Diffusion of Uranium Through Graphite

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Diffusion rates of uranium through graphite were determined in the temperature range of 3,000° to 4,350°F. The diffusion couples consisted of sintered UC_2 disks in contact with graphite rods. The observations indicated two distinct types of uranium transport which could be associated with volume diffusion and with migration along pores respectively.

Volume diffusion was characterized by steep concentration gradients and shallow penetration. The diffusion coefficient D_v, in sq. cm./sec. between 3,300° and 4,250°F., is given by an equation. Above 4,250°F. incipient melting of the UC_2 was evident and the diffusion coefficients were much higher than those given by the equation.

As an example of the penetration resulting from volume diffusion, calculations show that, after 1,000 hr. at 4,200°F. the uranium concentration at 0.1 cm. from the interface will be 1,000 mg./cc., compared with 10,000 mg./cc. for pure UC_2.

Pore migration resulted in uranium penetration far beyond that arising from volume diffusion at equivalent temperatures and diffusion times. However, uranium concentrations were very small compared with those corresponding to volume diffusion. Pore migration is strongly temperature dependent.

To estimate the practical importance of pore migration, the uranium flow through a graphite wall at 3,000°F. was measured. With a wall thickness of 0.32 cm., the average flow per unit area was 0.015 mg./(sq. cm.)/(hr.) for a 40-hr. test.

Graphite was used in the first nuclear reactor because it is a good moderator and because large amounts of pure graphite were obtainable. The early reactors were designed to operate at relatively low temperatures. However, graphite also is very well suited as a moderator and structural material for power-producing reactors. Except for its poor oxidation resistance, it has generally attractive properties for high-temperature service—high thermal conductivity, good strength, and excellent resistance to thermal shock and to creep.

There are several important areas in which more data are needed to extend the use of graphite in power reactors. Among these is the need for information on its compatability with nuclear fuels at high temperatures.

Uranium dioxide and uranium dicarbide are two high-melting fuel compounds which have been considered for use in contact with graphite. As the oxide reacts with graphite at high temperatures to form the carbide, uranium dicarbide appears to be the more suitable compound to use with graphite.

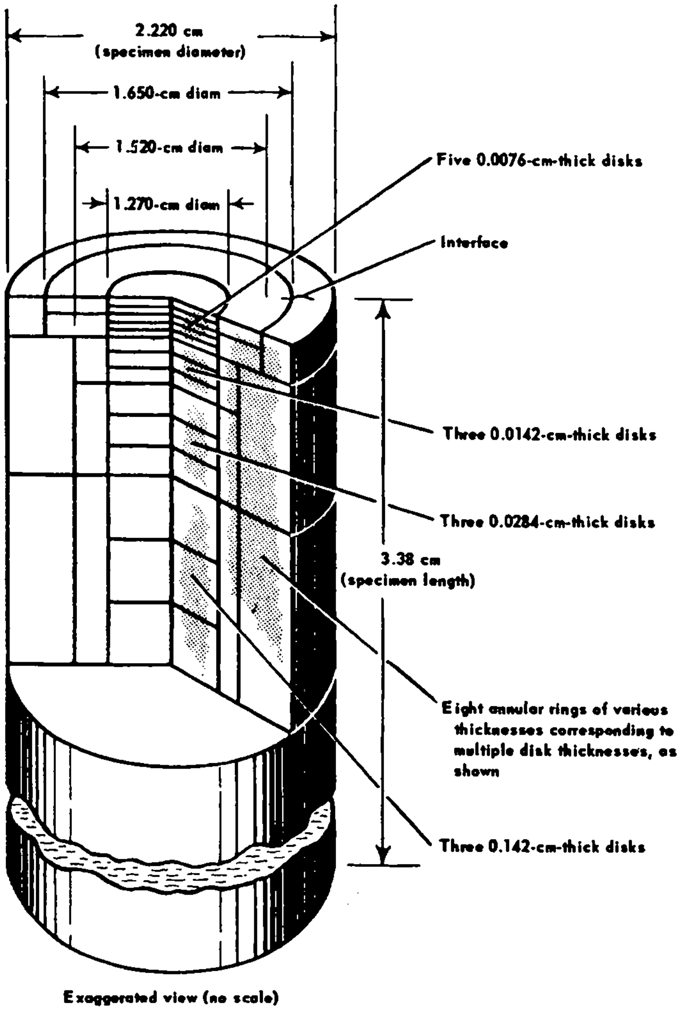
Uranium dicarbide, UC_2, is known to be relatively unreactive with graphite up to its melting point, but few data on the diffusion of uranium from UC_2 into graphite have been reported. In fact, prior to this investigation, the only systematic study of the problem appears to be that made by Loftness (*1*).

Loftness measured the diffusion of uranium from UC_2-impregnated graphite into pure graphite at temperatures between 3,900° and 4,700°F. The impregnated graphite had a uranium concentration of approximately 250 mg./cc. Loftness concluded that volume diffusion was the only important diffusion mechanism contributing to his results.

The present study deals with diffusion from massive UC_2 into graphite. The results should be applicable to a variety of reactor-design problems.

MATERIALS

Synthetic graphite, designated type AGOT by The National Carbon Company, was used in the experiments. This material, made and purified for use in reactor applications, is otherwise a typical high-grade commercial graphite, prepared by heating a mixture of petroleum coke and coal-tar pitch to graphitizing temperatures.



Exaggerated view (no scale) to show relative locations

Fig. 2. Cutting scheme for diffusion couples.

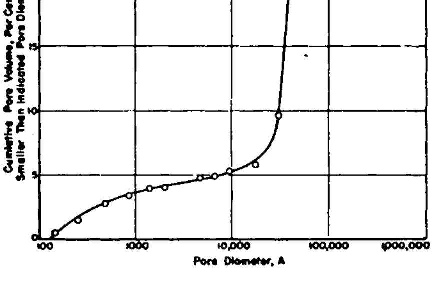


Fig. 1. Pore-size distribution in AUF graphite.

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Despite multiple impregnations by pitch to increase the density, the void content ranges from 23 to 27% of the total volume. The pores are largely interconnected and permeable to gases. Figure 1 gives the mercury pore spectrum of AUF graphite, which is structurally similar to AGOT. The grains of AUF and AGOT graphites range from 1 to 20 μ and contain crystallites 2,000 Å. long in the direction of the basal plane; the majority of the pores, 80%, are in the same size range as are the grains.

Massive uranium dicarbide was crushed in a steel mortar to pass a 200-mesh sieve. All handling of the UC_2 was performed under carbon tetrachloride to prevent oxidation. Chemical analysis of the UC_2 showed 8.44% carbon, compared with the theoretical carbon content of 9.16%.

To prepare specimens, the graphite was machined into cylinders 3.8 cm. long and 2.2 cm. in diameter. The axes of the cylinders were parallel to the direction of extrusion. End surfaces were polished with 600-grit silicon carbide abrasive paper.

The UC_2 powder and 0.75 wt. % paraffin, added as a carbon tetrachloride solution, were thoroughly mixed, and then the carbon tetrachloride was evaporated in air. The resultant powder was pressed at 22,600 lb./sq. in. into disks which were sintered in vacuum at 4,200°F. for 1½ hr. One side of each disk was polished under carbon tetrachloride with 600-grit SiC paper. The finished disks were 0.3 cm. thick and 1.8 cm. in diameter. They were stored under carbon tetrachloride until used.

EXPERIMENTAL PROCEDURES

Each diffusion couple consisted of a sintered uranium carbide disk resting on one end of a graphite cylinder. The UC_2 was held in place temporarily by an organic adhesive which carbonized during heating. The diffusion couple was placed in a carbon-tube resistor furnace with the axis of the cylinder vertical and heated to maximum temperature in about 2 hr. Furnace temperatures were read to ±20°F. with a Leeds-Northrup optical pyrometer. Corrections were made in the temperature readings for losses in the glass lens and mirror used in sighting. The furnace was cooled overnight to room temperature before the couple was removed.

Argon entering the furnace was passed over heated titanium granules to remove nitrogen and was dried with anhydrous magnesium perchlorate. Traces of carbon monoxide were present in the furnace atmosphere.

After each diffusion couple was removed from the furnace, the UC_2 disk was detached and the graphite was sectioned on a lathe in accordance with the diagram in Figure 2. In every case when the couple was separated, part of the graphite stuck to the UC_2, leaving an irregular graphite surface. Therefore the distance of each cut from the original interface was measured with reference to the periphery of the graphite face, which was undamaged. As the UC_2 disks were smaller in diameter than the graphite rods, the peripheral area was not in contact with UC_2 during heating.

The cutting operation permitted an accuracy of ±0.0005 cm. in measuring the thickness and penetration distance after each cut. Penetration distance was recorded as the distance between the original interface and the midpoint of the cut.

Material shaved off by the lathe was collected carefully and its uranium content analyzed by a fluorophotometer (*2*). The accuracy of the analyses was ±10% of the uranium content. The center cuts shown in Figure 2 were used to obtain concentration-penetration curves. The outer cuts were analyzed only to determine whether radial diffusion had an effect on the uranium concentrations resulting from linear diffusion.

TABLE 1. URANIUM CONCENTRATION-PENETRATION DATA

	Specimen 23, 3,800°F., 16 hr.		Specimen 32, 3,600°F., 8 hr.	
Cut	Uranium concentration, mg./cc.	Depth of cut, cm.	Uranium concentration, mg./cc.	Depth of cut, cm.
1	1,200	0.004	73.0	0.004
2	110	0.011	2.0	0.011
3	6.1	0.019	0.83	0.019
4	3.6	0.027	0.46	0.027
5	2.2	0.034	0.31	0.034
6	1.8	0.045	0.41	0.045
7	0.84	0.061	0.36	0.061
8	0.64	0.076	0.41	0.076
9	0.46	0.099	0.57	0.099
10	0.40	0.130	0.54	0.130
11	0.36	0.160	0.39	0.160
12	0.24	0.252	0.16	0.252
13	0.11	0.405	0.01	0.405
14	0.03	0.558	0.006	0.558
—	—	—	0.006	0.611

	Specimen 19, 4,350°F., 2 hr.		Specimen 15, 4,250°F., 12 hr.	
Cut	Uranium concentration, mg./cc.	Depth of cut, cm.	Uranium concentration, mg./cc.	Depth of cut, cm.
1	N.D.*	0.004	N.D.	0.004
2	920†	0.011	850	0.011
3	973	0.019	115	0.019
4	600	0.027	3.3	0.027
5	254	0.034	2.8	0.034
6	50	0.042	2.1	0.042
7	5.3	0.050	2.5	0.050
8	2.9	0.058	2.6	0.058
9	2.6	0.069	2.3	0.069
10	2.0	0.079	1.8	0.079
11	1.5	0.092	1.7	0.092
12	0.97	0.117	1.7	0.117
13	1.1	0.140	1.2	0.140
14	0.88	0.170	1.3	0.170
15	1.08	0.261	1.1	0.261
16	0.61	0.413	0.73	0.413
17	0.55	0.505	0.67	0.505

*N.D. = no determination.

†This point was not shown in Figure 3 as it was in obvious error and is less reliable than deeper points.

Complete tabular data are filed as document 4830 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

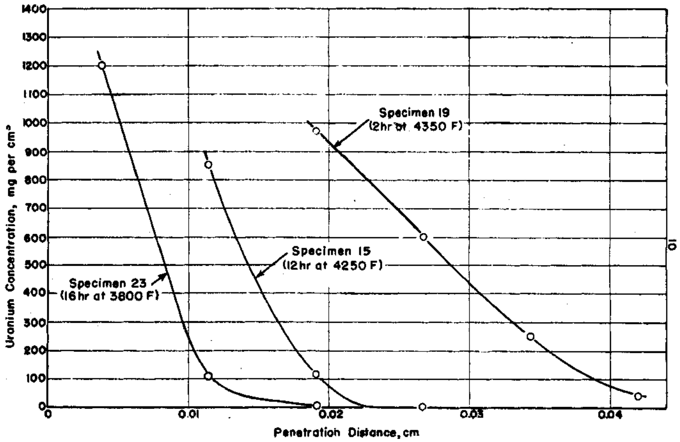

Fig. 3. Representative concentration-penetration curves for shallow penetration.

RESULTS AND DISCUSSION

The heating conditions and concentration-penetration data for the experiments are shown in Table 1. Representative penetration curves for the first few cuts are shown in Figure 3. The curves for specimens 15 and 23 in Figure 3 are typical of those obtained at and below 4,250°F. Experiments at 4,300° and 4,350°F. produced curves similar to the one shown in Figure 3 for specimen 19.

Figure 3 shows a strong dependence of penetration distance on temperature. At 4,350°F., which is near the melting point of uranium dicarbide (*3*), the penetration was 0.04 cm. after only 2 hr., and heating for 16 hr. at 3,800°F. produced a penetration of less than 0.02 cm.

An unusual feature of the results was the appearance of two types of concentration gradients: (1) large gradients near the interface, as shown in Figure 3, and (2) small gradients at deeper penetrations. The two types of gradients are illustrated in Figure 4 for specimen 15. Even though the concentrations at the deeper penetrations were small, they were significant. The data are plotted in Figure 4 as log concentration vs. distance only for convenience; the straight lines should not be taken as an indication that linear relationships were obtained with this type of plot.

The dependence of concentrations near the interface on depth and time was found to be consistent with diffusion equations and sufficiently well defined to permit the determination of diffusion coefficients. However, the data were not sufficient to answer secondary questions, such as whether the diffusion coefficient in the carbide was the same as in the graphite where the uranium concentration was much lower. Accordingly, analysis of the data was based on the equation

$$C(x, t) = \frac{C_0}{2}\left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

where $C_0 = 10{,}000$ mg./cc.

This equation is applicable to the results of the present investigation provided that (1) there is no very large dependence of the diffusion coefficient on concentration, (2) no appreciable change in concentration occurs at the extremities of the couple, and (3) the effect of radial diffusion is negligible. Auxiliary experiments showed that the diffusion times used in this work were sufficiently short to prevent depletion of uranium at the outer extremities of the UC_2 disks. Also the center cuts which were taken for analysis were shown to be close enough to the center line so that radial diffusion might be ignored.

In accordance with the foregoing equation, the concentration-penetration data were plotted as 100 C/C_0 on the probability scale vs. $x/(t)^{1/2}$ on a linear scale. Straight lines were drawn through the data for the shallow penetrations so as to intersect the point 100 $C/C_0 = 50$ and $x/(t)^{1/2} = 0$. In most cases it was not necessary to force this intersection, showing that the assumption of constant D on both sides of the interface was not unreasonable. The plots obtained for the experiments at 4,200° and 4,300°F. are shown in Figure 5. All the plots showed a definite tail marking the transition from shallow penetration to deep penetration noted in Figure 4.

For the experiments at 4,200°F. and above, there were enough points available and the straight-line fit was sufficiently good to calculate a diffusion coefficient with some certainty. For specimens 13 and 19, however, very little weight was given to the first cut because of the uncertainties in the concentration and in the penetration distance.

For the experiments at 3,300°, 3,600°, 3,800°, and 4,000°F. the first cut again was doubtful, leaving only one or two reliable points in each case. Straight lines were drawn to fit the points as well as possible. Under the circumstances, the values of D obtained from these experiments are not so reliable as those at the higher temperatures.

The values of D obtained for shallow penetration are shown in Table 2. A plot of log D vs. $1/T$ is shown in Figure 6 along with values obtained by Loftness (*1*) for comparison.

TABLE 2. DIFFUSION COEFFICIENTS FOR SHALLOW PENETRATION

Temperature, °F.	Diffusion coefficient D, sq. cm./sec.
4,350	1.9×10^{-8}
4,300	3.6×10^{-9}
4,250	1.0×10^{-9}
4,200	7.4×10^{-10}
4,000	6.8×10^{-11}
3,800	1.6×10^{-10}
3,600	4.1×10^{-11}
3,300	2.4×10^{-11}

A least-squares treatment of these data was not made because the substantial uncertainties at the four lowest temperatures could not be estimated at all well. The line shown in Figure 6 was drawn by inspection. Using this line, one finds that the diffusion coefficient D in sq. cm./sec. between 3,300° and 4,250°F. is given by the equation

$$D = 7.6 \times 10^{-3} \exp(-82{,}000/RT)$$

On the basis of close inspection of the data, it is estimated that the activation energy of 82,000 cal./g.-atom may be in

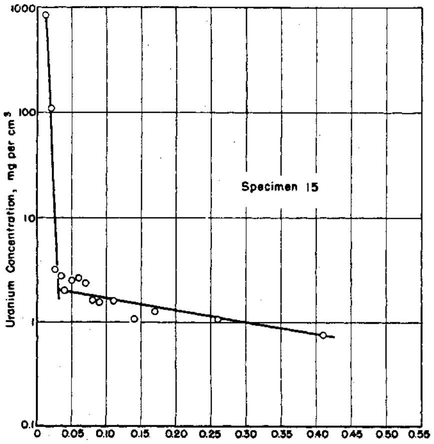

Fig. 4. Comparison of the two types of concentration gradients.

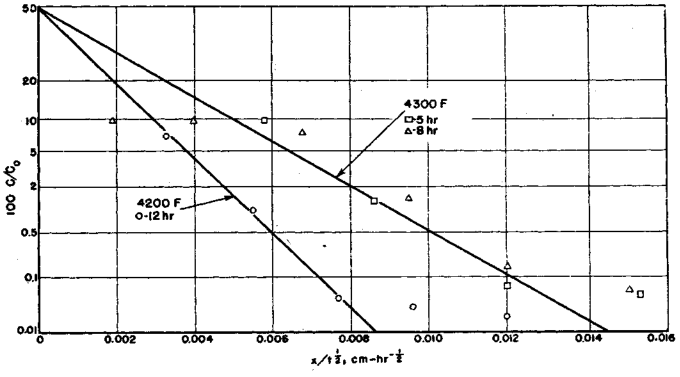

Fig. 5. Plots showing agreement of shallow-penetration data with Fick's Law.

error by as much as 20,000 cal./g.-atom, which is not unduly high for diffusion experiments of this type. The rather high value of the activation energy suggests that volume diffusion is the major contributor to shallow penetration of uranium.

The results obtained in this investigation are in general agreement with those reported by Loftness. His activation energy of 53,000 cal./g.-atom is not significantly different. The only important difference is seen in the results at temperatures above 4,250°F., where Loftness did not observe the sharp increases in diffusion rates noted in the present investigation. A possible reason for this may be that in Loftness's experiments the uranium dicarbide initially was distributed in thin layers on the pore walls in the graphite. Thus it easily could take up excess carbon, which prevented melting of the carbide (*3*). In the present experiments the amount of carbon available to the UC_2 was limited, and so some melting occurred at 4,300°F. and above.

Calculation of uranium penetrations by volume diffusion for long times indicates that this type of diffusion may be of less practical importance than the type referred to as *deep penetration*; for example, after 1,000 hr. at 3,200°F. the uranium concentration would be expected to decrease from 10,000 mg./cc. in the UC_2 to 1,000 mg./cc. at 0.01 cm. inside the graphite. After 1,000 hr. at 4,200°F. the concentration should be 1,200 mg./cc. at 0.1 cm. from the interface. Deep penetration, on the other hand, reaches a depth of a centimeter or more in a few hours at these temperatures.

Deep penetration must occur by way of the pores and may logically be called *pore migration*. Although it is presumably a type of diffusion, the available data give no evidence for this and do not justify the estimation of diffusion coefficients. To obtain some conception of the temperature dependence of the process, the data were plotted as log Q/t vs. $1/T$, where Q is the amount of uranium absorbed by the graphite as a result of pore migration and t is the time. In the present experiments volume diffusion was negligible at depths greater than 0.05 cm.; only the uranium which penetrated deeper than 0.05 cm. was used in calculating Q. The resultant plot is shown in Figure 7.

Pore migration shows a temperature dependence which is qualitatively similar to that observed for volume diffusion. A sharp increase in rate again was noted above 4,250°F.

One experiment was made to estimate the uranium loss through a graphite wall due to this form of transport. The uranium flow was measured through a thin-walled tube ½ in. in diameter and 4 in. long, closed at one end. Uranium dicarbide powder of 325 mesh was tightly packed in the ¼-in. bore of the tube to a depth of ½ in. and the bore closed with a graphite plug. The tube was placed in a carbon-black absorption bed contained by a tube 1 in. in diameter. The assembly was placed vertically in a vacuum furnace similar to that described by Smith (*4*), so that only that portion of the inner tube which contained the UC_2 was in the hot zone of the furnace. In this manner uranium leakage around the plug was minimized.

The uranium lost per unit area was 0.6 mg./sq. cm. after 40 hr. at 3,000°F. Under these conditions the penetration depth by volume diffusion would be about 0.004 cm. compared with the wall thickness of 0.32 cm. Therefore the uranium picked up in the carbon black must have reached the outer wall of the graphite tube by pore migration.

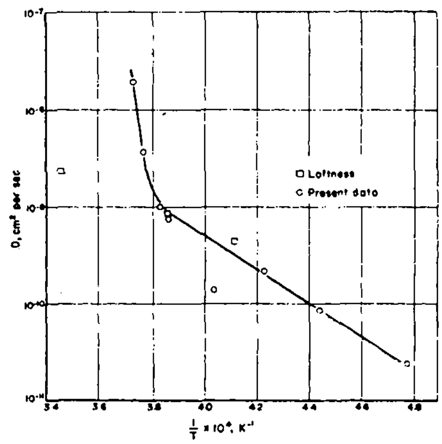

Fig. 6. Dependence of diffusion coefficient on temperature for shallow penetration.

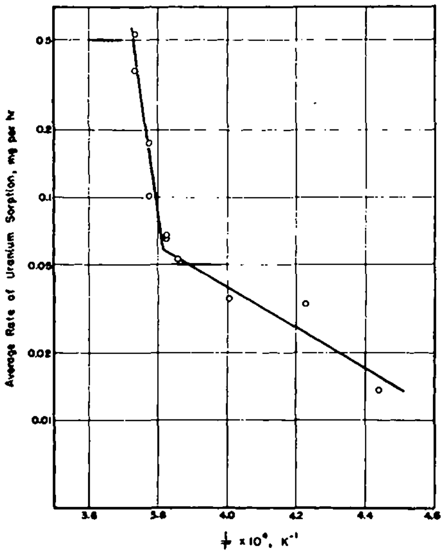

Fig. 7. Dependence of pore migration on temperature.

SUMMARY AND CONCLUSIONS

Uranium transport through polycrystalline graphite was measured in the temperature range of 3,000° to 4,350°F. Two forms of transport were observed: volume diffusion and pore migration. The volume-diffusion coefficients obtained in this investigation are in good agreement with those reported by Loftness (*1*). The activation energy of 82,000 ± 20,000 cal./g.-atom is not significantly different from Loftness's value of 53,000 cal./g.-atom. Within the time and temperature ranges studied, depths of penetration by pore migration were about 100 times as great as those by volume diffusion. Therefore, for practical purposes, pore migration may be the more important type of uranium transport.

A better understanding of pore migration is needed. More experiments, with graphites of widely different pore structures, will be helpful. It is of particular interest to determine whether pore migration occurs to the same extent in very dense graphites as it does in ordinary graphites.

NOTATION

C = uranium concentration, mg./cc.
C_0 = initial uranium concentration, mg./cc.
D = diffusion coefficient, mechanism unassigned, sq. cm./sec.
D_v = diffusion coefficient for volume diffusion, sq. cm./sec.
R = gas constant = 1.987 cal./(g.-atom)(°K.)
t = time, hr.
T = temperature, °K.
x = penetration distance, cm.
exp = base of the natural logarithms = 2.71828

$$y = \frac{x}{2\sqrt{Dt}}$$

$$\operatorname{erf} y = \frac{2}{\sqrt{\pi}} \int_0^y \exp(-z^2)\, dz,$$

where z is a variable of integration

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