only a few per cent error in measuring the interval.

A series of wafers was heated at 1880°, 2000°, 2100° and 2200° C. Attempts to heat the wafers at 2300° C resulted in the generation of large amounts of gas which sustained an arc between the graphite helix and shield.

Since uranium carbide decomposes in vacuo at about 2250°C ,⁴ this appears likely to be the cause of the arcing.

C. Sample Preparation

The handling procedure followed after heating the wafers to the desired temperature is similar to that given in Ref. 1. A flow diagram for the procedure is shown in Fig. 5. The wafers which were heated for the various intervals and one or two unheated wafers used for control were burned individually in small platinum boats at 800°C in an oxygen atmosphere to oxidize the graphite. The wafers were weighed before burning and the residue weighed after burning to obtain the uranium content in the form of U_3O_8 . The residue was then dissolved in HNO_3 , the boat thoroughly rinsed with HNO_3 and H_2O and the solution diluted to 50 milliliter volume for analysis.

1. For Total Activity Analysis - An aliquot of 1 cubic centimeter each of solution was evaporated on a 1-inch watch glass under an infra-red lamp. The glass was then mounted on a 3-1/4 inch by 2-1/2 inch cardboard card with a centered 1-1/16 inch hole. The glass was covered with a thin film of Kodapak II. The card was pressed down over the glass with the film tightly stretched. The card was then backed with scotch tape to hold everything in place (Fig. 6). The sample was counted by a thin end window Geiger-Mueller tube on a Berkeley Decimal Scaler, Model 2000.

Coincidence corrections were made, but corrections for absorption or back scattering were omitted since all samples were mounted in the same manner with approximately the same amounts of solids on the glass. Comparisons of results were made between the unheated control sample and the heated samples, thus cancelling any errors due to back scattering, absorption, etc. The half-life of the composite of fission products for the first heating, 20 days after irradiation, was approximately 10 days and the half-life of the composite of fission products for the last heating, 43 days after irradiation, was about 25 days. Therefore, corrections for decay were not necessary because the control and heated samples were counted within a few hours of each other.

2. For Ba^{140} , Sr^{89} and Zr^{95} Analysis - An aliquot was taken for radiochemical analysis of Ba^{140} and Sr^{89} and one for Zr^{95} . The chemical

separations followed were those described in CN-2815.⁵ The precipitates were filtered on prepared and weighed filter papers. These were reweighed to obtain the chemical yields. Each filter paper was placed on a one inch watch glass and mounted in the same manner as samples for total activity measurements. After corrections for the chemical yields, aliquot portions, sample weights or uranium content, the barium and strontium activities were compared for loss of activity due to the different heating times. Since the heated samples were compared with unheated or control samples all mounted in the same manner and counted at the same time, the effects of absorption, back scattering, etc., cancel out. Since Ba^{140} , Sr^{89} and Zr^{95} have half-lives respectively of 12.8 days, 53 days and 65 days, a difference in counting rate due to not more than two hours delay between counting the control and samples was insignificant. Hence corrections for decay were not necessary.

III. EXPERIMENTAL RESULTS

As a result of the data obtained in the earlier diffusion studies,¹ it was apparent that shorter time intervals would be desirable during the first hour of heating. Twelve to fourteen wafers were heated, one being removed at intervals of 5, 10, 15, 20, 40 and 60 minutes and at less frequent intervals thereafter for 4 or 5 hours.

The wafers were permitted to decay for about 3 weeks before they were heated in the vacuum furnace. The heatings were made after the following decay times:

<u>Temperature</u>	<u>No. of Days After Irradiation</u>
1880° C	20
2000°	21
2100°	23
2000°	34
2200°	42
2300°	43

At all of these temperatures, uranium oxide is transformed to uranium carbide.

The per cent of activity lost was obtained by the following calculation:

$$\% \text{ Loss} = \frac{A_c - A_h}{A_c} \times 100$$

where A_c = activity of the control sample

A_h = activity of the heater sample

The data obtained for the per cent of activity lost at 1800°, 2000°, 2100°, and 2200° C are presented in Fig. 1. The data are consistent with the findings of the earlier experiments.¹ Approximately 80 per cent of fission products can be removed by heating at temperatures up to 2200° C. The data obtained were for 4 hours of heating only. However, from the slope of the curve, it appears that very little more would diffuse as a result of longer heating.

It is interesting to note that the percentage of activity lost during the 2200° C run was slightly less than that lost during the heating at 2100° C. This may be due to the longer decay period before heating in the vacuum furnace took place - 23 days as compared to 42 days - indicating that the fission products which remain in the uranium-carbide graphite matrix tend to be those of longer half-life.

This was evident also when a second series of wafers was heated at 2000° C. (The heating at this temperature was repeated because the first series yielded a peculiar diffusion slope for the first 2 hours. It was thought that perhaps the temperature of the furnace might have been slightly lower during this time interval. To check this, the second series of wafers was heated at 2000° C.) The comparison of the same two sets of data is presented in Fig. 7. The slope of the curve during the first 2 hours of the second heating does indicate that the premise of poor temperature control during the first run was correct. However, after 4 hours at temperature, approximately 60 per cent of the activity diffused during the second heating for the samples which had "decayed" for 34 days, compared to 80 per cent for samples cooled for 21 days. This difference also lends evidence to the supposition that the fission products which tend to remain are some of the longer lived ones.

The radiochemical separations of barium and strontium were carried out only on the 1880° and 2100° C runs. It appears that no further information could be gained by analysis of the 2000° or 2200° C heatings. The per cent loss of activity for barium is presented in Fig. 2, and for strontium, in Fig. 3. Ninety-nine per cent of the activity diffused in 20 minutes for barium and in 10 minutes for strontium, at 1880° C, and in less than 5 minutes for both activities at 2100° C. The carbides of both barium and strontium are known to be volatile at these temperatures in vacuum.⁴ This may account for the rapid diffusion.

It was decided to check the loss of zirconium activity at the highest temperature, 2200° C. Zirconium forms a carbide which melts at a temperature considerably higher than this.⁴ Analysis of the zirconium loss is given in Fig. 8. Approximately 2 per cent had diffused after 4 hours of heating. The slope of the curve indicates that the zirconium activity would not have diffused to any greater extent at temperatures of 2200° C or lower, even after considerably longer heating periods.

IV. DISCUSSION

The experimental results for barium and strontium described above appear to be consistent with those found at lower diffusion temperatures, as shown in Figs. 2 and 3. Fig. 9 shows a plot of the logarithm of the diffusion rate of barium against the reciprocal of the absolute temperature, whose slope is based on the value of the Ba diffusion activation energy, 68,300 cal/mole.¹ A similar plot for strontium (activation energy = 26,400 cal/mole¹) is shown in Fig. 10. The times required for 20, 40 and 60 per cent of the barium and strontium activities to diffuse were selected for the plotting. It had been reasoned in the earlier work¹ that diffusion in this range was dominated by the diffusion from the uranium particles rather than from the graphite crystallite structure. A single diffusion process would be indicated by a straight line. For both the barium and strontium activities, the data for the higher temperature do not fall on the straight lines as determined by the data for the lower temperatures. An examination of the diffusion curves plotted in Figs. 2 and 3 shows that for both barium and strontium, 99 per cent of the activities diffused within

5 minutes at 2100° C. Data were not obtained for shorter heating periods. If a second diffusion process played a significant part in removing the last few per cent of diffusing material, the data would not be expected to fall on the same curves and a different activation energy would result. This may be the explanation for the non-conformity of the data at the higher temperatures.

The activation energy for the diffusion of total activity was obtained from the final slopes of the diffusion curves for the lower temperatures¹ and was found to be = 20,700 cal/mole. Fig. 11 shows the final slopes of the diffusion curves as given in Fig. 1, referred to a common origin. Following the procedure of Ref. 1, the logarithm of the diffusion rate of total activity is obtained from the slopes of Fig. 11, for plotting against the reciprocal of the absolute temperature as given in Fig. 12. Since the diffusion at the higher temperature apparently reaches a limit of approximately 80 per cent, the activation energy would not be expected to be the same as for the lower temperatures. This would account for the difference in slopes shown in Fig. 12. There no longer exists a quasi-steady state in which the concentration gradient of the diffusing particles is constant.

Also it should be realized that diffusion rates may be strongly sensitive to specimen configuration and size, temperature distribution and other environmental factors which were not carefully studied; and that the data in this report are intended to represent only a qualitative measure of the course of the diffusion in situations other than the specific ones studied.

The behavior of zirconium may be understood from the low volatility of ZrC .⁴ Since the uranium was present as oxide when fission occurred, there is some possibility that zirconium formed in fission could be either metal or oxide. In either of these cases, there would be a time interval, during the subsequent heating and conversion to carbide, in which the zirconium would be present in the form of the metal. The metal is more volatile⁴ than either the dioxide⁶ or carbide. It is perhaps this transient volatility which accounts for the small loss of zirconium activity (Fig. 8).

Although an improvement in techniques and an extension of experiments to temperatures higher than those of Ref. 1 has been achieved, the present study represents only an exploratory survey of the role of fission product diffusion in the use of homogeneous graphite reactor fuel at high temperatures.

An experimental study of the diffusion of xenon from such fuel has been made,⁷ which indicated that even at temperatures near 1500° C the diffusion of xenon from graphite is too slow to effect more than fractional removal of this neutron absorber. It would be of interest to investigate the diffusion of other activities such as the rare earths, and iodine (a precursor of xenon). It would also be of value to study the effect of irradiation on the diffusion, by exposing the homogeneous graphite fuel to radiation while maintaining it at high temperature.

V. CONCLUSIONS

The following results were obtained experimentally during the present study of the diffusion of barium, strontium, zirconium and total fission product activities, at temperatures from 1880° C to 2200° C:

1. More than 99 per cent of both barium and strontium activity diffused from the samples within the first 20 minutes of heating at 1880° C; and within the first 5 minutes, at 2100° C.
2. Approximately 2 per cent of the zirconium activity diffused at temperatures up to 2200° C, for a heating period of four hours. The slope of the diffusion curve indicates that very little more, if any, would diffuse for longer heating times.
3. For samples heated after 3 weeks of radioactive decay, approximately 80 per cent of total fission product activity diffused upon heating at 2200° C, with very little more lost up to 2200° C.
4. If a longer period of radioactive decay occurs before heating, less activity diffuses. This may indicate that those elements which remain are predominantly those which have longer half-lives.

The information obtained in this series of studies indicates that more data on the diffusion of fission products would be useful in evaluating homogeneous graphite fuel elements for high temperature reactor application. Among the specific problems are how other individual fission elements diffuse, especially bromine, iodine, xenon, krypton and the rare earths; and how the diffusion is affected if the impregnated graphite is at a high temperature while fission is occurring.

15

Figure 1.
Per Cent of Total Activity Lost During Heating

16

Figure 2.
Per Cent of Barium Activity Lost During Heating

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Figure 3.
Per Cent of Strontium Activity Lost During Heating

Figure 4.
Furnace Assembly

Figure 5.

Flow Chart of Procedure Used for Obtaining
Data at 1880°, 2000°, 2100°, and
2200° C

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NAA-SR-232
Page 20

20

Figure 6.
Cross Section of Mounted, Total Activity Sample

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Figure 7.

Per Cent of Total Activity Lost During Heating at 2000° C

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22

Figure 8.

Per Cent of Zirconium Activity Lost During Heating at 2200° C

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Figure 9.

Semilogarithmic Plot of the Time for Diffusion of a
Fixed Fraction of Activity vs 1/T, for Barium

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Figure 10.

Semilogarithmic Plot of the Time for Diffusion of a
Fixed Fraction of Activity vs $1/T$, for Strontium

25

Figure 11.
Final Slopes of Diffusion Curves from Fig. 1 Referred to a Common Origin

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Figure 12

Semilogarithmic Plot of the Time for Diffusion of a
Fixed Fraction of Activity vs 1/T, for Total Activity

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