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THE NOBLE GAS PERMEABILITY CHARACTERISTICS OF GRAPHITE MATERIALS FOR USE IN GAS-COOLED REACTORS*

by

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ABSTRACT

The theory of gas permeation through porous materials is reviewed in brief. Experimental data are presented on the permeation of helium and the fission product noble gases as a function of pressure, temperature and time of annealing through various graphite materials of interest for use to contain or hold back volatile fission products in gas-cooled reactors. This is essentially a status report of work in progress and includes data on British and American impervious graphites and certain carbide or pyrolytic carbon coated graphites.

INTRODUCTION

One of the alternate designs of the HTGR reactor calls for the fuel material to be essentially "clad" in graphite. The gaseous fission products can be expected to diffuse through the graphite at a rate dependent on the pore size and pore distribution. Of interest are diffusion rates through sleeve material, cladding material and compacts.

Although in the reactor the fission products would be diffusing through graphite in a helium atmosphere, for expediency, initial measurements have been made determining helium permeabilities. It was felt that this would be satisfactory as a screening test for determining the relative permeability of graphites and would indicate the effects of treatments such as irradiation, thermal cycling or aging at elevated temperatures.

PROCEDURE

Most of the permeability measurements have been made in an apparatus as shown schematically in Figure 1. The graphite specimen is attached to the metal tubing either by using a high melting point wax (Apiezon W) or by soldering, after copper plating. The entire system is evacuated to approximately 1 micron. Helium is then admitted to the bell jar and the rate of helium flowing through the graphite is measured with a mass spectrometer type helium leak detector. The flow rates which can be measured in this manner range from 2×10^{-9} to 4×10^{-5} cc-atm/sec.

Since the volumes in this system have been calibrated, the permeability can also be determined by pressure rise or pressure decay. The pressure rise technique is most suitable for the relatively impermeable graphites. Here the graphite separates a volume of helium at one atmosphere from a

closed evacuated volume. The permeability is calculated from the rate of pressure rise in the evacuated volume. Normally the change in pressure drop across the specimen is negligible (less than 1%) during a run. This method is suitable for other gases as well as helium, but the graphite must be sufficiently outgassed so that desorption during the run is negligible compared to the gas permeating the graphite.

On the more porous graphites, a pressure decay scheme has been used. Here the bell jar, as shown in Figure 1, is filled with helium and a vacuum is maintained on the other side of the graphite specimen. The permeability is then calculated from the rate of decrease in pressure in the bell jar. For permeation or diffusion measurements above one atmosphere an apparatus as shown in Figure 2 has been assembled. Permeabilities of the more porous graphites can be measured by measuring the rate of flow with the flow meter. The pressure rise or pressure decay systems described earlier can also be used.

The apparatus was primarily designed for diffusion measurements where the graphite separates two streams of gas which may be of the same or different pressures. If one of these streams contains an inert gas as a model of the fission product, the diffusion coefficient can be calculated from the concentration of this material found in the second stream. Also, the phenomenon of "back-diffusion" can be studied. Measurements have been made using argon as the model for the fission product gas. Here the concentration of argon which diffused was measured with a mass spectrometer. It is also planned to use Kr^{85} and Xe^{133} . Here the Kr or Xe will be collected in a charcoal-filled liquid nitrogen trap and the amount determined with a sodium iodide crystal and a gamma spectrometer system.

RESULTS

Results of permeability measurements are given in Tables I, II, III and IV. Table I gives the results of the permeability measurements of some assorted specimens in the as received condition.

Table II shows the effect of heat treating silicon carbide coated graphite at 1200°C for 1000 hours. Metallographic studies indicated a loss of silicon from the coating, presumably either through vaporization or by diffusion.

Table III shows no significant effect of radiation on four graphite specimens. The fast neutron dosage given is only approximate and is subject to revision.

Table IV gives a comparison of the results obtained by helium permeation and the results of a fission product xenon effusion experiment. (The Xe^{133} is produced by irradiation of a graphite capsule filled with uranium carbide powder (-325 mesh) as described in a paper given by Anderson, Burnette and Zumwalt at the November 1959 meeting of the American Nuclear Society¹.)

The results of helium permeability measurements on a specimen of National Carbon graphite RH0025 are shown in Figure 3. The measurements above 1 atmosphere were made with a flow meter; in this case, a pressure differential of 1 atmosphere was maintained. For the measurements below 1 atmosphere, the pressure decay technique was used and the pressure differential decreased with time.

DISCUSSION

Impermeable Graphites

For the low permeability graphites, the flow appears to be diffusional

(Knudsen flow). This is indicated by the lack of effect of pressure on the permeability as shown in Figure 4. The diffusional nature of the flow is also indicated by the time required for the flow to reach an equilibrium rate. This is illustrated for a typical sample in Figures 5 and 6. In Figure 5 the rate of flow is plotted vs. time, and in Figure 6 the accumulated flow is plotted vs. time. The asymptotic line for the flow can be described by the equation:

$$n = \frac{KA}{L} \frac{\Delta P}{RT} (t - t_1)$$

where

n = number of moles of gas which have passed through the specimen

K = permeability coefficient

A = area of the sample

ΔP = difference in gas pressure across the sample

If, as has been assumed, the flow is diffusional, the flow is in the Knudsen region. That is, the mean free path of the gas molecules is large compared to the radius of the capillaries, or openings, through which it passes. Thus, the presence of a second gas would not affect the permeation rate. Accordingly, results of helium permeability measurements can be extrapolated to the diffusion of fission products through graphite in the presence of a helium atmosphere as long as the mean free path remains large compared to the pore radius.

Various models have been considered in attempting to set up a diffusion equation adequately describing the phenomenon of a gas diffusing through graphite.

Case I

Assume that the flow channels are equivalent to a uniform tubular capillary and we are considering diffusion through a slab:

let

r = radius of each capillary

N = number of capillaries

L_e = length of the capillaries

x = a distance down a capillary

C = concentration of gas = $\frac{P}{RT}$

A = area of slab

L = thickness of slab

q = tortuosity of the capillary = $\frac{L_e}{L}$

l = a distance through the slab

D = the gas diffusion coefficient = $\frac{2}{3} \bar{v} r$

J = current of gas flowing

n = number of moles which have passed through the slab

Barrer² gives a solution of Ficks laws of:

$$J = - D \frac{\partial C}{\partial x}$$

and

$$\frac{\partial C}{\partial t} = - D \frac{\partial^2 C}{\partial x^2}$$

For our conditions of test, $C = 0$ at $x = 0$ for all t ; C is constant at $x = L_e$ for all t . The amount of gas which has flowed through a unit area of pore after a sufficiently long time

$$= \frac{D \Delta C}{L_e} \left(t - \frac{L_e^2}{6D} \right) .$$

The flow through a slab is then

$$n = N\pi r^2 A \frac{D \Delta C}{L_e} \left(t - \frac{L_e^2}{6D} \right)$$

since

$$\Delta C = \frac{\Delta P}{RT}$$

and

$$L_e = q L$$

$$n = \frac{N\pi r^2 A D \Delta P}{R T q L} \left(t - \frac{(qL)^2}{6D} \right) .$$

For a system of uniform tubular capillaries, the fraction of the volume available to a gas, $\epsilon = N\pi r^2 q$.

If we define the permeability coefficient, $K = \frac{N\pi r^2 D}{q}$

$$\frac{D}{q^2} = \left(\frac{K}{N\pi r^2} \right) \frac{1}{q} = \frac{K}{\epsilon}$$

thus,

$$n = \frac{K A \Delta P}{R T L} \left(t - \frac{L^2}{6K/\epsilon} \right) .$$

Case II

A somewhat more realistic model for graphite is to consider the capillaries to have access to a uniform number of "pockets" which are filled with the diffusing gas.

The same definition of terms as used in Case I can be used with the addition of:

ϵ = the fraction of volume available to gas
(available porosity)

C' = average concentration of gas in the graphite

Then,

$$C' = \epsilon C = \epsilon \frac{P}{RT} .$$

In terms of the pressure gradient in the specimen the diffusion current through slab is given by:

$$J_s = - \frac{K}{RT} \frac{\partial P}{\partial l} .$$

Average concentration in slab at distance l (where pressure is P) is:

$$C' = \epsilon \frac{P}{RT} .$$

By Ficks law

$$\frac{\partial C'}{\partial t} = \frac{\partial (J_s)}{\partial l}$$

and

$$\epsilon \frac{\partial P}{RT} = \frac{\partial \left(\frac{-K}{RT} \frac{\partial P}{\partial l} \right)}{\partial l}$$

$$\frac{\epsilon}{RT} \frac{\partial P}{\partial t} = \frac{-K}{RT} \frac{\partial^2 P}{\partial l^2}$$

$$\frac{\partial P}{\partial t} = - \frac{K}{\epsilon} \frac{\partial^2 P}{\partial l^2}$$

Therefore the asymptotic equation can be written:

$$n = \frac{K A \Delta P}{R T L} \left(t - \frac{L^2}{6K/\epsilon} \right) .$$

Case III

From a microscopic examination of a graphite the most likely model for the pore structure appears to be a number of large interconnected volumes.

If the restriction to flow is considered to be only the constrictions between these volumes, the treatment can be identical to that in Case II. Here the effective diffusion path is the sum of the constrictions and can be described as $q L$. However, in this case, q may be less than one.

In each of the cases considered, the equation,

$$n = \frac{K A \Delta P}{R T L} \left(t - \frac{L^2}{6K/\epsilon} \right)$$

was derived assuming the graphite to be of uniform structure. It is realized that in many cases of "impervious" graphites the material consists of a thin low permeability layer with the bulk of the material much more permeable. Although a rigorous treatment of such a composite material becomes quite cumbersome, it can be assumed that the permeable material has no effect. The ratio of the steady state pressure drop across each area is proportional to its thickness divided by the permeability constant, that is,

$$\frac{L_T}{K_T} = \frac{L_1}{K_1} + \frac{L_2}{K_2}$$

and

$$\frac{K_T \Delta P_T}{L_T} = \frac{K_1 \Delta P_1}{L_1} = \frac{K_2 \Delta P_2}{L_2} .$$

Thus, if there is an appreciable difference between the permeability of the bulk material and the "impervious" layer, the bulk material contributes little flow resistance and the ΔP across it is small.

For when

$$\frac{K_2}{L_2} \gg \frac{K_1}{L_1}$$

$$\Delta P_2 \ll \Delta P_1$$

and

$$\Delta P_1 \approx \Delta P_T$$

also

$$\frac{K_T}{L_T} = \frac{K_1}{L_1}$$

This, however, requires a knowledge of the thickness of the impervious layer since this is the L which should be used in the equation.

If it is not convenient to determine the thickness of the impermeable layer, effective values can be used, but they cannot be extrapolated to another thickness of graphite. Where the graphite is not uniform in structure, the calculated value of ϵ using the total length and average permeability constant could be expected to be considerably different from the porosity determined by helium free volume or mercury porosimetry measurements.

Porous Graphites

The more porous graphites do not lend themselves to as rigorous a treatment as the impervious ones because there is apt to be a broader distribution of pore sizes.

For flow with a pressure differential across the graphite, two components can be expected: one viscous and one diffuse, thus,

$$\frac{dn}{dt} = K \frac{A \Delta P}{L R T}$$

where K is not independent of pressure and

$$K = \alpha \frac{m^2}{\eta} \bar{p} + \beta D$$

where $\bar{m}$ is the mean hydraulic radius of the pores contributing to viscous flow, and η is the viscosity and $\bar{p}$ is the mean pressure, $\frac{P_1 + P_2}{2}$. The diffusive flow term enters in both by being a slip flow term in the larger pores and by being the diffusive flow term for the small pores.

Permeability measurements have been used to give an indication of the pore size by assuming that the pores are uniform tubes. Here the Poiseuille equation for flow with slip can be used:

$$\frac{dn}{dt} = \left[\left(\frac{N\pi r^2 \bar{p}}{8\eta q} \right) + \left(\frac{3\pi}{16} \right) \left(\frac{N\pi r^3}{q} \right) \left(\frac{2}{3} \right) \left(\frac{8RT}{M\pi} \right)^{1/2} \right] \frac{A\Delta P}{LRT} = K \frac{A\Delta P}{LRT} .$$

By plotting K vs. $\bar{p}$ a separation of the viscous and slip contribution can be made. Their ratio then yields a value for the effective r . This technique is reasonably valid if the range of pressures is small enough so that the change in mean free path is negligible compared to the distribution of pore sizes.

If the effective pore size for the specimen of National Carbon Co. RH0025 graphite is calculated by this method, it is found to be 0.2μ . This is in reasonable agreement with mercury porosimetry readings taken on a specimen from the same lot which indicated that most of the pores are in the 0.5μ range. This is also in agreement with the estimate of pore size from the mean free path. Pure Knudsen flow can be expected if the mean free path is ten times the pore radius and the mean free path at one atmosphere is about 2 microns.

A second method of estimating the size of the pore is to reduce the average pressure for the permeation measurement until the flow is predominantly diffusive flow. The mean free path of the helium molecules is of the order of magnitude of the pore radius in the region of transition from viscous to diffusive flow.

CONCLUSIONS

From the results obtained it can be concluded that the flow of helium through graphite can be either diffusional flow or viscous flow with slip depending on the relationship of pore size and mean free path of the helium.

For the diffusional case the equation

$$n = \frac{K A \Delta P}{R T L} \left(t - \frac{L^2 \epsilon}{K} \right)$$

is a very promising description of the amount of gas which has diffused through the graphite after a long time. The term $\frac{L^2 \epsilon}{K}$ is expected to be useful in estimating hold-up times of fission products diffusing through graphite.

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REFERENCES

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2. R. M. Barrer, Diffusion In and Through Solids , p. 15, 18 and 19, Cambridge University Press, 1951.

TABLE I

Results of Helium Permeability Measurements
of Some Relatively Impervious Graphites

(These are measurements on individual specimens, not necessarily representative)

Sample	ΔP mm Hg	Type of Measurement	Wall Thickness cm	K Permeability Coefficient cm ² /sec	Intercept Time min	L ² /6t: cm ² /sec	ϵ	Hg Porosimeter Determination Volume Fraction >.095 μ
RXLP1 No. 10 (National Carbon Company)	757 741 393 741	Pressure rise " " "	0.3 0.3 0.3 0.3	5.8 x 10 ⁻⁷ 5.7 x 10 ⁻⁷ 5.3 x 10 ⁻⁷ 5.6 x 10 ⁻⁷	7 9 7 8	3.6 x 10 ⁻⁵ 2.8 x 10 ⁻⁵ 3.6 x 10 ⁻⁵ 3.1 x 10 ⁻⁵	.016 .020 .015 .018	
Ave.				5.6 x 10 ⁻⁷		3.3 x 10 ⁻⁵	.017	
HS 1 AAEC6 (Hawker Siddeley)	730 730	Pressure rise "	0.475 0.475	1.9 x 10 ⁻⁵ 1.8 x 10 ⁻⁵	18 19	3.5 x 10 ⁻⁵ 3.3 x 10 ⁻⁵	.54 .54	0.06
CEY (National Carbon Company)	744 370	Pressure rise "	0.5 0.5	4.1 x 10 ⁻⁶ 3.2 x 10 ⁻⁶	8 10	8.7 x 10 ⁻⁵ 7.0 x 10 ⁻⁵	.047 .046	0.078
HS 143-1 (Hawker Siddeley)	780 760	Pressure rise "	0.32 0.32	1.2 x 10 ⁻⁸ 4 x 10 ⁻⁸	- 6	- 4.8 x 10 ⁻⁵	- .00084	0.03
HS 143-2	760 760 760	Pressure rise " Leak detector	0.32 0.32 0.32	2 x 10 ⁻⁷ 1.3 x 10 ⁻⁷ 1.9 x 10 ⁻⁷	- 2 -	- 1.42 x 10 ⁻⁴ -	- .00091 -	
HS 143-3	760 760 760	Pressure rise Leak detector Leak detector	0.32 0.32 0.32	2.6 x 10 ⁻⁶ 7.5 x 10 ⁻⁷ 9.3 x 10 ⁻⁷	2 - -	1.4 x 10 ⁻⁴ - -	.0145 - -	
HS 143-4	760	Pressure rise	0.32	4 x 10 ⁻⁹	7	4.1 x 10 ⁻⁶	.00098	
HS 143-4 Bored	760	Pressure rise	0.32	1.4 x 10 ⁻⁵	3	9.5 x 10 ⁻⁵	.15	
HS 143-4 Bored	760	"	0.32	1.8 x 10 ⁻⁵	3	9.5 x 10 ⁻⁵	.19	

Continued on next page -

TABLE I (cont'd)

Sample	P mm Hg	Type of Measurement	Wall Thickness cm	K Permeability Coefficient cm ² /sec	Intercept Time min	L ² /6t: cm ² /sec	€	Hg Porosimeter Determination Volume Fraction .095μ	
HS 143-9	1 Atm	Leak detector	0.32	3.6 x 10 ⁻⁷	8	3.5 x 10 ⁻⁵	.011		
	4 Atm	Leak detector	0.32	5.1 x 10 ⁻⁷	10	2.5 x 10 ⁻⁵	.020		
HS 143-11	1/2 Atm	Leak detector	0.32	2.35 x 10 ⁻⁷	-	-	-		
	1 Atm	Leak detector	0.32	2.6 x 10 ⁻⁷	-	-	-		
HS 143-14	1 Atm	Leak detector	0.32	2.64 x 10 ⁻⁷	-	-	-		
	4 Atm	"	0.32	2.2 x 10 ⁻⁷	40	8.3 x 10 ⁻⁶	.028		
	7 Atm	"	0.32	3.2 x 10 ⁻⁷	18	1.58 x 10 ⁻⁵	.020		
	4 Atm	"	0.32	4.98 x 10 ⁻⁷	18	1.58 x 10 ⁻⁵	.032		
	(143°C)								
	1/2 Atm	"	0.32	1.0 x 10 ⁻⁷	13	2.2 x 10 ⁻⁵	.0046		
	8 Atm	"	0.32	1.5 x 10 ⁻⁷	6	4.7 x 10 ⁻⁵	.0032		
Raytheon Pyrolytic	1 Atm	Leak detector	0.1	2.7 x 10 ⁻¹⁰	22	1.26 x 10 ⁻⁶	.00022		
GEC No. 1 "Impervious"	1 Atm	Leak detector	0.1	6.2 x 10 ⁻⁹	132	2.1 x 10 ⁻⁷	.0295		
GEC No. 3 "Low Per- meability"	750 cm	Pressure rise	.435	2.7 x 10 ⁻⁵	-	-	-		
	158	Pressure rise	.435	2.1 x 10 ⁻⁵	4	1.3 x 10 ⁻⁴	.162		
	20	Pressure rise	.435	1.7 x 10 ⁻⁵	3.5	1.5 x 10 ⁻⁴	.113		
(General Electric Co. of England)									

TABLE II

Helium Permeation Through Silicon Carbide Coated Graphite

Effect of Heat Treatment at 1200°C in Argon

Spec. No.	As Received	<u>Permeability Constant - cm²/sec</u>	
		After 350 hr at 1200°C	After 1000 hr at 1200°C
1	7×10^{-7} 2×10^{-7}	8.6×10^{-10}	7×10^{-4}
2	1.6×10^{-9}	1.5×10^{-9}	1×10^{-5}
3	5×10^{-9}	6.1×10^{-8}	2×10^{-5}
4	1.7×10^{-9}	9.2×10^{-11} 3×10^{-11}	1.4×10^{-6}
5	3.9×10^{-9}	5×10^{-7} 3.8×10^{-7}	
6	5.3×10^{-7} 4.9×10^{-7}	1.6×10^{-10}	2.5×10^{-6}

TABLE III

Effect of Irradiation on Helium Permeability

Specimens irradiated in the GA 311-1 Test
 (nvt = 1×10^{21} , at 327-660°C)

<u>Specimen</u>	<u>K Before</u>	<u>K After</u>
CEY (crucible)	$4 \times 10^{-7} \text{ cm}^2/\text{sec}$	$4 \times 10^{-7} \text{ cm}^2/\text{sec}$
RXLP2-19	$2 \times 10^{-10} \text{ cm}^2/\text{sec}$	$3 \times 10^{-10} \text{ cm}^2/\text{sec}$
RXLP2-6	$9 \times 10^{-9} \text{ cm}^2/\text{sec}$	$3 \times 10^{-9} \text{ cm}^2/\text{sec}$
CEY (specimen)	$2 \times 10^{-6} \text{ cm}^2/\text{sec}$	$6 \times 10^{-6} \text{ cm}^2/\text{sec}$

TABLE IV

Comparison of Fission Product Effusion Studies
with Helium Permeability

Sample	K He Perm. RT	t_c	Calculated		Measured Fraction Xe per day Effused
			K_{Xe}	Fraction Xe per day Effused	
HS 149-2	5.4×10^{-7}	5 min	2.1×10^{-7}	.4	.0014
HS 149-11	1.4×10^{-8}	10 min	5.4×10^{-9}	.01	.02
RXLP2-16	2×10^{-10}		7.7×10^{-11}	1.5×10^{-4}	.01

Fig. 1--Permeability Measurement Apparatus

Fig. 2--High Pressure, High-Temperature Permeability Apparatus

HELIUM
PERMEABILITY
 $K\text{-CM}^2/\text{SEC} \times 10^7$

HELIUM PERMEABILITY OF A LOW PERMEABILITY GRAPHITE

Fig. 4

Fig. 5

Fig. 6