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Characterization of Pyrocarbon Coatings of HTGR Fuel Particles by Inert Gas Intrusion

C. S. Morgan

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Fueled Graphite Development (189a 01330)

CHARACTERIZATION OF PYROCARBON COATINGS OF HTGR FUEL PARTICLES BY INERT GAS INTRUSION

C. S. Morgan

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CHARACTERIZATION OF PYROCARBON COATINGS OF HTGR FUEL PARTICLES BY INERT GAS INTRUSION

C. S. Morgan

ABSTRACT

Biso fuel particles used in the HTGR have a pyrocarbon coating designed to retain fission gases during reactor operation. The inert gas permeability of the pyrocarbon coating is variable and a measure of it is an important clue to fuel performance. A method was developed to measure the permeablity of pyrocarbon coatings by intrusion of light inert gases. The mole quantity of neon and helium entering the fuel particle at elevated temperature (1375°C for 1 h) from an equimolar mixture is determined by mass spectrometry after breaking the particle. The ratio of the two gases constitutes a useful measure of the pyrocarbon coating permeability. Activiation energies for intrusion of helium, neon, and argon show a sharp increase with atomic number. Pyrocarbon coatings have a measurable permeability for krypton only at very high temperatures and only then in the more permeable coatings. Neutron irradiation reduced the permeability of the pyrocarbon coatings on inert kernels. Neon and helium ratios measured on hundreds of fuel particle batches ranged from 0.03 to greater than 1.0, and we estimate that a pyrocarbon with neon-helium ratio below 0.30 or 0.35 will be gastight under HTGR operating conditions.

INTRODUCTION

The fuel form for the High Temperature Gas-Cooled Reactor (HTGR) consists of small fissile and fertile particles about 800 μm in diameter in a carbon-base matrix suitably arranged in a graphite structure. The fissile-fertile particle mixture permits utilization of a large heat generating column, which with the high efficiency of the helium coolant results in a relatively low temperature gradient. The fuel particle-graphite structure operates with a large reserve heat capacity, reducing the danger of damaging temperature excursions. A spherical fissle or Triso particle has a uranium-containing kernel, a low-density pyrocarbon

buffer layer, a dense inner pyrocarbon layer, a SiC layer, and a dense outer pyrocarbon layer. The function of the SiC coating is to retain all fission products generated in the fuel particle. A fertile or Biso particle consists of a ThO_2 kernel, a buffer layer, and a dense pyrocarbon outer coating. The dense coating of both the Biso and Triso particles is a low-temperature isotropic (LTI) pyrocarbon.

The outer pyrocarbon coating of the Biso particles is permeable to some metal fission products, such as cesium, but is expected to be quite impermeable to gaseous fission products. This coating thus functions as a pressure vessel and is designed so as to retain fission gases and other gaseous materials, such as carbon monoxide. In some cases this may lead to pressures above 0.7 MPa (>100 psi). Retention of the volatile fission products in the fuel particle is important in minimizing radioactive contamination of the primary coolant system in the reactor.

The performance of pyrocarbon coatings, and specifically the retention of gaseous fission products, depends primarily on two properties of the coating. First is the permeability to inert gases, particularly krypton and xenon in the "as-fabricated" condition. The question here is whether significant quantities of radioactive gases will diffuse or permeate through the pyrocarbon coating and enter the primary coolant during the tenure of the particle in the reactor. The second important property of the pyrocarbon with respect to fission gas retention is the potential for crack development during irradiation. During reactor operation the high temperature and neutron fluence will cause densification and anisotropic crystallization in pyrocarbons. This may cause cracks to develop in the coatings.

This report addresses the first of these properties. The pyrocarbon coatings on HTGR Biso fuel particles are permeable to helium and neon at elevated temperatures. If the particles are intruded with a helium-neon mixture for a time and temperature such that helium in the pores of the buffer coating reaches equilibrium with the intruding atmosphere while the more slowly diffusing neon does not, the ratio of these two gases in the particle provides a sensitive measure of the permeability of the outer coating.

INERT GAS PERMEABILITY OF PYROCARBON COATINGS

Measurement of Permeability

The obvious way to determine the permeability of pyrocarbon coatings of Biso fuel particles is to measure directly the movement of inert gases through the pyrocarbon coating. This is possible for light inert gases, and we have developed a permeability determination method. The Biso fuel particles (Fig. 1) are annealed at high temperature in an inert gas atmosphere. The amount of gas diffusing through the coating into the buffer layer is then determined by breaking the pyrocarbon coating in a mass spectrometer and measuring the quanitity of the gas released. The particles are crushed individually in a single-action anvil in a dynamically pumped vacuum system containing a quadrupole mass spectrometer, and the inert gas pressure transient is monitored and integrated.[1] The mass spectrometer was calibrated by introduction of

[1]C. S. Morgan and G. L. Powell, "Preliminary Examination of the Helium Permeability of Pyrocarbon Coatings," *Nucl. Technol.* 35: 337–39 (1977).

ORNL-DWG 78-10349

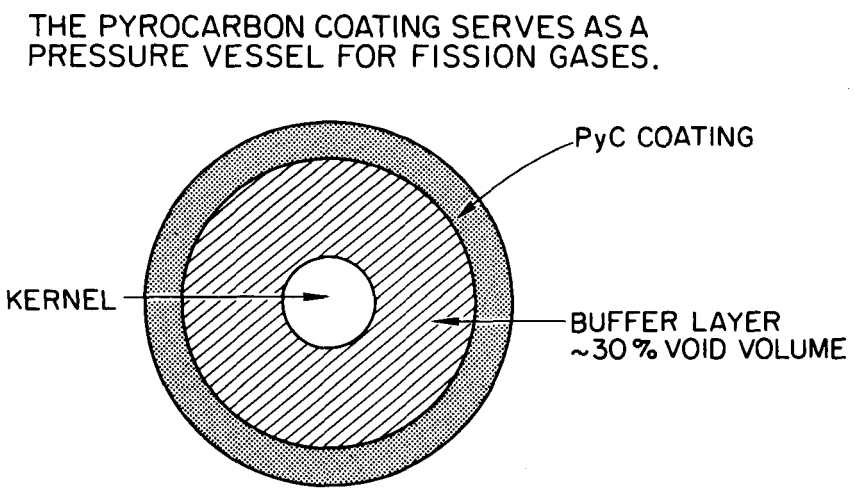

Fig. 1. Biso Fuel Particle.

known amounts of gas and was shown to be sensitive to 10 fmol He. The mass spectrometer response to helium from a typical fuel particle after saturation with the gas is shown in Fig. 2. The principles of operation of the mass spectrometer measurement system have been reported.[2,3]

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[2]J. B. Condon, R. A. Strelow, and G. L. Powell, "An Instrument for Measuring the Hydrogen Content of Metals," *Anal. Chem.* 43: 1448 (1977).

[3]G. L. Powell, F. W. Postma, C. Cook, H. Tucker, and A. L. Williamson, "Mass Spectrometric Determination of Hydrogen Thermally Evolved from Titanium," *Anal. Chem.* 47: 679 (1975).

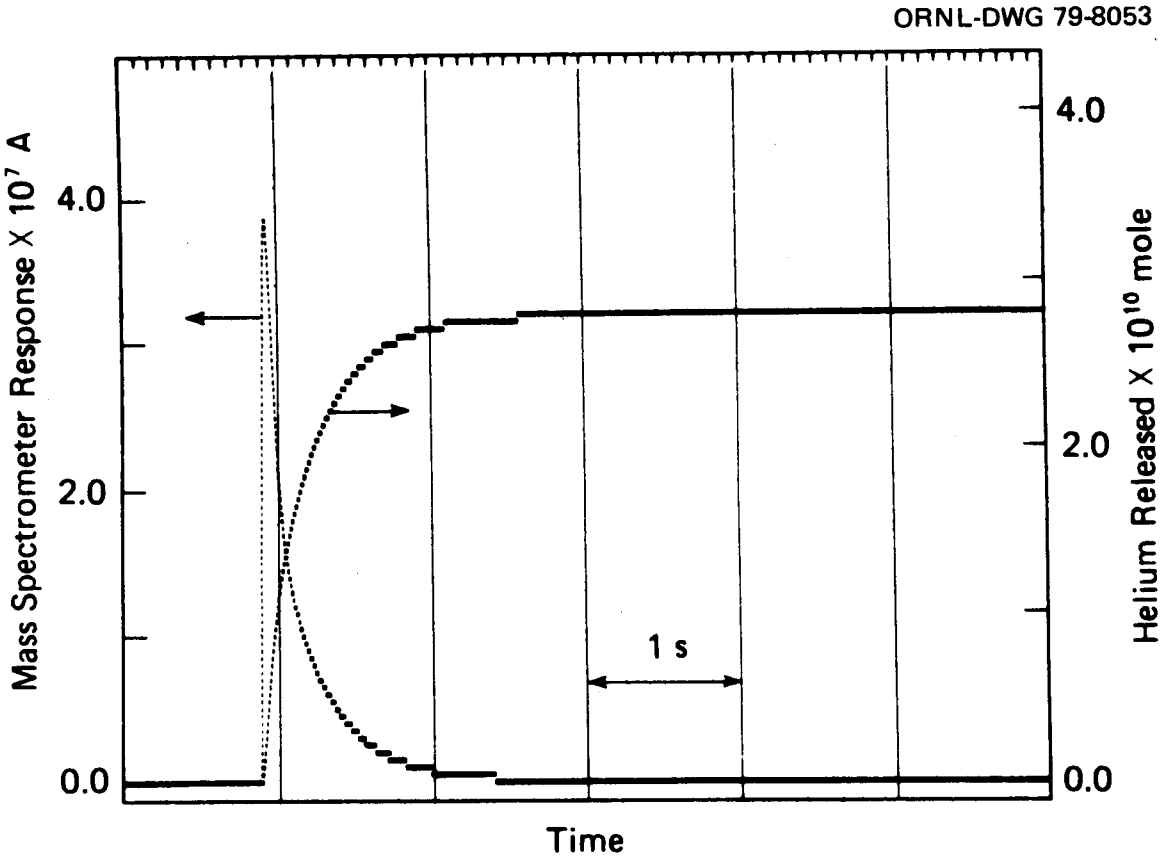

Fig. 2. Helium Release Measurement for a Biso Fuel Particle from Batch OR-2261-HT after Annealing for 1 h in Vaccum at 1800°C (2073 K) and 1 h in Helium at 96 kPa and 1100°C (1373 K).

After the pyrocarbon coating is broken the gas is released and analyzed in about 2 s. Only a crack in the pyrocarbon coating is required. Further repetitive crushing results in release of an additional 1 to 2% gas. This indicates that the bulk of the gas is in connected void volume in the buffer layer. The additional gas release on further crushing comes from small pores in the dense pyrocarbon coating and in the buffer layer.

The possibility of very permeable coatings must be considered. If the pyrocarbon coating is permeable at room temperature, the measured helium content would be reduced and depend on elapsed time after gas input. To determine if this was happening, several tests were made on a moderately permeable pyrocarbon coating by vacuum pumping on coated particles for time periods ranging from overnight to one week before breaking the particle in the mass spectrometer; no decrease in helium content was noted. (Some highly permeable coatings will leak helium after coating; this possibility is mentioned later.)

Helium Permeability of Batch OR-2261-HT

Table 1 shows results for diffusion of helium into batch OR-2261-HT fuel particles as a function of annealing temperature and heat treatment time.

Table 1. Helium Content of OR-2261-HT Fuel Particles Annealed in Helium at 97.3 kPa

Temperature (°C)	Time (h)	Helium Content, pmol			Number of Particles Tested
		As Measured	Corrected[a] to 20°C, 98 kPa	Standard Deviation	
750	1	11	39	2	10
840	1	66	258	19	11
970	1	230	1004	30	10
1100	1	211	1015	77	16
1200	1	300	1549	80	10
1800	0.5	220	1599	38	6
1800	2	230	1671	49	8
1800	4	220	1597	31	10

[a]To give a basis for comparing results at different temperatures, the content of the same volume at 98 kPa and 20°C was calculated.

These results, each of which is the average for about ten particles, show that with this fuel particle batch sufficient helium has diffused into the particles after 1 h at 1200°C to fill the void volume in the buffer layer. The standard deviation is included in Table 1 to indicate the variation observed in fuel particles of this batch. This deviation results primarily from dimensional variation in the individual fuel particles.

Determination of Particle Void Volume

Fuel particles acting as effective pressure chambers must have adequate void volume in the buffer layer to accommodate fission gases. The required volume, of course, depends on the quantity of thorium in the fuel particle.

The intrusion of helium through the LTI layer of Biso fuel particles can be used to determine the void volume of the buffer layer. The quantity of helium contained in a fuel particle affords a measure of the buffer coating void volume, and Table 2 gives buffer coating void volumes for

Table 2. Fuel Particle Volume Determined by Helium Intrusion for 1 h at 1800°C and 97.3 kPa (730 torr) Compared with Volumes Measured by Mercury Porosimetery and with Radiographic Buffer Volumes

Fuel Particle Batch	Helium, pmol		Void Volume, m^3		Buffer Volume by Radiography (m^3)	Void (% of buffer)
	Content	Std Dev	by Helium Intrusion	by Mercury Porosimetry[a]		
OR-1972-HT	87	11	15.4×10^{-12}	15.9×10^{-12}	71.5×10^{-12}	21.5
OR-1975-HT	88	12	15.6	16.2	70.5	22.1
OR-1978-HT	89	10	15.8	19.4	71.9	22.0
OR-1985-HT	77	12	13.6	12.7	73.5	18.5
OR-1986-HT	82	14	14.5	14.4	71.2	20.4
OR-1987-HT	75	14	13.3	12.4	75.3	17.7
OR-2010-HT	240	17	42.5	41.4	183.4	23.2
OR-2013-HT	96	10	17.0	17.7	85.7	19.8
OR-2251-HT	220		38.9		109.9	35.4

[a]Unpublished measurement by R. L. Beatty, ORNL.

several particles determined in this manner. These fuel particle batches were first heated at 1800°C to remove any helium retained from the coating preparation process. They were then heat-treated in helium at 97.4 kPa (730 torr) at 1800°C for 1 h. As shown in Table 1, this treatment is actually more rigorous than required to achieve pressure equilibrium between helium in the void volume and the surrounding atmosphere. The average helium mass value obtained on 15 particles of a given batch was selected as being a satisfactory average of the helium content. The buffer void volumes are calculated by use of the ideal gas law as follows in the example for batch OR-2010-HT:

$$\text{Void Volume} = 240 \times 10^{-12} \times \frac{22.412}{1000} \times \frac{2073}{273} \times \frac{101.3}{97.3}$$

$$= 42.5 \times 10^{-12}\ \text{m}^3\,, \qquad (1)$$

where 240×10^{-12} is the number of moles of helium in the particle at equilibrium at a helium pressure of 97.3 kPa (730 torr) at 1800°C (2073 K) and 22.412/1000 is the molar volume of a gas (in m^3) at 101.3 kPa (760 torr) and 273 K. The void volumes agree quite well with values determined by mercury porosimetry. The table also gives the buffer volume determined from radiographic measurements and the percentage of this volume that is void space.

Neon-to-Helium Ratio

A standard procedure that would consistently give a reproducible value for pyrocarbon coating permeability based on light inert gas intrusion was needed to evaluate fuel particles. After considerable experimentation, we decided that the most useful permeability test involved determining the amounts of helium and neon diffusing into the fuel particle in 1 h at 1375°C from an equimolar mixture of neon and helium at atmospheric pressure. The coating is then broken, and the quantity of each gas that had diffused into the fuel particle is determined with a mass spectrometer.

The ratio of neon to helium in the fuel particle constitutes a measure of the permeability of the pyrocarbon coating. Under these conditions, for most pyrocarbon coatings of interest for HTGR applications, helium in the porous buffer coating will come to equilibrium with the furnace atmosphere. The rate of neon diffusion at 1375°C, however, is very sensitive to the pyrocarbon structure, and thus the ratio measured when the dense pyrocarbon coating is broken is a sensitive measure of the pyrocarbon coating permeability. Simultaneous use of two gases avoids the uncertainty about whether the pyrocarbon coating is very permeable or very impermeable when the particle contains only a small amount of gas after heat treatment in a gas atmosphere. This problem arises because if the pyrocarbon coatings are too permeable some of the intruded gas could diffuse out of the test particle before it is tested in the mass spectrometer. The use of a ratio of two gases also partially erases permeability distortion by particle geometry differences. This problem is discussed later in this report.

The neon-to-helium ratio of a selected group of fuel particle batches is given in Table 3 along with deposition conditions. As indicated in the table, fuel particle batches have a wide range of permeabilities depending on preparation techniques used to make the LTI layer.

Normalized Neon-to-Helium Ratio

The neon-to-helium ratios determined on Biso fuel particles that have roughly the same diameter and void volume represent a satisfactory measure of the relative permeability of the pyrocarbon coating. Typically, the as-measured ratio is used to compare the permeabilities of different batches of particles with similar dimensions. However, where there is a large difference in the ratio of particle surface area to buffer void volume the neon-to-helium ratios can be significantly distorted. This results from the fact that during the heat treatment in the neon-helium atmosphere, the void volume usually fills with helium regardless of the geometry, whereas for a given instrinsic permeability the extent of neon filling will be proportional to the ratio of surface

Table 3. Deposition Conditions and Neon-to-Helium Ratios for Selected HTGR Fuel Particle Batches

Fuel Particle Batch	Deposition Conditions				Gas Quanitity and Standard Deviation[b]		Ne/He
	Temperature (°C)	Hydrocarbon[a]	Coating Rate				
			(pm/s)	(μm/min)	Helium	Neon	
OR-1978-HT	1245	50% Propylene	13	0.8	66 ± 3	2 ± 0.3	0.03
OR-2261-HT	1375	50% MAPP	123	7.4	163 ± 39	38 ± 4	0.23
OR-2262-HT	1275	50% MAPP	108	6.5	166 ± 38	33 ± 4	0.20
OR-2263-HT	1325	25% MAPP	60	3.6	151 ± 17	19 ± 3	0.13
OR-2269-HT	1325	50% MAPP	208	12.5	181 ± 32	74 ± 10	0.40
OR-2274-HT	1325	100% MAPP	467	28.0	203 ± 31	102 ± 16	0.50
OR-1967-HT	1300	50% Propylene	87	5.2	62 ± 11	6.6 ± 4	0.11
OR-1979-HT	1315	50% Propylene	198	11.9	60 ± 6.5	10.5 ± 1.1	0.19
OR-2013-HT	1325	33% Propylene[c]	185	11.1	67 ± 6.7	8.5 ± 1.3	0.14
A-758	1350	33% Mixed	82	4.9	62 ± 7	30 ± 5	0.48
A-762	1225	33% Mixed	55	3.3	45 ± 9	16 ± 2	0.36
A-770	1225	33% Propylene	22	1.3	55 ± 12	8 ± 1	0.15

[a]Inert diluent (He or Ar) except where indicated.
[b]Helium and neon uptake from equimolar Ne + He at 1375°C and ambient atmospheric pressure for 1 h.
[c]Diluent CO_2.

area to void volume. Thus, even though the pyrocarbon coating of two fuel particle batches might have the same intrinsic permeability characteristics, the neon-to-helium ratio would be higher for the batch that has the larger surface area and smaller buffer void volume.

Several procedures can be used to adjust permeability for particle geometry. One method for permeability correction developed by Eatherly[4] uses a one-dimensional model of a coated particle. Experimentally, gas flows from an infinite volume through a barrier of admittance F, area A, and thickness L into a finite void volume v_0. Then the number of moles N in the void at any time t will be:

$$N = N_\infty[1 - \exp(-FAt/Lv_0)] \ , \tag{2}$$

where N_∞ is the number of moles of gas within the particle void volume at equilibrium (infinite time). Neon-to-helium ratios are normally used as mole ratios

$$\frac{\mathrm{Ne}}{\mathrm{He}} \equiv f = \frac{N(\mathrm{Ne})}{N(\mathrm{He})} \ . \tag{3}$$

If the infinite reservior contains equal numbers of moles (partial pressures) of neon and helium, then in equilibrium

$$N_\infty(\mathrm{Ne}) = N_\infty(\mathrm{He}) \ , \tag{4}$$

and the time-dependent ratio f becomes

$$f(t) = \frac{1 - \exp(-F_{\mathrm{Ne}}At/Lv_0)}{1 - \exp(-F_{\mathrm{He}}At/Lv_0)} \ . \tag{5}$$

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[4]C. S. Morgan, G. L. Powell, W. P. Eatherly, M. Reeves, and J. S. Tolliver, "Permeability Determinations Using Inert-Gas Intrusion," *HTGR Base-Technology Program Annu. Prog. Rep. Dec 31, 1977,* ORNL-5412, pp. 32–48.

Experimentally we can select a value for t, say τ, such that

$$(F_{He}A/Lv_0)\tau >> 1, \qquad (F_{Ne}A/Lv_0)\tau = O(1) \quad , \tag{6,7}$$

where O(1) symbolizes a number of order unity. The $\exp(-F_{He}A\tau/Lv_0)$ term can be eliminated because the much more rapid permeation by helium causes it to become small while the term reflecting Neon permeation is still significant. The heat treatment conditions, 1 h at 1375°C, were selected to take advantage of this diffusion rate behavior. Then

$$f(\tau) \approx 1 - \exp(-F_{Ne}A\tau/Lv_0) \quad , \tag{8}$$

which permits a unique determination for the neon admittance F_{Ne}. The result is

$$F_{Ne} = \frac{-Lv_0}{A\tau} \ln(1 - f) \quad . \tag{9}$$

Equation (9) must be considered with some care: f is an experimentally determined number, a ratio of gas entry into the particle. It clearly must depend on the time at which the measurement is made, the volume v_0 into which the gas is flowing, and the area A and thickness L of the barrier interface through which the gas must flow. Hence, the right hand side of the equation "corrects" the experimentally determined quantity f to a true material constant F. The admittance F (in units of m^2/s) is the amount of gas flowing through a 1-m cube of material in 1 s. Values of F are of the order of 10^{-13} m^2/s at 1375°C.

Another method of determining an intrinsic measure of permeation was developed by Toliver and Reeves of the ORNL Computer Sciences Division.[5] In this analysis the diffusion of gas atoms through a spherical shell has been evaluated by a combined analytical and numerical approach. The diffusion equation for gas into a spherical shell of finite volume was solved by a Laplace transform technique. This technique has been applied in determining diffusion coefficients for helium in the pyrocarbon coating of fuel particles and the results are included under "Characteristics of Inert Gas Intrusion."

The two methods discussed are procedures for determining intrinsic measures for movement of gases through pyrocarbon coatings of interest for use in HTGR fuel. However, the measures obtained from different fuel particle batches are not as easily calculated or as conveniently compared as are the simpler neon-to-helium ratios. For these reasons a method was needed to adjust the ratios to eliminate distortion by fuel particle dimensional variations, and a procedure for normalizing neon-to-helium ratios was developed. For a given intrinsic coating permeability, the neon-to-helium ratio increases with increasing particle surface area and decreases with increasing void volume in the buffer layer. To make the neon-to-helium ratio comparable from fuel particle batches of different geometry we use normalization factors proportional to the buffer void volume and inversely proportional to the particle surface area. The permeability so adjusted is still not a property of the deposited coating material that can be compared with other properties of the material, so a third normalization factor proportional to the coating thickness is included.

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[5]M. Reeves and J. S. Toliver *Transient Diffusion Through a Spherical Shell into Its Finite Spherical Core,* ORNL/CSD/TM-60 (March 1979).

Our normalization procedure is based on a "normal" particle having the following parameters:

1. particle diameter 814 μm,
2. pyrocarbon thickness 75 μm, and
3. void volume corresponding to 90 pmol He in equilibrium with 50.7 kPa (0.50 atm) He at 1375°C.

Since surface area is proportional to diameter squared and void volume to helium intrusion, the normalization equation is

$$\frac{\mathrm{Ne}}{\mathrm{He}}_{\mathrm{Norm}} = \frac{\mathrm{Ne}}{\mathrm{He}}_{\mathrm{Exp}} \times \frac{L}{75} \times \frac{814^2}{D^2} \times \frac{V}{90} , \tag{10}$$

where

L = pyrocarbon coating thickness, μm;

D = particle diameter, μm; and

V = helium content of particle, pmol.

This equation reduces to:

$$\frac{\mathrm{Ne}}{\mathrm{He}}_{\mathrm{Norm}} = 98.2 \frac{\mathrm{Ne}}{\mathrm{He}}_{\mathrm{Exp}} \frac{LV}{D^2} . \tag{11}$$

Normalized and experimental values of neon-helium permeabilities of several fuel particle batches are shown in Table 4. The average diameters and LTI coating thicknesses of the particles included in the table are determined by x-ray microradiography. As can be seen in the table, the normalized neon-to-helium ratios do not differ significantly from the as-measured ratios for some of the fuel particle batches, and this is true for most fuel particle batches evaluated to date. For batches with unusual dimensions, as in the case of OR-1840-HT, where the neon-to-helium ratio changes from an experimental value of 0.49 to a normalized value of 0.22, this adjustment can be important in comparing the permeability of different coatings.

Table 4. Comparison of Ne/He Ratios with Normalized Ne/He Values for Several HTGR Biso Fuel Particle Batches

Fuel Particle Batch[a]	Helium (pmol)	Diameter (μm)	Pyrocarbon Coating Thickness (μm)	Ne/He Ratio		BAF_o
				As Measured	Normalized	
OR-2261-HT	118	792	88.9	0.23	0.38	
OR-1840-HT	28.0	552	50.1	0.49	0.22	
OR-1837-HT	6.9	452	24.4	0.59	0.05	
OR-2722-HT	81.4	766	82	0.29	0.32	
A-339	56.6	827	86	0.35	0.24	1.047
A-358	84.0	800	93	0.38	0.45	1.036
A-382	66.1	786	91	0.30	0.29	1.057
A-391	83.1	748	89	0.34	0.44	1.048

[a]OR-samples made in 75-mm coater; A-samples made in 0.13-m coater with cone distributor.

Influence of Deposition Parameters on Noble Gas Diffusion

The permeability of pyrocarbon coatings as indicated by the measured neon-to-helium ratio has been found to vary from 0.03 to greater than 1 depending on deposition conditions for the pyrocarbon. (Neon-to-helium ratios greater than 1 indicate that the pyrocarbon coating is sufficiently permeable for some of the helium to diffuse out at room temperature before the coating is cracked in the mass spectrometer.) The permeability depends in part, of course, on coating thickness, but the prime determinant is the status of the pyrocarbon structure. Apparently if the pyrocarbon had a perfect graphite structure, the neon-to-helium ratio would be zero or very small. The permeability increases with

increasing disorder in the pyrocarbon and departure from an ideal graphite lattice. The pyrocarbon structure and hence its permeability depend strongly on deposition conditions. The structure depends on the hydrocarbon gas used, diluent gas concentration, temperature, and deposition rate. Of these variables, the deposition rate of the pyrocarbon on the fuel particles appears to exert a dominating influence. The size of the coating furnace also may be an important factor as it influences pyrocarbon deposition conditions. Figure 3 shows the neon-to-helium ratio as a function of deposition rate for sets of fuel particles made in the 76-mm-diam, and 0.13-m coaters. Each set of fuel particles shows a fairly uniform increase of permeability with increasing deposition rate, although the neon-helium values cover a larger range for particles coated in the larger coater. The set of particles coated in the 0.13-m coater were part of a study[6] of coating permeability as a function of several variables including temperature, hydrocarbon gas, diluent (argon, helium, or hydrogen), and percent diluent. The dependence of the neon-to-helium ratio on other variables was less clear than on deposition rates. The neon-to-helium ratio decreases with increasing pyrocarbon coating density but typically shows more scatter than when plotted against deposition rate. The neon-to-helium ratio for several coatings is shown as a function of density in Fig. 4.

Permeability of Pyrocarbon Coatings for Argon and Krypton

The permeability of the pyrocarbon for inert gases decreases rapidly with increasing atomic number. The neon-to-helium ratio makes use of this fact in furnishing a measure of permeability with values as low as 0.03. Table 3 shows neon and helium contents after heat treatment in

---

[6] D. P. Stinton, W. J. Lackey, and B. A. Thiele, *Influence of Process Variables on Permeability and Anisotropy of Biso-Coated HTGR Fuel Particles*, ORNL/TM-6087 (November 1977).

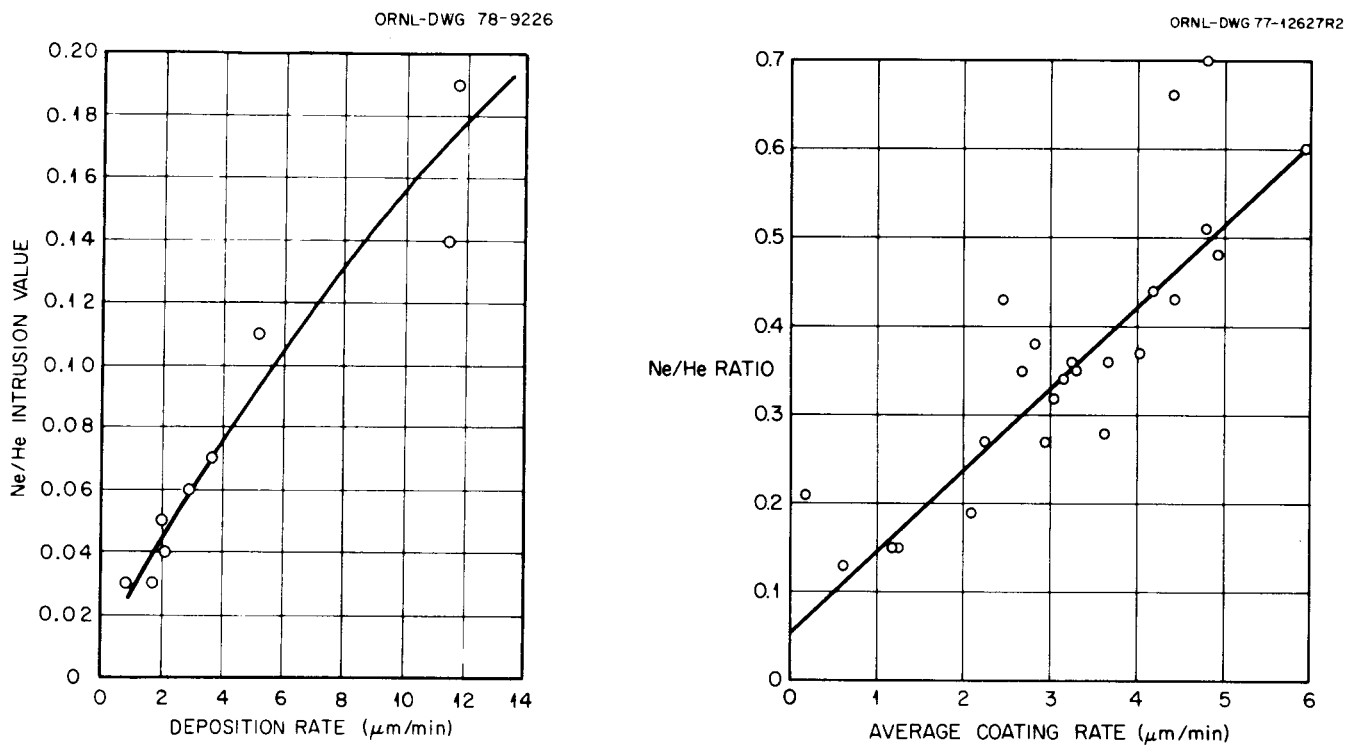

Fig. 3. Neon-to-Helium Ratio as a Function of Deposition Rate for Fuel Particles Coated in (a) the 76-mm Coater and (b) the 0.13-m Coater.

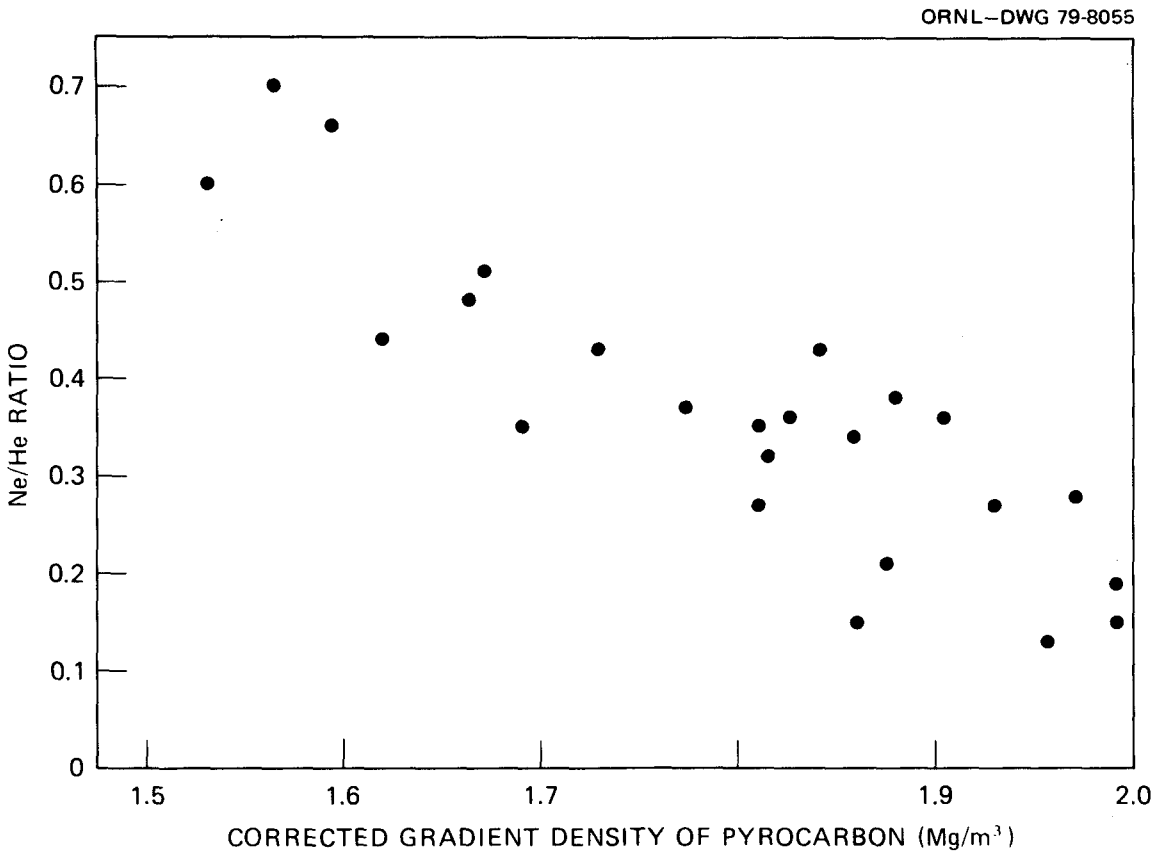

Fig. 4. Neon-to-Helium Ratio vs Density for Particles Coated in the 0.13-m Coater for Irradiation Experiment HT-34.

equimolar helium and neon at atmospheric pressure. Note that the difference in values does not truly reflect the difference in permeability for the two gases. The helium values are reduced by saturation effects while the quantity of neon diffusing into the void volume is little affected by saturation except for the most permeable particles.

While neon-helium values reflect reduced permeability for neon compared with helium, the permeability for argon gas undergoes a further sharp reduction. Argon diffusion through pyrocarbon coatings is so slow at 1375°C, which is typically used to determine neon-to-helium ratios,

that it is not practical to use this gas for most pyrocarbon coatings of interest. Data available indicate that argon diffusion becomes appreciable at 1800°C only in the more permeable coatings. This is indicated in Table 5, where data for four batches of fuel particles are given. The particles were evacuated at 1800°C for 1 h and then heat-treated at 1800°C in argon at atmospheric pressure. Argon used in particle preparation remained in the fuel particles during the vacuum heat treatment, and the amount increased significantly during subsequent heat treatment in an argon atmosphere only in the case of the two more permeable particle batches.

Table 5. Argon Permeation of Pyrocarbon Coatings

Fuel Particle Batch	Argon Content and Standard Deviation, pmol		Ne/He Ratio
	After 1 h at 1800°C in Vacuum	After 1 h at 1800°C in Vacuum, Then in Ar	
OR-2261-HT	99 ± 23	101 ± 21	0.23
OR-2264-HT	162 ± 33	151 ± 23	0.13
OR-2265-HT	28 ± 10	38 ± 10	0.32
OR-2274-HT	25 ± 9	51 ± 8	0.50

The permeability of pyrocarbon coatings for krypton is so low as to be unmeasurable with our equipment under temperature-time conditions that do not alter the structure of the pyrocarbon coatings. Krypton permeation tests were made on fuel particles held in a krypton atmosphere at 1700°C and 2300°C. At 1700°C a heat treatment time of 40 h was necessary for sufficient krypton diffusion to occur to allow dependable measurements in the mass spectrometer. The krypton intrusion data in 1 h at 2300°C and in 40 h at 1700°C are given in Table 6. The krypton values were determined from mass 84, and mass ratios observed verify that the masses being measured were krypton; however, in the cases where

Table 6. Krypton Diffusion Through Pyrocarbon Coatings on HTGR Fuel Particles and Comparison with Ne/He Ratios

Fuel Particle Batch	Intrusion Conditions		Measured Kr Content[a] (pmol)	Ne/He Ratio
	Temperature (°C)	Time (h)		
OR-2261-HT	1700	40	1.6 (0.4)	0.23
OR-2263-HT	1700	40	0.3 (0.2)	0.13
OR-2269-HT	1700	40	10.2 (3.4)	0.40
OR-2274-HT	1700	40	18.6 (8.4)	0.50
OR-2261-HT	2300	1	1.4 (0.5)	0.23
OR-2263-HT	2300	1	0.3 (0.1)	0.13
OR-2269-HT	2300	1	8.6 (2.1)	0.40
OR-2274-HT	2300	1	16.4 (11.7)	0.50

[a]Numbers in parentheses are standard deviations.

krypton quantities are small, that is, about 0.3 pmol, a significant part of the measured krypton could have been from organic impurities having the same mass. Krypton intrusion values are shown in Fig. 5 as a function of the neon-to-helium ratios for several pyrocarbon coatings. The krypton permeation in 40 h at 1700°C is almost the same as that at 2300°C for 1 h. An interesting part of this figure is the extremely small amount of krypton diffusion in the fuel particle batches with neon-to-helium ratios below 0.3. The low diffusion rate of krypton at 1700°C suggests that the diffusion of krypton and xenon through pyrocarbon coatings with neon-to-helium ratios less than about 0.3 will be very low if not completely negligible at HTGR temperatures.

Characteristics of Inert Gas Intrusion

Neon-to-helium ratios have been determined on hundreds of fuel particle batches during the course of this work, but a detailed examination of inert gas intrusion involving permeation isotherms has been made only on one particle batch, OR-2261-HT, with less complete measurements

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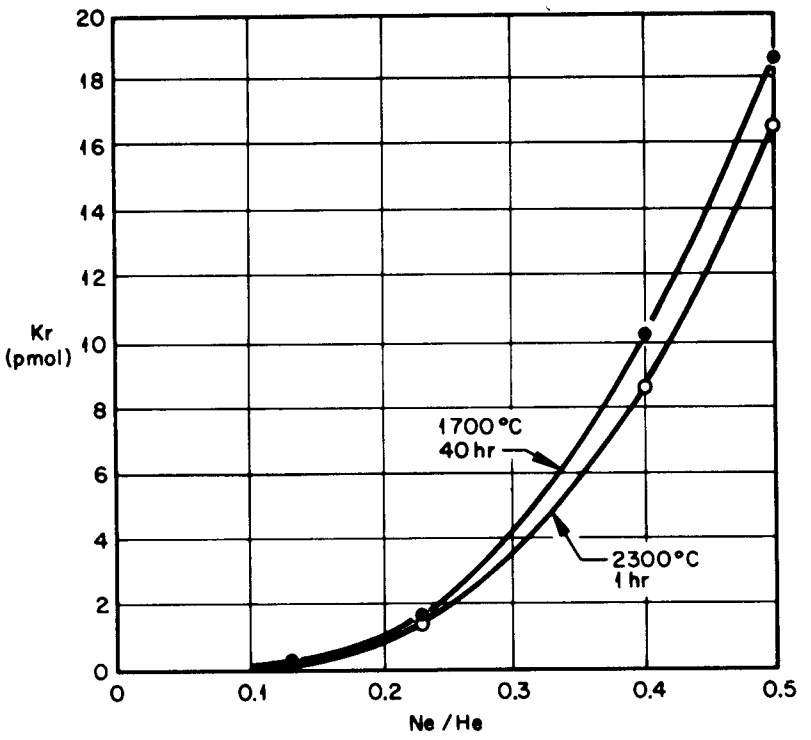

Fig. 5. Krypton Intrusion as a Function of Ne/He Ratio for Various Pyrocarbon Coatings.

carried out on six additional fuel particle batches. Powell (Y-12 Development Division)[7] used intrusion isotherms measured at several temperatures to determine values of the diffusion coefficient for the gas and the activation energies for the process. The data of each permeation isotherm were fit to the equation

$$n = n_{\infty}\{1-\exp[-k(t - t_1)]\} , \tag{12}$$

[7]G. L. Powell, *Helium Permeability of Biso High-Temperature Gas-Cooled Reactor (HTGR) Fuel Particles*, Y/DA-8035 (Sept. 22, 1978).

where

n = moles of gas permeating,

n_∞ = moles of gas in fuel particle at equilibrium,

k = first-order rate constant for filling the particle free void volume,

t = time, and

t_1 = time to achieve steady-state diffusion across the pyrocarbon coating.

The time to reach steady difffusion across the pyrocarbon coating, t_1, primarily consists of the time required to fill the porosity of the coating. Powell's analysis leading to the diffusion equations is included in the Appendix. It is based on the assumption that permeation occurs through a plane surface of area equivalent to the area of the pyrocarbon shell calculated from the gemoetric mean radius of the pyrocarbon shell.

The mathematical procedure developed by Reeves and Tolliver[8] for handling the problem of diffusion through a spherical shell into a finite volume can be used to determine diffusion coefficients. Tolliver had applied this solution to permeation data using a computer program that, in effect, determines the diffusion coefficient, D, which fits the gas uptake indicated by the experimental isotherm.[9] Other parameters are derived by use of the value of D.

The study of fuel particle batch OR-2261-HT provided data for helium permeation to apply this method at several temperatures. The diffusivites, shown in Figure 6, are described well by the Arrhenius relation except at very high or very low temperatures, where the experimental measurement is not dependable. Measurements required to obtain the graph in Fig. 6 were very time consuming, requiring several

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[8]M. Reeves and J. S. Toliver, *Transient Diffusion Through a Spherical Shell into Its Finite Spherical Core,* ORNL/CSD/TM-60 (March 1979).

[9]J. S. Tolliver, *Numerical Determination of Inert Gas Permeability Parameters of High-Temperature Gas-Cooled Reactor (HTGR) Fuel Particles,* ORNL/CSD/TM-78 (in press).

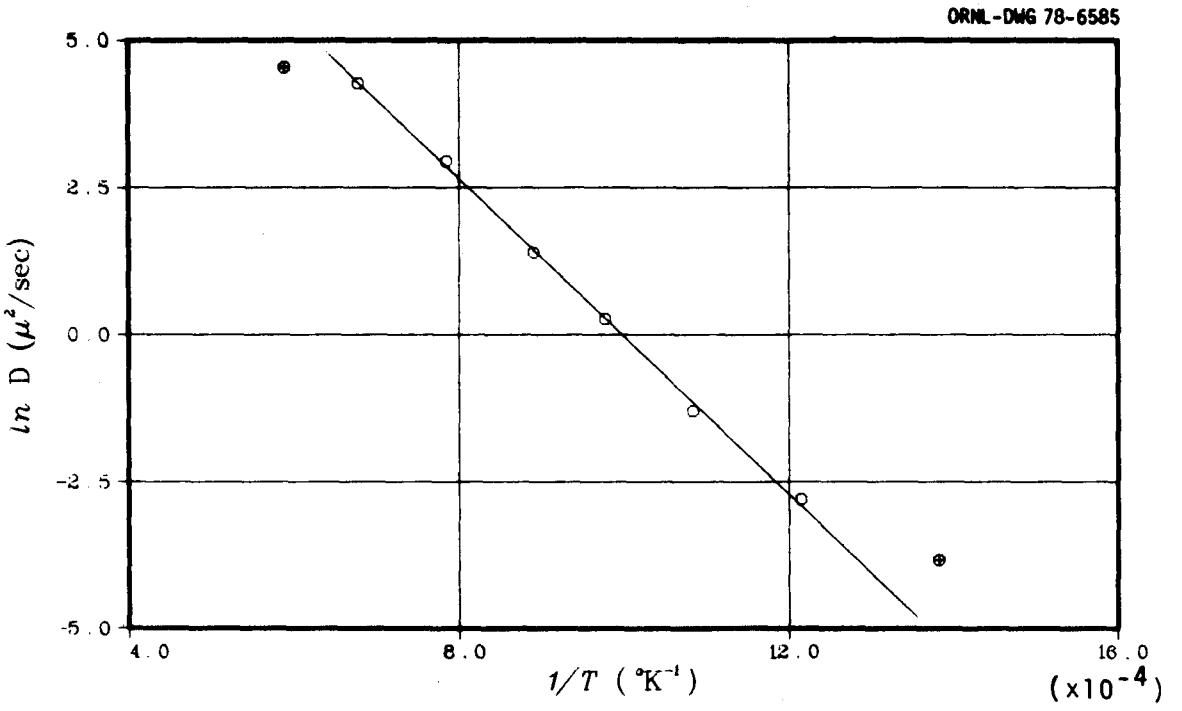

Fig. 6. Plot of Log D vs $1/T$ Demonstrating Fit of the Arrhenius Relationship for Diffusivities (D) of Helium in Fuel Particle Batch OR-2261-HT. Crossed points were not used in the fit.

weeks to complete at some temperatures. This makes this procedure impractical for comparing the permeabilities of a large number of HTGR fuel particle batches.

Helium diffusion characterization values determined by both methods of analysis are given in Table 7. Both methods can be manipulated to allow a range of values depending on the exact nature of the fit to isotherm curves. Analyses reported in Table 7 show good agreement between the two methods for determination of activiation energies for the pyrocarbon coatings on each batch of fuel particles except OR-2269-HT and J-606, and in these cases the differences are not large. For D_0 the differences are greater, but all except J-606 are the same order of magnitude. For coating J-606 diffusion coefficients were determined at only three temperatures, making it more difficult to obtain precise values of D_0 and Q.

Table 7. Characteristics of Helium Diffusion in Pyrocarbon Coatings, as Determined by the Analysis Methods of Powell and Tolliver

Fuel Particle Batch	Ne/He Ratio		D_0,[a] Preexponential Coefficient, mm^2/s		Q,[a] Activiation Energy, kJ/mol(kcal/mol)		Porosity,[b] %	
	As Measured	Normalized	Powell	Tolliver	Powell	Tolliver	Powell	Tolliver
OR-2261-HT	0.20	0.36	1.0	0.66	116(27.6)	111.7(26.7)	4.6	4.3
OR-2261-HT[c]			0.5	1.0	116(27.6)	124.5(29.7)	9.7	7.4
OR-2263-HT	0.13	0.24	0.3	1.3	109(26.1)	120.4(28.8)	4.3	3.9
OR-2269-HT	0.41	0.90	3.5	0.19	110(26.3)	81.4(19.5)	2.6	1.5
J-596	0.05	0.04	0.38	0.10	120(28.7)	109.1(26.0)	1.0	1.4
J-598	0.64	0.55	1.3	2.1	104(24.8)	104.8(25.0)	2.1	1.6
J-605	0.31	0.23	2.4	10.0	122(29.2)	129.6(31.0)	3.5	1.6
J-606	0.22	0.16	0.13	2.2	105(25.1)	130.2(31.1)	4.7	8.7

[a]The symbols are defined by the equation $D = D_0 \exp(-Q/RT)$.
[b]These values represent the percent void volume in the pyrocarbon coatings.
[c]Heat-treated 48 h at 2000°C.

Activation Energy Considerations

Activation energies for helium diffusion shown in Table 7 for several fuel particle batches do not vary significantly, even though the permeability of the pyrocarbon coatings varies extensively, as indicated by neon-to-helium ratios. The absence of a correlation between activation energy and permeabiity suggests that the actual gas movement through different pyrocarbon coatings is through similar geometric spaces or passages in the coating. Variation in permeability depends on the number of passages available for the gas. The nature of the gas passages apparently changes for all coatings similarly with temperature, so that the change of gas flow with temperature (indicated by the activation energy) is similar regardless of the actual gas permeability or diffusion value for the coating.

Sufficient inert gas intrusion measurements have been made on fuel particle batch OR-2261-HT to calculate activation energies for neon and argon as well as helium.[10] The activation energies are

helium, 116 kJ/mol (27.6 kcal/mol);

neon, 176 kJ/mol (42 kcal/mol);

argon, 268 kJ/mol (64 kcal/mol).

The krypton intrusion data in Table 6 could be used to determine an activation energy; however, the high temperatures required for measurable krypton permeation decrease the permeability of the coating, particularly at 2300°C, so any calculated activation energy would be meaningless.

Activation energies in the range from 113 to 268 kJ/mol (27—64 kcal/mol) are very high compared with activation energies for processes that reflect changes in the velocity of gas atoms. Therefore, the activation energies for helium, neon, and argon permeation suggest that the

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[10] G. L. Powell, *Inert Gas Permeability of High-Temperature Gas-Cooled Reactor (HTGR) Coated Fuel Particles from Batch OR-2261-HT*, Y/DA-7885 (May 25, 1978).

temperature variation of the movement of the gas atoms through the pyrocarbon coatings is primarily controlled by change of spacing in the permeation passages rather than by the velocity of motion of the gas atoms. The activation energies thus appear to depend on thermally activated structural changes in the pyrocarbon coatings.

The activiation energies for helium, neon, and argon permeation or diffusion through the dense pyrocarbon coatings of OR-2261-HT are plotted against atomic number in Fig. 7. The straight line obtained is extrapolated to show anticipated values for krypton and xenon (open circles). Extremely high activation energies are indicated for the diffusion of these gases. Regardless of the physical cause of the correlation shown in Fig. 7, it suggests that diffusion of krypton and xenon through pyrocarbon structures having reasonably low neon-to-helium ratios will be insignificant at anticipated HTGR fuel operation temperatures.

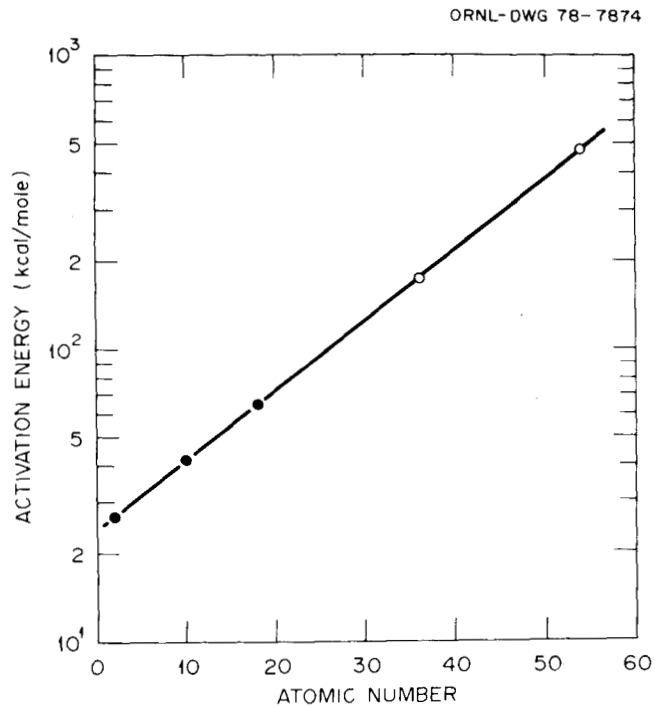

Fig. 7. Correlation of Calculated Activation Energies for He, Ne, and Ar (solid points) vs Atomic Number. The extrapolation of activation energies for Kr (At. No. 36) and Xe (At. No. 54) indicate unreasonably high values. 1 kcal = 4.184 kJ.

Correlation of Neon-to-Helium Ratios with Small-Angle X-Ray Scattering

Krautwasser[11] has studied extensively small-angle x-ray scattering (SAXS) of pyrocarbon coatings and, among other evaluations, has compared the SAXS results with neon-to-helium ratios. The relative amount of highly disordered fibrous material in the pyrocarbon structure is derived from the SAXS analysis of the quantity of pores with diameters in the neighborhood of 10 nm. A correlation between SAXS and neon-to-helium ratios, shown in Fig. 8 taken from Krautwasser and Nickel,[11] reveals a simple relation of inert gas permeability for pyrocarbon coatings and the amount of the fibrous component in the pyrocarbon structure.

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[11]P. Krautwasser and H. Nickel, "Influence of Porosity on Irradiation Performance of Pyrocarbon Coatings," *Nucl. Technol.* 35 310–19, (1977).

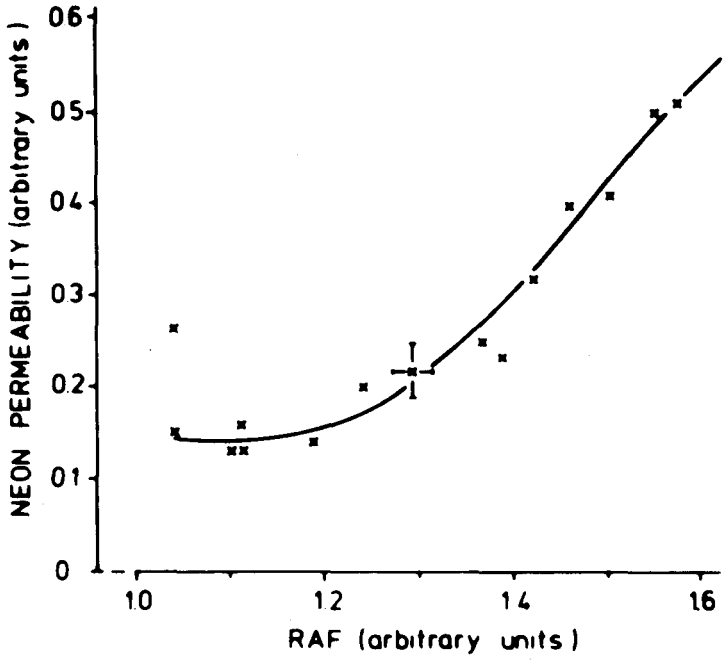

Fig. 8. Neon-to-Helium Ratio Plotted Against RAF (a measure of fibrous content derived from small-angle x-ray scattering) for a Series of HTGR Pyrocarbon Coatings Deposited from Propylene and from MAPP Gas. Copied from Krautwasser and Nickel, *Nucl. Technol.* 35: 310 (1977), by permission of the American Nuclear Society.

Comparison of Neon-to-Helium Ratios and Chlorine Leach Results of HTGR Pyrocarbon Coatings

Defects such as cracks or holes in pyrocarbon coatings on thorium-bearing kernels can be detected by a chlorine leach technique. At elevated temperatures chlorine gas moves through the defect, it reacts with a ThO_2 kernel to form $ThCl_4$, and the $ThCl_4$ diffuses out of the particle. The number of defective particles in a population can be estimated by the fraction of thorium released for given test conditions or can be determined by x-ray transmission radiography, which easily reveals particles where the thorium has been removed or has been deposited in the buffer coating. Any movement of the thorium is a direct indication that chlorine has diffused through the high-density pyrocarbon coating. Recently Thiele[12,13] has demonstrated that a chlorine leach at 1500°C can be used to measure permeability of pyrocarbon coatings on HTGR fuel particles. The quantity of thorium removed during the first 2-h leach represents primarily the removal of thorium from particles with defective pyrocarbon coatings. If the leach is continued for longer times, additional thorium removed is primarily due to permeation of chlorine through the pyrocarbon coating. Figure 9 demonstates the viability of the chlorine leach technique for differentiation of fuel particle batches into permeable and nonpermeable groups. In each case the chlorine leach indication of permeability agrees with neon-to-helium ratio measurement results on pyrocarbon coatings of the same fuel particle batch. Thorium was leached from particles with neon-to-helium ratios of 0.60 and greater, while those with lower ratios exhibited no thorium loss. The neon-to-helium ratios provide an indication of rather subtle permeability differences, while the chlorine leach tests tend to indicate an abrupt measurable distinction between permeable and nonpermeable pyrocarbon coatings.

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[12] B. A. Thiele, D. A. Costanzo, and D. P. Stinton, "Permeability Determination Using Chlorine Leach Techniques," *HTGR Base-Technology Program, Annu. Prog. Rep. Dec. 31, 1977,* ORNL-5412, pp. 46–48.

[13] D. P. Stinton and B. A. Thiele, "Permeability Studies," *HTGR Base-Technology Program, Annu. Prog. Rep. Dec. 31, 1978,* ORNL-5536, pp. 52–55.

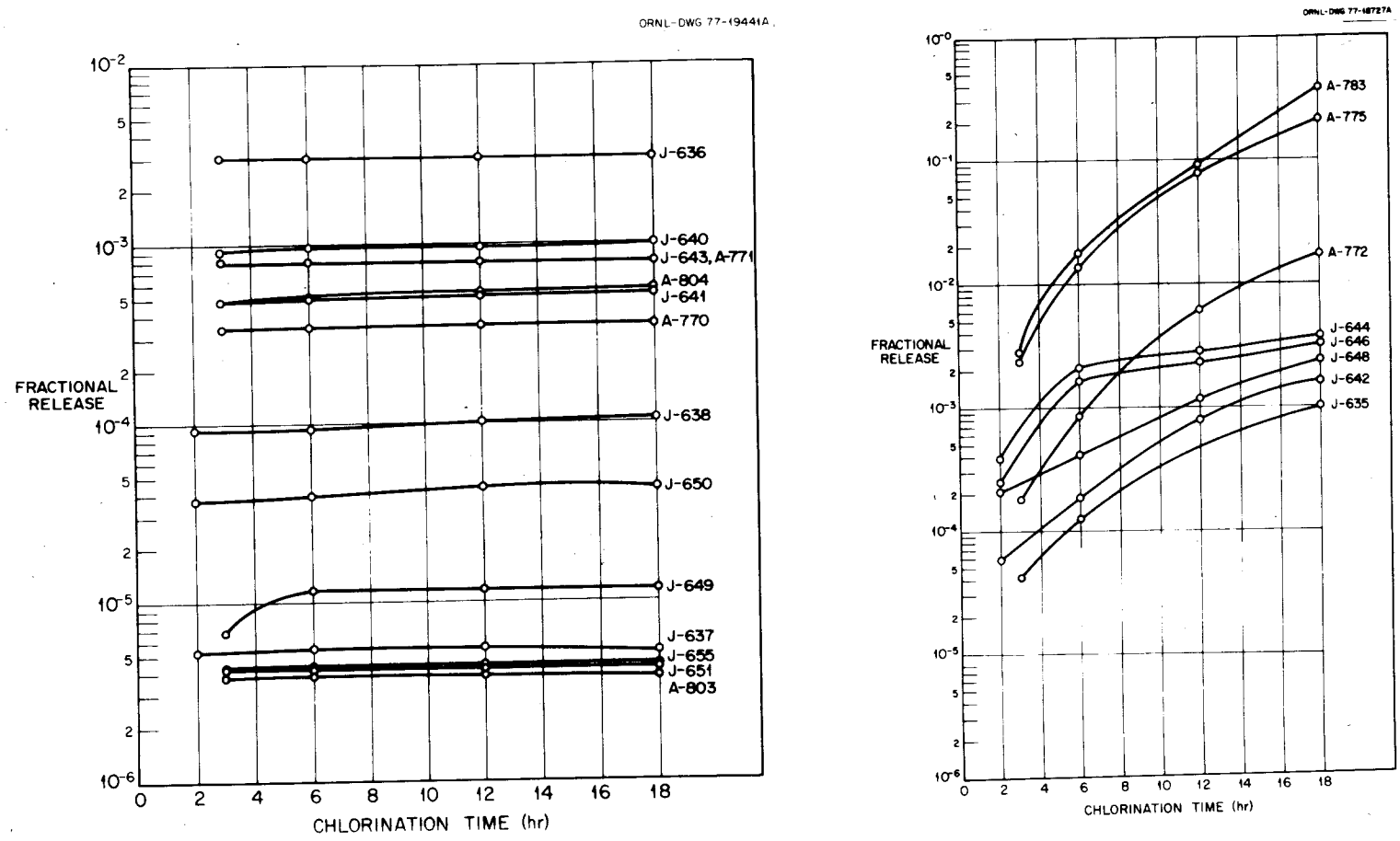

Fig. 9. Thorium Release from Fuel Particle Batches during Chlorine Leach at 1500°C. (a) Fuel particle batches with Ne/He values of 0.15 to 0.55. (b) Fuel particle batches with Ne/He values of 0.60 to 0.70.

A more sensitive measure of permeability is obtained through chlorine leach by radiographic examination of leached fuel particles. Thiele[14] has found that for fuel particles with neon-to-helium ratios above about 0.4, chlorine permeation can be observed by movement of thorium into the buffer layer. Experimental results indicate that chlorine leaching of fuel particles does not alter the permeability of the pyrocarbon coatings. In one test the permeability indicated by the neon-to-helium ratio of two fuel particle batches was not significantly changed after 16 h of chlorine leaching at 1500°C. Shorter time leaching in hot chlorine also showed no change in noble gas permeability of these pyrocarbons.

EFFECT OF POSTDEPOSITION HEAT TREATMENT AND IRRADIATION OF PYROCARBON COATINGS ON NOBLE GAS PERMEABILITY

Effect of Heat Treatment at 1800 and 2000°C

Pyrocarbons slowly undergo further crystallization and become more structurally ordered at elevated temperatures. This process would be expected to decrease the gas permeability. Significant decrease of permeability due to high-temperature annealing is evident in the data in Table 8, which shows the neon-helium permeability for fuel particles prepared in the 0.13-m coating furnace before and after heat treatment at 1800°C for 0.5 h. Generally, the noble gas permeability decreases measurably after such a 1800°C heat treatment. The decrease in neon-to-helium ratio averaged 0.069, which is a change of about 14%. The short 1800°C heat treatment also causes a small decrease in the void volume in the buffer layer. For the fuel particles in Table 8 the decrease averages 7.4%.

In another case, fuel particles of OR-2261-HT were annealed at 2000°C for 48 h. The helium diffusion through the pyrocarbon coating

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[14]B. A. Thiele, D. P. Stinton, and D. A. Costanzo, *Detection of Gas Permeable Biso-Coated Fuel Particles for High-Temperature Gas-Cooled Reactors*, ORNL/TM-6696 (April 1979).

Table 8. Neon-Helium Permeability of Pyrocarbon Coatings Before and After Annealing at 1800°C for 0.5 h

Fuel Particle Batch[a]	Ne/He Ratio		Reduction (%)
	As deposited	1800°C 0.5 h	
J-589	0.21	0.10	52
J-590	0.48	0.46	4.2
J-591	0.36	0.30	17
J-592	0.35	0.32	8.5
J-594	0.51	0.35	31
J-595	0.13	0.04	69
J-596	0.15	0.05	67
J-597	0.44	0.32	27
J-598	0.66	0.64	3.0
J-600	0.37	0.33	11
J-601	0.27	0.26	3.7
J-602	0.60	0.54	10
J-603	0.43	0.32	26
J-604	0.32	0.31	3.1
J-605	0.36	0.31	14
J-606	0.35	0.22	37
J-607	0.43	0.28	35
J-608	0.27	0.17	37
J-609	0.38	0.28	26
J-610	0.28	0.22	21

[a]Fuel particle batch designation after 1800°C, 0.5 h-heat treatment.

was measured and had a value 50% lower than the value before annealing. The void volume of OR-2261-HT decreased from 3.7×10^{-11} m^3 (per particle) to 3.1×10^{-11} m^3 during this heat treatment. (The long time allowed for helium permeation guaranteed equilibrium and assured this decrease to be real and not merely a reflection of reduced permeability).

Effect of Irradiation

The behavior of the permeability of the pyrocarbon coating during irradiation to neutron fluences of the order of 8.6×10^{25} n/m^2 is of prime importance in the behavior of Biso fuel particles. A key question

is whether fission gases will be released from the fuel because of radiation-induced permeability. In this work, the permeability of irradiated pyrocarbon coatings was determined on several batches of fuel particles in which the high-density pyrocarbon coatings were deposited on inert (carbon) kernels. The high radioactivity of irradiated particles with thorium- or uranium-containing kernels made it impossible to obtain neon-helium permeability measurements because of the mass spectrometer location. Results of measurements on particles with inert kernels clearly demonstrate that inert gas permeability of the pyrocarbon coatings decreases with increasing neutron fluence, at least to a fluence as high as 11.6×10^{25} n/m^2 (>0.18 MeV). These data are shown in Table 9 for inert kernel particle batches tested in several irradiation experiments. In each irradiation test the neon-helium permeability decreases with increasing neutron fluence except for two of the batches irradiated in capsule HT-33. This conflicting result has been explained tentatively as being due to a sample interchange at some point. These results are shown in Fig. 10, where the neon-helium permeability is represented as percentage of the unirradiated permeability as a function of fluence. The permeability decrease exceeds 60% in several cases. There is considerable scatter in the plot, which includes data from four experimental irradiation tests and five different particle batches, all of which contain inert kernels. Because of the limited number of tests and absence of control specimens, it is not feasible to deduce different irradiation behavior as a function of temperature or of particle batch. Fission products and gas pressure could affect the behavior of fuel particle coatings with uranium- or thorium-containing kernels, but results of this work using inert kernels clearly demonstrate that disorder created by the neutron damage does not cause the pyrocarbon coatings to become more permeable to inert gases.

Table 9. Pyrocarbon Coating Permeability of Irradiated Biso Particles

Particle Batch	Irradiation Experiment	Specimen Designation	Neutron Fluence >0.18 MeV (n/m^2)	Irradiation Temperature (°C)	Gas Uptake per Particle, pmol		Ne/He Ratio	Ne/He Ratio (% of Preirradiation Ratio)
					He	Ne		
OR-2294-HT	HT-31		0		107	20.5	0.19	
OR-2294-HT	HT-31		4.0×10^{25}		110	13	0.12	63
OR-2291-HT	HT-32		0		155	36	0.23	
OR-2291-HT	HT-32	14-3	4.3×10^{25}	1000	107	13	0.12	52
OR-2291-HT	HT-32	15-3	8×10^{25}	1300	75	4.2	0.06	26
OR-2294-HT	HT-33		0		107	20.5	0.19	
OR-2294-HT	HT-33	1-T	5.6×10^{25}	900	120	11.3	0.09	47
OR-2294-HT	HT-33	1-B	9.3×10^{25}	900	99	11.8	0.12	63
OR-2294-HT	HT-33	2-B	11.6×10^{25}	1250	59	3.3	0.06	32
OR-2722-1-H	HT-34		0		81	24	0.29	
OR-2722-1-H	HT-34	28-3 Top	4.8×10^{25}	900	101	13	0.15	52
OR-2722-1-H	HT-34	26-3 Top	9.1×10^{25}	1250	114	15	0.11	28
OR-2725-1-H	HT-34		0		84	26	0.31	
OR-2725-1-H	HT-34	28-3 Bottom	4.8×10^{25}	900	126	15	0.12	39
OR-2725-1-H	HT-34	26-3 Bottom	9.1×10^{25}	1250	125	14	0.11	36
OR-2730-1-H	HT-34		0		117	35	0.30	
OR-2730-1-H	HT-34	28-1	8.2×10^{25}	900	149	36	0.24	80
OR-2730-1-H	HT-34	26-1	10.2×10^{25}	1250	165	28	0.17	57

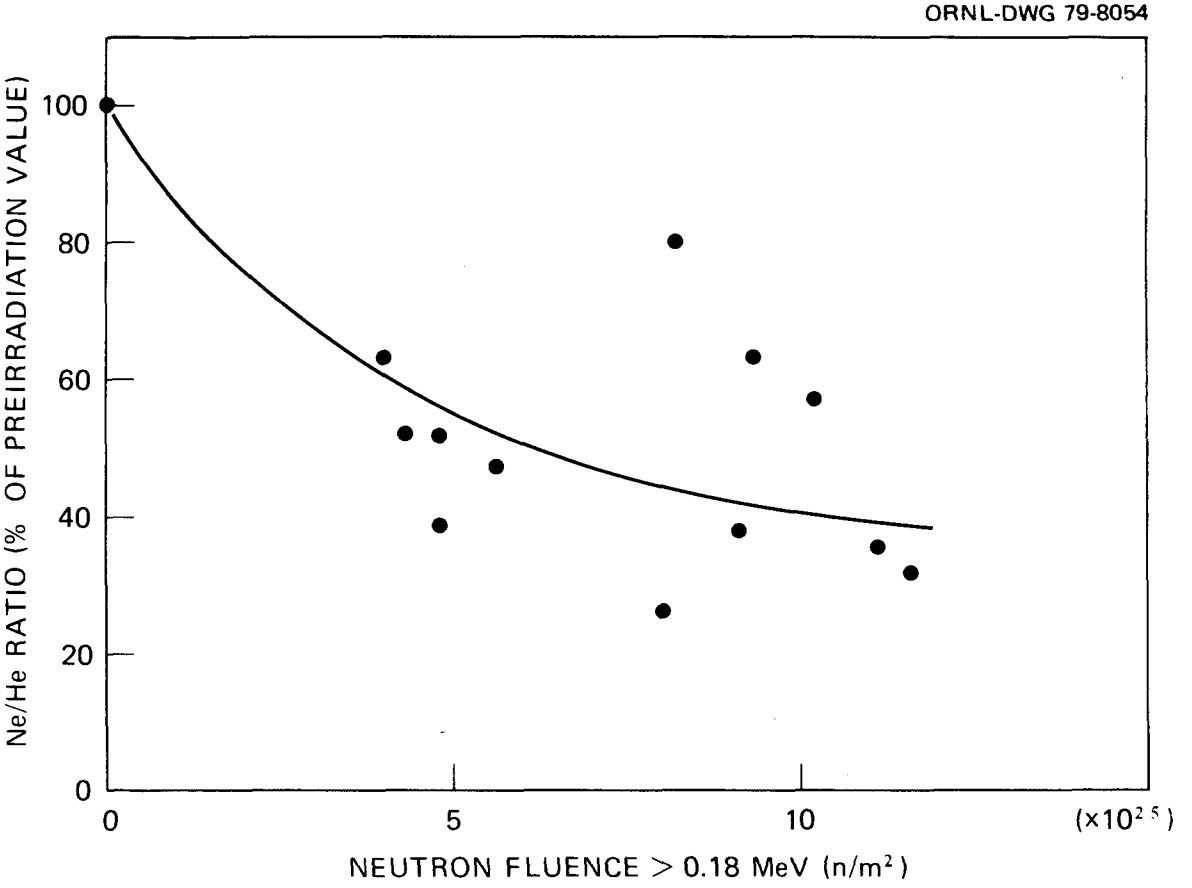

Fig. 10. Neon-Helium Permeability of Pyrocarbon Coatings as a Function of Neutron Fluence.

Effect of Fuel Particle/Fuel Rod Processing, Including Fuel Rod Consolidation and Deconsolidation

Fuel elements are prepared for HTGRs that use a prismatic core by consolidating fuel particles into a carbon-based matrix. Eighteen fuel particle batches prepared for use in irradiation experiment HRB-14 were consolidated and subsequently chemically deconsolidated by leaching with a solution of 20 wt % ammonium persulfate in 98% H_2SO_4. The neon-to-helium ratios of the deconsolidated particles decreased 11 to 54% from those of the original particles. The decrease in noble gas permeability can possibly be explained by assuming that the binder used in the carbonaceous consolidation mixture infiltrates at least some of the open

porosity of the pyrocarbon coating, and thus reduces the inert gas permeability. No evident correlation between initial pyrocarbon coating density and permeability changes during fuel rod fabrication was detected during this work.

THE NEON-HELIUM PERMEABILITY REQUIREMENTS FOR HTGRs

In order to minimize radioactive contamination of the primary coolant in an HTGR, diffusion of krypton and xenon through the pyrocarbon coatings should be essentially zero during particle lifetime in the reactor. Because of the extremely slow diffusion of krypton and xenon in pyrocarbon coatings, an experimental correlation of xenon diffusion with neon-helium measurements was not possible. In addition, correlation of krypton data is very limited. But neon-to-helium ratios do afford a basic indication of the permeability of pyrocarbon coatings. As previously pointed out, if the pyrocarbon coating had a perfect (or near perfect) graphite lattice, the permeabilty for helium at HTGR fuel temperatures would be nonexistent or very low. The permeability results from disorder and structural defects in the lattice, and obviously the disorder must be greater for heavier, larger, and more polarizable atoms such as krypton and xeonon to get through.

Based upon available data, one comparison of neon-to-helium ratio with permeability for heavy gases can be made from the krypton permeability measurements. For the rather permeable fuel particle batch OR-2274-HT (Ne/He = 0.50; data in Table 6), the krypton uptake in 40 h at 1700°C in 0.1 MPa (1 atm) was 18.6 pmol. Estimating the activation energy at 376 kJ/mol (90 kcal/mol), the release from a particle with 0.1 MPa (1 atm) Kr at 1300°C in a reactor for 180 d would be 4 pmol. If the activation energy were assumed to be the same as that for argon, 268 kJ/mol (64 kcal/mol), a more conservative assumption, the krypton release would be 32 pmol. For fuel particle batch OR-2261-HT, which had a neon-to-helium ratio of 0.23, the krypton release under these conditions would be 0.3 and 2.7 pmol, respectively. (The krypton pressure in the fuel particle will average more than 0.1 MPa (1 atm) and the time

may be longer than 180 d). These evaluations, based on measured krypton permeability, indicate that there will be only very small release of krypton from particles with neon-to-helium ratios below about 0.3.

The plot of permeation activation energy versus atomic number in Fig. 7 demonstrates that for both heavy gases, krypton and xenon, the activation energy values lie well above that for argon. Thus, available data does clearly show that releases of krypton and xenon will be very low for pyrocarbon coatings with initial neon-to-helium ratios below 0.3. For the activation energies in Fig. 7, there would be essentially no krypton release from OR-2263-HT and xenon release would be substantially less than for krypton.

Chlorine leach tests also indicate that diffusion of heavy inert gases through pyrocarbon coatings will be very small for neon-to-helium ratios below about 0.35. Chlorine leach tests[15] for 16 h at 1500°C for this type of coating detected no leaching (after a small initial amount due to mechanically defective particles in the sample population) when the neon-to-helium ratio of the pyrocarbon did not exceed 0.35.

The significance of prediction of very low krypton and xenon releases under HTGR operating conditions for pyrocarbon coatings with neon-to-helium ratios no greater than 0.30 is augmented by the significant decrease in inert gas permeability in the pyrocarbon with increasing neutron fluence. Unfortunately, further experimental determination of heavy gas atom diffusion through pyrocarbon coatings is not practical with the present procedure because the higher temperatures required for measurable effects would alter the pyrocarbon structure.

In this discussion pyrocarbon coating permeability is considered to be a process of gas atoms diffusing through the coating. Movement of gas atoms through cracks in the coating constitutes another transport process. Under some conditions, cracks tend to develop in the pyrocarbon during irradiation. In an irradiation experiment in the BR2-Mol reactor, permeability of Biso-coated ThO_2 particles increased as the

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[15]E. L. Long, Jr., R. L. Beatty, JM Robbins, M. J. Kania, and W. P. Eatherly, *Irradiation Performance of HTGR Biso Fertile Particles in HFIR Experiments HT-17, -18 and -19,* ORNL/TM-6414 (November 1978).

irradiation continued.[16] The "permeability" observed may be due to cracks formed as a result of pressure-induced stresses. However, a more likely cause is microcracks resulting from fast-neutron-induced anisotropy in the pyrocarbon coating, since transmission electron microscopy did show that microcracks had formed during irradiation.[16] In general the same deposition conditions that lead to low neon-to-helium ratios also cause high BAF_o values. Thus, if the neon-to-helium permeability is low enough to meet noble gas release criteria the pyrocarbon may have too high a BAF_o to be sufficiently stable to the required neutron fluence. That this need not be the case was verified for several fuel particle batches that had low neon-to-helium ratios and performed satisfactorily in various irradiation experiments: OR-2262-HT and OR-2273-HT exceeded HTGR design fluence in experiment HT-28 without failure,[17] and OR-2013-HT went to a fluence of 11.6×10^{25} n/m^2 in experiments HT-17 through -19 without failure.[15] The initial neon-to-helium ratios of these batches were low — 0.20, 0.14, and 0.14, respectively. Postirradiation measurements[15] showed that OR-2013-HT retained fission gases after substantially exceeding the design fluence.

The capability of pyrocarbon coatings on HTGR fuel particles to withstand irradiation is closely related to the initial anisotropy in the coating. The anisotropy as indicated by BAF_o and the permeability as indicated by the neon-to-helium ratio have a qualitative inverse relation, but, as Fig. 11 shows, in the important BAF range of 1.01—1.06 available data show no obvious correlation between BAF_o and neon-to-helium ratios.

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[16]R. A. Bradley and B. A. Thiele, "Neutron-Induced Pemeability of Pyrocarbon-Coated High-Temperature Gas-Cooled Reactor Fuel Particles," *Nucl. Technol.* 35: 353—58 (1977).

[17]E. L. Long, Jr., R. L. Beatty, P. Krautwasser, M. J. Kania, C. S. Morgan, R. L. Hamner, and C. S. Yust, *Characterization Studies and Performance of Biso-Coated Fertile Particles Irradiated in Capsules HT-28 Through HT-30*, in preparation.

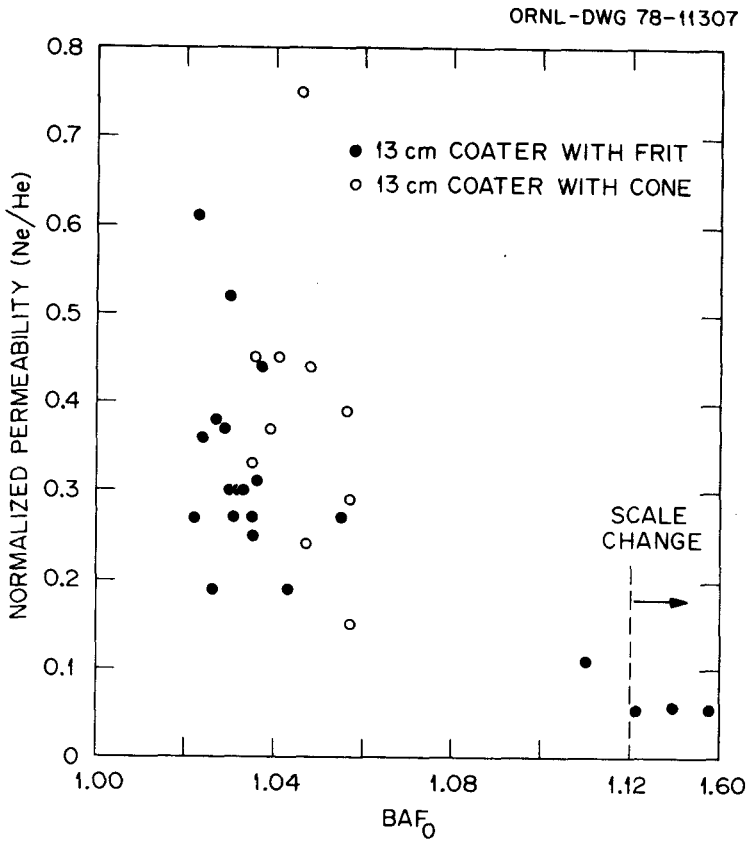

Fig. 11. Relation of Normalized Ne/He Ratio with BaF_o, the Optical Bacon Anisotropy Factor.

CONCLUSIONS

1. Pyrocarbon coatings used on HTGR fuel particles are permeable to neon and helium at elevated temperatures. A useful method to measure this permeability semiquantitatively in pyrocarbon coatings was developed.

2. The neon-to-helium ratio measure of permeability represents a measure of disorder or extent of the turbostatic condition in the pyrocarbon coating. Correlation with small-angle x-ray scattering results suggests that neon and helium permeabilities increase with increasing amount of the fibrous material in the pyrocarbon structure.

3. Neon-helium measurements show that the permeability of the pyrocarbon coating of particles with inert kernels decreases with irradiation, at least to a fluence of 11.6×10^{25} n/m^2 ($\leq$0.18 MeV). This result demonstrates that disorder created by the neutron fluence does not increase the gas permeability.

4. High activation energies for inert gas permeation of pyrocarbon coatings indicate that the process is thermally activated, with a rate change depending primarily on pyrocarbon structure changes with temperature. Similar activation energies for permeation of fuel particle batches with widely differing permeabilities suggest that gas passages through various pyrocarbon structures are similar in different coatings and that the permeability to gas depends on the number of passages, rather than variation of passage properties.

5. The relationship of neon-to-helium ratio measurements and the measured krypton permeability and chlorine leach test results, the increase of permeation activation energy with atomic number of the permeating gas, and the satisfactory radiation performance of some fuel particle batches with low neon-to-helium ratios indicate that an initial ratio of 0.3 to 0.35 for the pyrocarbon coating is low enough to assure very low krypton and xenon releases under HTGR operating conditions provided that the coating does not crack.

ACKNOWLEDGMENTS

All neon-and-helium measurements were made by G. L. Powell (Development Division, Oak RIdge Y-12 Plant), and without Powell's early help the project probably would not have been started. Powell also contriubted to the permeation experimental work and did a large part of the analysis of results. All fuel particles studied in this project were made and properties such as density, microscopy, chlorine leach, and BAF_o determined by other people, with D. P. Stinton, B. A. Thiele, E. L. Long, Jr., and W. P. Eatherly making substantial contributions. V. J. Tennery, E. L. Long, Jr., D. P. Stinton, F. J. Homan, and Sigfred Peterson and Joan Taylor contributed in preparation of the manuscript.

APPENDIX

Powell's Treatment of Permeation Data for Seven Fuel Particle Batches

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Powell's Treatment of Permeation Data for Seven Fuel Particle Batches

The intrusion of an inert gas into the buffer of a Biso HTGR fuel particle under isothermal conditions can be approximated by

$$n = n_\infty [f(t) - g(t)] \ ,$$

where:

$$f(t) = 1 - \exp\left[-k(t - t_1)\right] \ , \tag{2}$$

$$g(t) = \frac{12kt_1}{\pi^2} \sum_{i=1}^{\infty} \frac{(-1)^i}{i^2} \exp\left(-\frac{i^2\pi^2 t}{6t_1}\right) \ , \tag{3}$$

$$n_\infty = PV/RT \ , \tag{4}$$

$$t_1 = l^2/6D \ , \tag{5}$$

$$k = abD/lV \ , \tag{6}$$

and

P is the equilibrium gas pressure (Pa),
b is the volume fraction of voids in the pyrocarbon barrier,
D is the diffusion coefficient $D = D_0 \exp(Q/Rt)$ (m^2/s),
V is the free-void volume of the buffer determined from n_∞ (m^3),
l is the pyrocarbon barrier thickness (m),
r is the radius of the fuel particle (m),
a is the surface area of the pyrocarbon barrier $a = 4\pi r(r - 1)$ (m^2),

and

R is the ideal gas law constant (8.3144 J/mol K), provided $kt_1 < 0.05$.

The function $f(t)$ describes the filling of the buffer void volume by steady-state permeation and $g(t)$ describes the approach to steady-state permeation. The function $g(t)$ is significant only at early times and is negligible for $t > 2t_1$. Neglecting $g(t)$ and discarding data for which $n/n_\infty < 0.05$ yields $n = n_\infty f(t)$, from which n_∞, t_1, and k can be determined. The exact solution for helium permeation of OR-2261-HT fuel particles as calculated by Tolliver fits the model as described in Eq. (1) within a limit of error of ±0.1% with t_1 being determined with similar precision. However, the values for D and b deduced from Eqs. (5) and (6) were 2% greater for D and 10% smaller for b than those obtained by Tolliver using the mathematically exact method.[1,2] Thus, this expression is emperically valid within the experimental uncertainty (primarily due to particle-to-particle variability) of the data obtained from fuel particles. Equation (1) reduces to that of Eatherly when t_1 is neglected.

The values for Q (Table 7, Powell's results) were determined by using the data for k. Since the Q values from the t_1 data were not significantly different from those for the k data, D_0 was determined from the value for t_1. After D_0 and Q_1 were determined, b was then determined with Eq. (6).

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[1]G. L. Powell, *Inert Gas Permeability of High-Temperature Gas-Cooled Reactor (HTGR) Coated Fuel Particles from Batch OR-2261-HT,* Y/DA-7885 (May 25, 1978).

[2]J. S. Tolliver, *Numerical Determination of Inert Gas Permeability Parameters of High-Temperature Gas-Cooled Reactors (HTGR) Fuel Particles,* ORNL/CSD/TM-78 (in press).

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