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**CARBON TRANSPORT AND CORROSION IN HIGH-TEMPERATURE
GAS-COOLED REACTORS**

by

L. R. Zumwalt, R. D. Burnette, and A. B. Riedinger

April 12, 1962

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L. R. Zumwalt, R. D. Burnette, and A. B. Riedinger

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ABSTRACT

In high-temperature graphite reactors that are necessarily cooled by an inert gas such as helium, gaseous impurities can lead to transport and corrosion effects. In the reactor core, at the high temperatures involved, gaseous impurities of carbon, oxygen, hydrogen, and nitrogen occur principally as CO, H₂, and N₂. Depending on the temperature, the radiation level, and the catalytic effects, however, the following reactions (forward or reverse) involving these impurities will occur in the reactor coolant system:

Theoretical calculations are presented on the transport of carbon to be expected across gaps in the core region. These indicate reaction (3) to be important at reactor core temperatures (1000° to 1500°C). Experimental results of corrosion studies involving reaction (3) at high temperatures in and out of an irradiation field are given. Studies of the effects of steam on impermeable graphites at temperatures of the order of 1000°C are reported. Finally, the results of experimental studies on the effect of iron and of fission products such as cesium in catalyzing reactions (4), (5), and (6) are given.

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INTRODUCTION

In high-temperature graphite reactors that are cooled by helium, sufficiently high levels of gaseous impurities can lead to transport and corrosion effects. In the reactor core, at the high temperatures involved, gaseous carbon, oxygen, hydrogen, and nitrogen containing impurities will exist principally as carbon monoxide, hydrogen, and nitrogen. Depending on the partial pressures of impurities, the temperature, the radiation level, and the presence of catalysts, the following reactions (forward or reverse) involving these species may occur in the reactor coolant system; the heat of formation^[1] for each reaction is shown:

The possible effects of these reactions in the advanced class of graphite-moderated reactors designed to operate at a helium-coolant pressure of about 20 atm and exemplified by the O. E. C. D. Dragon reactor^[2] and the General Atomic HTGR (High-temperature Gas-cooled Reactor)^[3] have been the subject of the preliminary experimental and theoretical explorations reported here. Two features of these reactors pertinent to carbon mass transfer and corrosion are:

1. That the fuel elements are purged by a small fraction of the total coolant stream, so that the leakage of gaseous fission products into the primary coolant stream is minimized and thus the coolant impurities have a chance to attack the graphite within the fuel element and to transport carbon across gaps; and
2. That an effective coolant purification system is provided, so that, if necessary, the impurities can be maintained at quite low levels-- 10 to 100 ppm.

CARBON TRANSPORT ACROSS GAPS IN THE FUEL ELEMENT

A rather unique carbon-transport problem may exist in reactors operating with purged graphite fuel elements. The cylindrical fuel rods, composed of compacts made of (U, Th) C_2 particles dispersed in a graphite matrix, are sheathed in a graphite sleeve, and the coolant is allowed to purge the space between the sleeve and the fuel. The annular gap in this type of element is 5 to 10 mils (1 mil equals 0.0025 cm), and the expected temperature gradient across the gap is 50° to 200°C, depending on the axial position along the fuel element and the actual gap width. A maximum temperature gradient of the order of 200°C/10 mils (8000°C/cm) is expected. Under normal operation, the purge-gas-gap temperature of the hottest fuel element might be as high as 1800°K and as low as 700°K. Recent calculations for General Atomic HTGR fuel elements indicate that the upper gap temperature is more like 1550°K.^[4] Assuming that the chemical reaction rates are fast enough, different concentrations of the various species will develop at the two graphite surfaces, owing to an equilibrium shift, and gas-phase diffusion will tend to occur. Thus, by endothermic reactions (1) through (5), above, carbon will be eroded from the fuel bodies and deposited on the cooler sleeve. Exothermic reaction (6) will transport carbon in the opposite direction.

When the chemical reaction rates at the surfaces are sufficiently high, chemical equilibrium is attained, and diffusion across the gap will

determine the rate of carbon transport. Neglecting the generally small effect due to thermal diffusion, the transport may then be approximately calculated using the following equation, where i refers to the molecular species-- C_2N_2 , C_2H_2 , HCN, H_2O , CO_2 , and CH_4 , respectively, for reactions (1) through (6)--whose diffusion will determine carbon transport:

$$\frac{\Delta n_c}{\Delta t A} = \frac{D_{He-i}}{RT} \left| \frac{\Delta P_i}{\Delta x} \right| \frac{\text{equivalents}}{\text{cm}^2 \text{-sec}}, \quad (7)$$

where Δn_c = amount of carbon transferred (equivalents*),

Δt = time for transfer process (sec),

D_{He-i} = mutual diffusion coefficient of species i and He at temperature T and total gas pressure P (cm^2/sec),

ΔP_i = difference in partial pressure of species i across gap assuming chemical equilibrium is attained at each surface (atm),

A = area (cm^2),

R = gas constant ($\text{cm}^3 \text{-atm/mole-}^\circ\text{K}$),

T = average temperature across the gap ($^\circ\text{K}$),

x = gap width (cm).

Where chemical kinetics may be limiting, the carbon transport calculated using Eq. (7) is an approximate upper limit and, as such, may be useful in estimating the possible effect that carbon transport and deposition may have on fuel-element operation.

The above discussion is for radial transport; the question arises, is there appreciable axial transport due to the flow of the helium purge gas? Linear purge-gas velocities may be of the order of 150 cm/sec. In the case where the mutual diffusion constant, D_{He-i} , is $0.20 \text{ cm}^2/\text{sec}$, the characteristic diffusion time, $(\Delta x)^2/D_{He-i}$, would be 3.1×10^{-3} sec for a 10-mil gap, and an axial transport (distance of travel) of the order of 0.5 cm might be expected.

*An equivalent corresponds to two gram-atoms of carbon in the case of reactions (1) and (2) and one gram-atom of carbon for the other reactions.

To estimate carbon transport, equilibrium constants, K_p , were calculated for each of the six reactions at the surface temperatures of interest. Then, for two given surface temperatures, the difference in partial pressure of species i , ΔP_i , was obtained from ΔK_p and the partial pressures (P_j , P_k , etc.) of the impurities (j , k , etc.). Thus, for the calculation of carbon transport by reaction (3),

$$\Delta P_{\text{HCN}} = \Delta K_p^{(3)} (P_{\text{H}_2})^{1/2} (P_{\text{N}_2})^{1/2};$$

and for the calculation of carbon transport by reaction (4),

$$\Delta P_{\text{H}_2\text{O}} = \Delta K_p^{(4)} (P_{\text{CO}}) (P_{\text{H}_2});$$

Values of the mutual diffusion constant, $D_{\text{He}-i}$, were calculated using the equation

$$D_{\text{He}-i} = \frac{D_{\text{He}-i}^0}{P} \left(\frac{T}{273} \right)^{1.75}, \quad (8)$$

where P = total gas pressure (atm),

T = average temperature across the gap ($^{\circ}\text{K}$),

$D_{\text{He}-i}^0$ = mutual diffusion coefficient for molecular species i in helium at 1 atm total pressure and 0°C (cm^2/sec).

The values of $D_{\text{He}-i}^0$ shown in Table I were obtained from the rigid-elastic-sphere model approximation, [5]

$$D_{\text{He}-i}^0 = \frac{8.3 \times 10^{-16}}{(\sigma_{\text{He}-i})^2} \left[\frac{4 + M_i}{4M_i} \right]^{1/2}, \quad (9)$$

where M_i = molecular weight of species i ,

$\sigma_{\text{He}-i}$ = mean molecular diameter for helium and i (cm).

The value of $\sigma_{\text{He}-i}$ was estimated from atomic radii of Pauling [6] and molecular diameters based on viscosity measurements, using a method

Table I
CALCULATED MUTUAL DIFFUSION COEFFICIENTS
AT 1 ATM AND 0°C

<u>Molecular Species i</u>	<u>D_{He-i} (cm²/sec)</u>
C ₂ N ₂	0.49
C ₂ H ₂	0.66
HCN	0.53
H ₂ O	0.53
CO ₂	0.46
CH ₄	0.57

proposed by Merten.^[7] This method takes into account the fact that experimentally the mean molecular diameters determined directly in interdiffusion measurements are about 10% lower than those calculated for viscosity measurements, the rigid-elastic-sphere model being used in each case.

The results of the calculation of carbon transport across a 10-mil (0.025-cm) gap, assuming the presence of 10 ppm each of H_2 , N_2 , and CO in helium at 20 atm, are given in Table II.

It is to be noted that the reactions involving the formation of HCN, H_2O , and CO_2 are likely to be the most important ones leading to carbon transport. Also, it is to be noted that, with an equal increase of all impurities, the diffusion-controlled transport would increase linearly for reactions (1), (2), and (3), and as the square of the impurity level for (4), (5), and (6).

The transport values obtained, as indicated above, are approximate values of the upper limit of actual transport, since in most cases the rate of chemical reaction at the graphite surface will be limiting. In high-radiation fields, however, chemical reactions will tend to be accelerated, and diffusion-controlled transport may be approached. Furthermore, sorbed fission products such as cesium, strontium, and barium may catalyze the reactions. Accordingly, exploratory experiments on the most important carbon-transport and deposition reactions were carried out under simulated reactor conditions. This was done to get an idea both of the reaction kinetics involved and of the physical nature of the deposits. Carbon transport across the purge-gas passageways of a fuel element might lead to deposits which would ultimately obstruct the passageways; also, gap thicknesses might change, which would lead to changes in temperature drop and the possible development of undesirable hot spots.

Experimental Studies of the HCN Reaction

The reaction involving the formation of HCN from the elements, reaction (3), was investigated as long ago as 1879 by Dewar; however,

few data for this reaction or its reverse appear to be available. Therefore, several experiments were designed to roughly determine both the reaction rate of (3) and the carbon deposition by the reverse reaction, under conditions simulating reactor conditions.

The experimental approach was to use a simulated fuel-rod-sleeve assembly, depicted schematically in Fig. 1. The rod was affixed between the electrodes of a graphite resistance furnace and could be heated to temperatures up to 2000°C , while the sleeve experienced temperatures that were $\sim 200^{\circ}$ lower because of the heat losses across the 0.020-in. annular gap. The rod was composed of eight threaded sections, which were outgassed and weighed prior to starting the run. After the furnace was brought to the desired temperature in vacuo, a gas mixture consisting of Bureau of Mines helium to which hydrogen and nitrogen were added was allowed to purge the annular gap of the simulated fuel element. The gas stream was then passed through a caustic solution, which collected the HCN in the effluent. For each run at a particular temperature, a control run was made using helium (similar to that employed in making up the gas mixture) as the purge gas in order to determine the weight loss of the samples due to outgassing and/or reaction with impurities in the helium. By subtracting the control weight-loss rate from the total weight-loss rate, a true HCN-reaction rate could be arrived at. The weight-loss data for each of the graphite specimens for three separate runs are listed in Table III.

For purposes of extrapolation to reactor conditions, the weight-loss data for specimens 5, 6, 7, and 8 are to be used, since the other segments, 4, etc., are not under the sleeve. Why specimen 4 invariably loses more weight than the others is not entirely clear. A possible explanation is that H_2O and O_2 contamination of the large (90-liter) dome of the furnace leads to higher weight losses outside the sleeve, whereas those specimens inside the sleeve (5, 6, 7, and 8) are continually bathed with clean gas.

An Arrhenius plot of the average weight-loss rates for the three experiments is shown in Fig. 2. The apparent activation energy calculated from the slope is 13.7 kcal/mole.

Table II

CALCULATED CARBON TRANSPORT ACROSS A TEN-MIL GAP

Transporting Species i	Surface Temperature* (°K)	ΔP_i (atm)	D_{He-i} (cm ² /sec)	$\Delta n/\Delta tA$ (equiv. /cm ² -sec)	Equivalent External Surface Area, Mass Transfer in 1000 Days	
					mg/cm ²	mils†
C ₂ N ₂	2000 → 1800	3.0×10^{-10}	0.73	5.5×10^{-14}	0.11	0.026
C ₂ H ₂	2000 → 1800	$1.2_0 \times 10^{-7}$	0.98	3.0×10^{-11}	62	13
	1800 → 1600	3.1×10^{-8}	0.81	7.0×10^{-12}	15	3.2
	1600 → 1400	5.2×10^{-9}	0.65	1.1×10^{-12}	2.2	0.50
	1400 → 1200	$1.3_2 \times 10^{-7}$	0.41	2.0×10^{-11}	21	4.5
HCN	2000 → 1800	2.4×10^{-6}	0.79	4.8×10^{-10}	500	110
	1800 → 1600	$1.1_4 \times 10^{-6}$	0.65	2.1×10^{-10}	220	47
	1600 → 1400	4.8×10^{-7}	0.52	8.0×10^{-11}	83	18
	1400 → 1200	2.4×10^{-8}	0.31	3.2×10^{-12}	3.3	0.72
H ₂ O	1200 → 1000	-1.5×10^{-8}	0.30	2.0×10^{-12}	2.1	0.45
	1000 → 800	$-1.0_8 \times 10^{-6}$	0.21	$1.2_3 \times 10^{-10}$	128	28
CO ₂	1200 → 1000	-2.2×10^{-8}	0.26	2.6×10^{-12}	2.7	0.58
	1000 → 800	-5.0×10^{-6}	0.19	4.9×10^{-10}	513	111
CH ₄	1200 → 1000	-3.2×10^{-9}	0.33	4.6×10^{-13}	0.48	0.10
	1000 → 800	-6.6×10^{-8}	0.23	8.1×10^{-12}	8.5	1.9

* The direction of the arrow indicates the direction of diffusion of the transporting species.

† One mil equals 0.025 cm; thickness of a graphite with density of 1.8 g/cm³.

Fig. 1--Simulated fuel-rod-sleeve assembly for HCN reaction experiment

Table III

WEIGHT LOSS DUE TO THE HCN FORMATION REACTION
(Experimental conditions: 1.0% H₂ and 1.0% N₂ in helium
at a pressure of 1 atm and flowing at the rate of 50 cm³/min)

Specimen No.	Temp. (°C)	Reaction Rates (μg/cm ² -hr)*			HCN Analysis Data† (μg C/hr)
		Total	Helium Control	Net	
Run A (200 hr)					
4	1300	16	8.8	7.2	7.5
5	1400	1.7	0.6	1.1	
6	1380	1.8	0.3	1.5	
7	1300	1.8	0.4	1.4	
8	1250	1.4	0.4	1.0	
				Avg. 1.3**	
Run B (117 hr)					
4	1500	40.1	3.0	37.0	10.0
5	1600	11.4	2.2	9.2	
6	1580	12.6	2.0	10.6	
7	1500	12.3	2.2	10.1	
8	1450	13.6	2.8	9.8	
				Avg. 10.0*	
Run C (69 hr)					
4	1700	64	7.1	57.9	23.0
5	1800	38	6.0	32.0	
6	1780	48	4.2	43.8	
7	1700	50	5.4	45.6	
8	1650	59	4.7	54.3	
				Avg. 44.0*	

* μg/cm²-hr of external graphite surface.

† To translate the HCN analysis figures to μg C/cm²-hr, one must divide by the total active graphite surface--approximately 200 cm².

** Average reaction rate under sleeve, Specimens 5, 6, 7, and 8 only.

Fig. 2--Reaction rate for the HCN reaction

The total carbon weight loss calculated from the total amount of HCN collected during each run was invariably less than 1% of the observed weight loss, which would seem to indicate that the back reaction (decomposition of HCN) was rapid. Further evidence of this back reaction was the observation of a sooty carbon deposit on the inner surface of the sleeve after each run.

Extrapolation of the experimental weight-loss results to reactor conditions for 1000 days and comparison with the theoretical calculations based on diffusion-controlled transport rate reveal that for specimen surface temperatures ranging from 1800° to 1600° K the experimental loss rate was 20 mg/cm^2 , compared with the theoretical value of 220 mg/cm^2 . For temperatures ranging from 1600° to 1400° K, the experimental rate was 4.2 mg/cm^2 , compared with the theoretical value of 83 mg/cm^2 . For temperatures ranging from 1400° to 1200° K, the experimental versus theoretical rate was 0.6 versus 21 mg/cm^2 , respectively. The fact that the experimental values are much lower than those of the theoretical calculations indicates that the carbon loss is limited by the chemical reaction rate rather than diffusion-limited.

Some preliminary experiments were performed to determine whether, under reactor conditions of intense radiation, the HCN reaction rates are enhanced. The furnace was set up at a beam port of the General Atomic electron linear accelerator (Linac). The electron beam was focused on a tungsten target, producing a cone of 10 to 15 Mev X-rays which impinged on the central portion of the graphite assembly (segments 4, 5, and 6; see Fig. 1) with a radiation dose rate of approximately 10^5 r/min . The temperature of the specimens was held at 1250°C to 1400°C ; the gas mixture used was 0.25% H_2 and 1.0% N_2 in helium flowing at a rate of 200 ml/min at a pressure of 1 atm. Three separate runs were made--one run used the radiation field and two were control runs. In the control runs, the specimens were exposed to the same conditions as in the irradiation experiment, with the exception of the radiation field. The results are given in Table IV.

Table IV

RESULTS OF HCN FORMATION REACTION IN LINAC IRRADIATION
(Experimental conditions: 0.25% H₂ and 1.0% N₂ in helium at a pressure of 1 atm and flowing at the rate of 200 ml/min)

Run	Experiment	Run Length (hr)	Reaction Rate Under Sleeve ($\mu\text{g}/\text{cm}^2\text{-hr}$)	HCN Analysis Data* ($\mu\text{g C/hr}$)
D	LINAC run (10^5 r/min)	9.3	28	19
E	Control No. 1	23	41	23
F	Control No. 2	65	7.1	13

*The HCN analysis data should be divided by approximately 200 to translate to $\mu\text{g}/\text{cm}^2\text{-hr}$.

Although there is considerable scatter in the data shown in Table IV, there does not appear to be an appreciable increase in reaction rate due to the radiation field; i. e., the radiation-field experimental result (run D) is intermediate between those of the two control runs (runs E and F).

Another point which should be noted is that the reaction rates listed for runs D, E, and F are considerably higher than those observed in run A (see Table III), where the temperatures were identical. If anything, run A should be higher because the H_2 concentration was higher--1.0% as compared with 0.25%. It has been our experience, however, that very short runs yield higher apparent specific reaction rates than longer runs, which is probably due to initial outgassing of the graphite as well as to the reaction of the graphite with gas-phase impurities in the furnace dome. This explanation would also explain the discrepancy between runs E and F.

Experiments on Reactions Involving H_2O , CO_2 , and CH_4 Formation

In experiments concerned with the question of carbon transport and deposition in purge passageways, graphite was found to be catalytically inactive with respect to the reverse steam-graphite reaction, the Boudouard reaction, and the methane synthesis reaction, respectively:

Several graphite specimens were exposed to 3.3% CO and 3.3% H_2 in helium at temperatures ranging from 400° to $850^\circ C$. The effluent was analyzed for CO_2 and CH_4 , using a gas chromatograph. No CO_2 or CH_4 was observed. The limit of sensitivity for the instrument (about 1 ppm for CO_2 and 2 ppm for CH_4) indicates that the Boudouard reaction rate was $<0.03 \mu g C/cm^2-hr$, and the methane synthesis reaction rate was $<0.06 \mu g CH_4/cm^2-hr$ for all of the temperatures studied. Examination of the

samples for weight changes after each run (100 to 300 hr) revealed that the samples almost invariably showed a weight loss (up to 10^{-2} wt-%), even though they were outgassed at 1000°C for 2 to 3 hr and were weighed immediately before starting each run. This negative gain indicates negligible carbon deposition by reactions (4R) and/or (5R).

Since metals are known to be active catalysts of the carbon deposition reactions, fission products such as barium, strontium, or cesium, which will be sorbed in the core graphite, may accelerate carbon deposition. Accordingly, the experiments were repeated using graphite specimens loaded with 0.013 wt-% barium, which roughly corresponds to end-of-core-life loading for the HTGR, assuming all the barium is sorbed in the core graphite. (The specimens were prepared by adding BaCO_3 to the graphite matrix material prior to hot-pressing.) The experimental conditions were similar to the above runs in which plain graphite was tested. The effluent CO_2 partial pressure sets the Boudouard reaction rate for various temperatures, as listed in Table V. No CH_4 was detected and weight gains of the sample were negligible (or negative), indicating extremely low carbon-deposition rates.

Extrapolation of these data to reactor conditions (where it is assumed the CO and H_2 impurities are at 10 ppm) leads to low carbon-deposition rates, i. e., 0.12 mg C/cm^2 (equivalent to a 0.025-mil layer) in 3 yr at 761°C , the temperature at which the highest reaction rate was observed experimentally. Thus, it appears that the catalytic effect of barium (0.013% barium in graphite) is negligible.

An experiment similar to the barium experiment described above was performed using a graphite specimen loaded to ~ 1.0 wt-% cesium. No CO_2 was observed in the temperature range 500° to 800°C . Methane formation, however, was observed, as listed in Table VI.

Extrapolation of the methane synthesis data to HTGR conditions, i. e., 10 ppm CO and 10 ppm H_2 in helium at 23 atm, shows that at 700°C about $2.4 \text{ mg CH}_4/\text{cm}^2$ -1000 days will be formed. This corresponds to

Table V

RESULTS OF EXPERIMENT ON THE EFFECT OF BARIUM
IN GRAPHITE ON BOUDUARD REACTION

(Experimental conditions: 3.0% CO and 3.0% H₂ in helium
at a pressure of 1 atm and flowing at the rate of 20 ml/min;
graphite loaded with 0.013 wt-% barium)

<u>Temperature</u> <u>(°C)</u>	<u>Reaction Rate</u> <u>($\mu\text{g C/cm}^2\text{-hr}$)</u>
400	>0.04
450	>0.04
500	0.05
540	0.08
589	0.07
646	0.18
700	0.24
734	0.43
761	0.60
821	0.40
871	0.35
900	0.32

Table VI

RESULTS OF EXPERIMENT ON THE EFFECT OF CESIUM
IN GRAPHITE ON METHANE SYNTHESIS

(Experimental conditions: 3.3% H₂ and 3.3% CO in helium
at a pressure of 1 atm and flowing at the rate of 75 ml/min;
graphite loaded with 1 wt-% cesium)

<u>Temperature</u> <u>(°C)</u>	<u>Reaction Rate</u> <u>($\mu\text{g CH}_4/\text{cm}^2\text{-hr}$)</u>
500	10
600	17
700	20
800	15

about 0.5 mil of erosion during one reactor-core lifetime (1000 days).

STEAM-GRAPHITE REACTION--RATES AND EFFECTS

In any gas-cooled reactor producing power by means of high-pressure steam, the possibility exists of a steam leak into the gas system. The HTGR is being designed to allow for a continuous in-leakage of 0.01 lb water/hr. This is equivalent to approximately 1.5% weight loss of reactor-core graphite in 3 yr. Since only a small fraction of the helium flow is passed through the purification system, essentially all of the water that enters the gas system can be expected to react with fuel-element graphite in contact with the coolant. The actual magnitude of the steam-graphite reaction rate is of little concern because a portion along the length of the graphite sleeve of the fuel element is quite hot (order of 1000°C) and will tend to completely react with water in the coolant. The question is thus the relative reaction rate as a function of temperature along the length of the sleeve and the effect of the reaction on the properties of the sleeve graphite.

Possible consequences of the steam-graphite reaction are (1) erosion of the surface of fuel elements, with a resultant enlargement of the coolant flow channels and a decrease in heat transfer and (2) an increase in the permeability of the graphite sleeve, and consequent increase of fission-product diffusion through the sleeve. It is expected that the relationship of temperature to reaction rate can be described in the manner of Wicke,^[8] shown in Fig. 3 as consisting of three distinct zones which are: I, controlled by the chemical reactivity of the graphite; II, controlled by diffusion into the pores together with the chemical reactivity of the graphite; and III, controlled by diffusion of reactants and products throughout the gas phase (through the boundary layer in the case of turbulent flow).

It is interesting to note that this rate behavior can be expected for each of the above reactions (1) through (6). In the previous discussion, it was assumed that the diffusion in the gas phase was limiting, i. e., that the rate versus the reciprocal temperature relation corresponded to zone III.

Fig. 3--Relative reaction rate of gases with graphite, according to Wicke^[8].

For reaction (4) in zone II ($\sim 1000^{\circ}$ to 700°C), the rate should be proportional to the square root of the rate of diffusion of steam into the graphite and the square root of the true chemical reaction rate. Thus, the activation energy is one-half that for the chemical reaction. In this case it can be expected that the major effect on the graphite will be enlargement of existing pores.

In the highest-temperature zone, III, the rate is difficult to measure because it is set by the thickness of the boundary layer; hence, meaningful measurements require a mockup of the reactor fuel element and gas flow rates (Reynolds number of $\sim 20,000$). Fortunately, this region can be calculated with reasonable accuracy. The effect of steam on the graphite in this region will be primarily to reduce sleeve thickness.

For HTGR operations, it appears that the effects corresponding to the two higher-temperature zones (II and III) are of most concern. The major portion of the reaction will occur above 800°C , with the maximum external temperature of the fuel-element sleeve not exceeding 1100°C .

Experimental Studies--Observed Reaction Rate and Effect on Graphite Permeability

Rate measurements have been carried out on specimens of various sizes and shapes, at various water levels and temperatures. The results of the measurements were similar to those reported in the literature, [9-13] showing considerable variation with material. Only those results on material similar to that which is planned for use in the HTGR fuel-element sleeve are presented here.

Weight loss of two samples of graphite as a function of time is shown in Fig. 4. These samples were 3-in. sections cut from a 3-1/2-in. diameter, 3/8-in. -wall tube of Great Lakes HLM-85 impregnated and regraphitized base stock and were exposed to 2.8% water vapor in helium. The activation energy was approximately 20 kcal/mole, indicating zone II or perhaps the zone II and zone III transition region. It is interesting to note that there was no detectable change in weight-loss rate with loss of graphite.

Fig. 4--Weight loss of fuel-element graphite due to reaction with water; samples exposed at 1000° and 900°C to 2.8% H₂O vapor in helium

The specimens were periodically removed from the furnace and weighed, and helium permeability measurements were made (pressure drop, 1 atm to vacuum). The results are shown in Fig. 5. The helium permeability of both specimens increased regularly with weight loss. The difference between these curves is believed to be due to differences in the initial structure of the graphite, even though the samples were cut from a single tube.

Perhaps more meaningful than the helium permeability measurements are the measurements of noble-gas diffusion through the sleeve against a forced flow. Here the diffusion of argon into helium was determined in an apparatus where the graphite sample separates a stream of helium from a stream of argon. Apparent permeation coefficients of argon were measured for the graphite sample before and after exposure to steam at 900°C as a function of the total pressure differential ($P_{\text{He}} - P_{\text{Ar}}$) across the sample; these results, which are shown in Fig. 6, indicate that the pores were being enlarged by the steam attack. The similarity of the curves, however, indicates that the 1.5% weight loss of graphite at this 900°C temperature (see Fig. 5) would not appreciably increase the loss of noble-gas fission products through the sleeve.

Catalytic Effect of Strontium and Barium

Strontium and barium sorbed by graphite at reactor conditions may catalyze the steam-graphite reaction by acting as an intermediary in successive oxidation-reduction reactions, which together give reaction (4). Thus, where M = strontium or barium,

Aside from such local action, there may be a distant action due to interactions with the electrons of the graphite lattice. Such catalytic activity

Fig. 5--Helium permeability of sleeve graphite versus weight loss; samples exposed at 1000° and 900° C to 2. 8% H₂O vapor in helium

Fig. 6--Apparent argon permeability of sleeve graphite before and after steam-graphite reaction

has been reported to have been observed in connection with Dragon project studies,^[14] and we have observed an apparent catalytic effect when a steam leak occurred in an apparatus where the permeation of barium through graphite was being studied. Accordingly, some exploratory experiments were carried out to investigate this effect.

Several barium- and strontium-impregnated graphite and untreated graphite specimens at various temperatures were exposed to steam in helium. The samples were prepared by adding BaCO_3 to the graphite recipe before hot-pressing. In effect, these samples simulated the graphite matrix material used in the HTGR fuel compacts. Prior to starting the experiment, the samples were conditioned at 1000°C in helium for 3 days to convert the BaCO_3 to barium (and possibly some BaO) and to ensure uniformity of the catalyst throughout the sample. The catalyst concentrations were chosen because they represent reasonable loadings expected in the HTGR--a loading of 0.01% to 0.02% barium or strontium, for instance, is the calculated end-of-life loading for the HTGR after 3 yr of operation, assuming that all of the barium or strontium stays in the core graphite.

That barium and strontium catalyze the steam-graphite reaction is indicated by Figs. 7 and 8. These graphs show the effect of increasing catalyst loading. The photographs reproduced in Fig. 9 very dramatically illustrate this same effect. These specimens at 990° and 1005°C were exposed to 0.33% steam in helium for 117 hr. Their weight-loss rates are plotted in Fig. 8. Samples 1, 2, 3, and 4 (barium) were exposed in a separate quartz tube from samples 1, 5, 6, and 7 (strontium). The leading-edge effect is quite obvious, considering that there were two specimens of each kind in tandem. The specimens which bore the brunt of the inlet steam were obviously eroded the most; indeed, they consumed at least 90% of the total water vapor entering the combustion tube. The tandem specimens were subsequently exposed to depleted gas and experienced much lower weight losses.

Arrhenius plots for the data in Fig. 7 are shown in Figs. 10 and 11

Fig. 7--Steam-graphite reaction of barium- or strontium-impregnated graphite compacts exposed to 3.5% H₂O vapor in helium at 1 atm and at a flow rate of 110 ml/min

Fig. 8--Steam-graphite reaction of barium- or strontium-impregnated graphite compacts exposed to helium at 1 atm and at a flow rate of 240 ml/min, containing either 0.33% or 0.03% H₂O vapor

Fig. 9--Photograph of the effect of steam on barium - or strontium-impregnated graphite compacts exposed for 117 hr to 0.3% H₂O vapor in helium at 1 atm and at a flow rate of 240 ml/min; exposure temperature of 1008° and 991° C for the barium and the strontium specimens, respectively

Fig. 10--Arrhenius plot of the steam-graphite reaction of strontium-impregnated graphite compacts

Fig. 11--Arrhenius plot of the steam-graphite reaction of barium-impregnated graphite compacts

and indicate that the activation energy for the reaction is a constant, regardless of catalyst loading. The apparent activation energy calculated from the slope is ~ 40 kcal/mole, which corresponds to zone II of Wicke's analysis (see Fig. 3). It appears that some of the curves are bending over slightly at higher temperatures, indicating the beginning of zone III.

CARBON DEPOSITION ON METAL SURFACES AND ON ACTIVATED CARBON

The reverse water-gas and Boudouard reactions,

will deposit carbon throughout the cooler (400° to 750°C) sections of the reactor. There are two areas of concern (apart from the purge passageways, as discussed) regarding this carbon-deposition problem:

1. The metal parts of the reactor, i. e., the main thermal shroud ($\sim 750^\circ\text{C}$) and the heat-exchanger surfaces (250° to 625°C);
2. The activated carbon and/or other reagents in the internal traps of the fuel element.

Carbon Deposition on Metal Surfaces

That metals are active catalysts for the carbon-deposition reactions is well known. Pure iron, especially in a finely divided form, is the most active catalyst. P. L. Walker^[15] has observed that finely divided iron powder when exposed to CO and H_2 will pick up several times its own weight in carbon at 500° to 600°C . P. P. Das and B. Chatterjee^[16] have determined that the iron carbide arising from these reactions subsequently causes a decrease in the reaction rate. They found that H_2 treatment at 900°C decomposes the carbide and reactivates the spent catalyst.

Of primary concern to a nuclear reactor in terms of carbon deposition is, of course, the possible damage to the heat-exchanger tubes resulting from

carburization. A discussion of this metallurgical problem is beyond the scope of this paper, however. For purposes of this discussion, we shall present some kinetic data for pure iron wire as compared with some alloys.

Pure iron wire and other metal wires of about 10-mil diameter were exposed at various temperatures to flowing helium containing H_2 and CO. The effluent was frequently analyzed for CO_2 throughout the run; these analyses yielded rate data on the Boudouard reaction. The total weight gain of the sample revealed the total carbon-deposition rate, and the reverse water-gas reaction rate was obtained by subtracting the Boudouard rate from the total rate. Carbon analysis, by combustion of the samples at the end of each experiment, verified that the weight gains were due to carbon. Some of the principal results of these studies are listed in Table VII.

Figures 12 and 13 show how the Boudouard reaction rate decreases with time, presumably because of contamination of the surface with carbide and carbon. Figure 14 is an Arrhenius plot for the Boudouard reaction. The apparent activation energy is 28 kcal/mole.

In interpreting the significance of these data for the HTGR, it is necessary to extrapolate to conditions of pressure, impurity concentrations, and temperature expected for the reactor. The heat-exchanger total surface is about $7 \times 10^6 \text{ cm}^2$ in area and experiences temperatures from 248° to 645°C . Of this total surface, some $1 \times 10^6 \text{ cm}^2$ endures temperatures from 425°C ; therefore, for estimating carbon-deposition rates in the heat exchanger only 10^6 cm^2 need be seriously considered.

For extrapolation to reactor conditions, the following assumptions are made:

1. A uniform 625°C temperature over the 10^6 cm^2 area.
2. A linear reaction-rate dependence on both H_2 and CO partial pressure.
3. An average $20 \mu\text{g}/\text{cm}^2\text{-hr-atm}$ reaction rate (from experimental data).
4. Impurities comprising 10 ppm of CO and 10 ppm H_2 at 23 atm.

Table VII
RESULTS OF CARBON-DEPOSITION STUDIES

Metal Wire	Temp. (°C)	Partial Press. CO (atm)	Partial Press. H ₂ (atm)	Gas Flow Rate (ml/min)	Bouduard Reaction		Reverse Water-Gas Reaction, Avg. Rate*
					Initial Rate*	Avg. Rate*	
Iron (pure)	590	1.8×10^{-2}	1.8×10^{-2}	28	1.05	0.86	----
Iron (pure)	690	1.8×10^{-2}	1.8×10^{-2}	28	2.9	2.1	----
Iron (pure)	790	1.8×10^{-2}	1.8×10^{-2}	28	7.4	4.4	----
Iron (pure)	890	1.8×10^{-2}	1.8×10^{-2}	28	17.9	12.3	----
Iron (pure)	550	3.4×10^{-2}	3.4×10^{-2}	28	0.7	0.2	7.0
Iron (pure)	650	3.4×10^{-2}	3.4×10^{-2}	29	3.4	1.8	23.0
Iron (pure)	749	3.4×10^{-2}	3.4×10^{-2}	29	14.0	9.2	35.0
Iron (pure)	850	3.4×10^{-2}	3.4×10^{-2}	30	61.0	29.0	60.0
Iron (pure)	500	1.2×10^{-2}	$\sim 10^{-5}$	25	5.7	3.8	----
Iron (pure)	527	1.2×10^{-2}	$\sim 10^{-5}$	25	4.8	2.4	----
Iron (pure)	626	1.2×10^{-2}	$\sim 10^{-5}$	25	3.8	3.7	----
Type 302 SS	750	3.3×10^{-2}	3.3×10^{-2}	25	3.7	3.0	28.0
0.85% C Steel	748	3.3×10^{-2}	3.3×10^{-2}	25	8.7	8.7	16.0
Inconel	750	3.3×10^{-2}	3.3×10^{-2}	25	1.8	2.5	16.0
Monel	750	3.3×10^{-2}	3.3×10^{-2}	25	9.5	9.5	62.0

* ($\mu\text{g}/\text{cm}^2\text{-hr-atm}$)

Fig. 12--Boudouard reaction rates on pure iron wire (127 cm²) exposed at various temperatures to 3.0% H₂ and 3.0% CO in helium at 1 atm flowing at a rate of 28 ml/min

Fig. 13--Boudouard reaction rates on pure iron wire (127 cm^2) exposed at various temperatures to 1.5% H_2 and 1.5% CO in helium at 1 atm flowing at a rate of 28 ml/min

Fig. 14--Arrhenius plot for Boudouard reaction on pure iron wire

From these considerations, we calculate a reaction rate of $40 \mu\text{g C/cm}^2\text{-yr}$ or 40 g C/yr over the heat-exchanger surface. We believe the extrapolation to be pessimistic because assumptions (1) and (3) are certainly pessimistic. The assumption of a first-order reaction rate, however, may not be valid, but it is the best assumption that can be made until further data are available.

Long-term (500-3000 hr) exposures of various alloys to 230 ppm CO-H_2 at 1 atm (corresponding to a 10 ppm reactor level of impurities at 23 atm total pressure) and 2300 ppm CO-H_2 at 625°C (maximum heat-exchanger temperature) and 725°C (thermal-shroud temperature), with subsequent metallurgical examination for carbon increase, microstructural changes, and physical-strength changes, have been carried out. The results of these tests are encouraging and show that there should be less cause for concern over this problem (at reactor impurity levels up to 100 ppm at 23 atm) than previously anticipated. [17]

Carbon Deposition on Internal-trap Reagents

In order to retain as much of the condensible fission products such as I_2 , tellurium, cesium, etc., in the reactor core, the fuel-element purge channels terminate at the bottom of the element in an internal trap. This trap in the case of the HTGR is comprised of sixteen 0.1-in.^2 grooves, 12 in. long, which will be filled with activated carbon and/or other reagents. Silver- or copper-coated activated carbon are logical candidates for the internal trap because of the ability of such material to retain electronegative fission products.

If activated carbon or the other reagents appreciably catalyze the carbon-deposition reactions, plugging could conceivably occur. The formation of fission-product-laden carbon aerosols, which might penetrate the internal trap, is another reason for concern. Therefore, carbon deposition on proposed internal-trap reagents has been studied. One experiment measured carbon-deposition rates on cesium-impregnated

activated carbon (Barnebey-Cheney MI-1), since cesium is an abundant, volatile fission product and is expected to be present in the internal trap. The experiments were conducted at temperatures expected for the internal trap in the reactor, i. e., with an upper limit of approximately 540°C .

The conditions and results of the experiments are listed in Table VIII. These data show that pure activated carbon (Barnebey-Cheney MI-1), even high specific-surface-area carbon, is quite inert to the carbon-deposition reactions. On the other hand, the metals copper, silver, and cesium accelerate the reaction. What is most interesting is that cesium is an extremely active catalyst for the carbon-transport reactions, including methane formation. When the weight gain for the cesium-activated-carbon reaction is extrapolated to reactor conditions (i. e., 10 ppm CO and 10 ppm H_2 at 23 atm) it is seen that about a gram of carbon will be deposited in each internal trap channel in 3 yr. This extrapolation is, of course, pessimistic because of the relatively high cesium loading of the activated carbon in the experiment.

TENTATIVE CONCLUSIONS

1. Carbon transport across gaps in a helium-cooled high-temperature graphite reactor appears to be a less serious problem than previously anticipated. The experimental results indicate that reactor impurity levels (CO, H_2 , and N_2) of the order of 100 ppm at 23 atm can be tolerated.

2. In the case of the steam-graphite reaction, data on the magnitude of the actual reaction rate are less important than data on graphite permeability (to noble gases) as a function of weight loss. Changes in effective permeability are small up to 1.5 wt-% loss.

3. The catalytic effect of strontium and barium fission products on the steam-graphite reaction is probably not serious.

4. Long-term data on the effects of carbon deposition on metal surfaces exposed to low partial pressures of CO and H_2 are needed. Available results from shorter-term experiments are encouraging and

Table VIII
RESULTS OF CARBON-DEPOSITION STUDIES ON
INTERNAL-TRAP REAGENTS

(Experimental conditions: 3.0% H₂ and 3.0% CO in
helium at a pressure of 1 atm and flowing at the rate
of 25 ml/min)

Activated Carbon Reagent Tested	Temperature (°C)	Weight Change (mg/cm ³ -hr)	Boudard Reaction Rate (mg/cm ³ -hr)	Methane Formation (mg/cm ³ -hr)
MI-1	525	0.013	0.0003	0.0006
MI-1	525-480	0.003	0.0005	0.0006
MI-1	480-260	0.024	0.0005	0.0006
Cu-coated MI-1 (40 wt-%)	520-516	0.076	0.0055	0.0006
Ag-coated MI-1	520-516	0.028	0.0037	0.0006
Cs-loaded MI-1 (24 wt-%)	558	0.24*	0.03*	0.0073

* This number is probably inordinately high because the cesium-loaded activated carbon was weighed in air, allowing the cesium to partially oxidize.

indicate that the stringent helium impurity requirements (of 10 ppm CO and H₂ at 23 atm) could be relaxed to at least 100 ppm.

5. Carbon deposition on the internal-trap reagents studied does not seem to be serious.

REFERENCES

1. Lewis, G. N., and M. Randall, Thermodynamics, 2d ed., revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, 1961.
2. Lockett, G. E., and R. A. Huddle, "The Dragon Reactor Development and Design of the HTGC," Nuclear Power, Vol. 5, February, 1960, pp. 112-117.
3. Fortescue, P., D. Nicoll, C. Richard, and D. Rose, "HTGR-- Underlying Principles and Design," Nucleonics, Vol. 18, No. 1, 1960, p. 86.
4. Rockenhauser, W., General Atomic, private communication.
5. Chapman, S., and T. G. Cowling, The Mathematical Theory of Non-Uniform Gases, 2d ed., Cambridge [Eng.] University Press, 1952.
6. Pauling, L., "Atomic Radii and Interatomic Distances in Metals," J. Am. Chem. Soc., Vol. 69, 1947, p. 542; The Nature of the Chemical Bond, 2d ed., Cornell University Press, Ithaca, N. Y., 1940.
7. Merten, U., General Atomic, private communication.
8. Wicke, E., "Contributions to the Combustion Mechanism of Carbon," Fifth Symposium (International) on Combustion, Reinhold Publishing Corp., New York, 1955; E. Wicke and K. Hedden, Z. Elektrochem., Vol. 57, 1953, p. 636.
9. Boulangier, F., X. Duval, and M. Letort, "The Kinetics of the Reactions of Carbon Filaments with Carbon Dioxides and Water Vapor at High Temperatures and Low Pressures," Proceedings of the 1957 Conference on Carbon, Pergamon Press, London, p. 257.

10. Strickland-Constable, R. F., Trans. Faraday Soc., Vol. 43, 1947, p. 769.
11. Blyholder, G., and H. Eyring, "Kinetics of the Steam-Carbon Reaction," J. Phys. Chem., Vol. 63, 1959, p. 693.
12. Johnstone, H. F., C. Y. Chen, and D. S. Scott, "Kinetics of the Steam-Carbon Reaction in Porous Graphite Tubes," Ind. Eng. Chem., Vol. 44, 1952, p. 1564.
13. Antill, J. E., and K. A. Peakall, "Thermal Reactions of Gaseous Impurities in Flowing Argon Leading to Carbon Transport," US/UK Gas Coolant Compatibility Conference, 1960, GCM/UK/13.
14. de Bruijn, H., private communication.
15. Walker, P. L., Jr., J. F. Rakaszawski, and G. R. Imperial, "Carbon Formation from Carbon Monoxide-Hydrogen Mixtures over Iron Catalysts. I. Properties of Carbon Formed; II. Rates of Carbon Formation," J. Phys. Chem., Vol. 63, 1959, pp. 133, 140.
16. Das, P. P., and B. Chatterjee, Trans. Indian Inst. of Met., Vol. 6, 1952, p. 279.
17. Weinberg, A. F., private communication.