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LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO

GRAPHITE CORROSION STUDIES FOR THE
ULTRA HIGH TEMPERATURE REACTOR EXPERIMENT

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GRAPHITE CORROSION STUDIES FOR THE
ULTRA HIGH TEMPERATURE REACTOR EXPERIMENT

by

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ABSTRACT

Experiments have been conducted to study graphite corrosion in an atmosphere of helium containing low concentrations of carbon dioxide (0 to 70 ppm). The test loop, operating at 500 psig with a maximum gas temperature of 2400°F for 30 days, has performed well for four tests.

The extent of graphite corrosion is described approximately by

$$\text{Rate} = 1.0 \times 10^{-2} C$$

where "Rate" is the loss in weight in milligrams per square centimeter per hour and C is the concentration of carbon dioxide in parts per million by volume.

In this report, the test loop and experimental procedures are described and the results obtained are discussed.

INTRODUCTION

The reaction between graphite and oxidizing gases at very low (parts per million) concentrations has been a subject¹ of concern for several years to designers of helium-cooled, graphite-moderated nuclear reactors with high core temperatures, e.g., Dragon, EGCR, UHTREX, etc. Even if there were no other source, the gaseous oxidizing impurities emitted by the heated graphite itself would be present. These contaminants are capable of reacting with the graphite structure to cause loss of strength or to create untenable heat transfer or fluid flow situations. Knowledge of the rates of the reactions and of the effects associated with them is essential in planning the design of the reactor and its operating procedures.

Graphite-gas reactions have been under study for decades.^{2, 3} Nevertheless, there are still unresolved contradictions in the results and the reaction characteristics are not understood.³ In particular, there is a dearth of experimental information on dilute systems in the region where mass transfer of the oxidant through an inert gas film plays a significant role. Since analytical prediction of corrosion rates under a particular set of conditions is little more than guesswork, experimental methods are required.

Most of the data published hitherto⁴ have been derived from small-scale test furnaces using gram samples, relatively low temperatures, and often

indefinite flow characteristics. This information has been useful in defining the problems and, by extrapolation of the data, in making gross calculations as to the extent of damage to be expected. However, extrapolation to UHTREX conditions from such data is not trustworthy and cannot be used to predict allowable contamination limits.

For these reasons it was decided to perform a series of experiments in which the actual UHTREX reactor geometry and environmental conditions were duplicated as closely as possible. It was felt that only in this way would sufficient information be obtained to assist in preparing operating procedures, i.e., allowable temperature levels, for the UHTREX system.

APPARATUS

The cylindrical core of the UHTREX system⁵ has 312 channels, each 1.1 in. in diam, with four fuel elements, 5-1/2 in. long, in each channel at full loading. The elements are hollow graphite cylinders with outer and inner diameters of 1.0 in. and 0.5 in., respectively. It was postulated that corrosion of the fuel elements would not be detrimental, since they are replaceable. But, corrosion of the graphite constituting the channel walls would limit the life of the core and influence the operation of the reactor. It was decided, therefore, that the most important condition to simulate in the corrosion experiments was the channel wall or annulus of the UHTREX core. The primary objective of the present work was to study the effect on the graphite of the channel wall of small concentrations of CO₂ in the helium gas.

The apparatus used (Fig. 1) was a closed loop in which helium was recycled continuously; it consisted essentially of a blower, a preheater, the simulated core, and several water-cooled heat exchangers. Details of these components and accessories are described below.

Fig. 1. UHTREX CORROSION TEST LOOP

Blower

The blower was a 1.5-hp industrial vacuum cleaner housed in a mild steel pressure vessel. The latter consisted of a 12-in. welding end cap, a 4-in. length of 12-in. pipe, and a 12-in. welding neck flange. A 12-in. blind flange was bolted to the vessel for access to the blower motor and impeller.

Preheater

The helium gas which entered the simulated core of the test loop was nominally 1600°F to correspond to the inlet gas temperature of the UHTREX core. Since the blower could not operate above 150°F, it was necessary to cool the gas before recirculation and subsequently to reheat it. For this purpose, a preheater is employed, with a heating element consisting of a graphite resistance rod 60 in. long and 13/16 in. in diameter. The helium is carried through 1/8-in. diam holes extending along the length of the heating rod. The electric current through the rod was controlled by means of a chromel/alumel thermocouple situated in the gas stream at the outlet of the preheater.

Simulated Core

The electrically-heated channel used in the experiments was necessarily a compromise of the real geometry (Fig. 2). Since the annulus or channel wall was selected as being the area most sensitive to corrosion, the fuel elements were simulated by a solid graphite rod, without the 1/2-in. hole through the center. The rod, which was fabricated of Graph-i-tite Grade "G" made by Graphite Specialties Corporation, served as an electrical-resistance type heating element. Since the heating element could not be permitted to touch the channel wall, as the fuel elements do, the rod was made 3/4 in. instead of 1 in. in diameter and

Fig. 2. TEST LOOP CORE SECTION

positioned on the same center as the fuel elements. This left a 1/8-in. minimum space between the channel wall and the heating element.

The graphite rod was supported and electrical contact made at each end of the heating element by graphite slip joints. The latter were supported in turn by discs, aluminum oxide at the gas inlet end and graphite at the gas outlet end. At the high-temperature (gas outlet) end, the slip joint was grounded and the joint at the cold end was connected to a copper electrode. The electrical connections at both ends were cooled with coils through which water was passed.

For ease of experimental diagnostics, the channel was simulated by five test specimens, each being a graphite cylinder 5-7/8 in. long and 2.1 in. o.d. The material used was Type H4LM graphite made by Great Lakes Carbon Co. In the first test of the series the graphite cylinders were 4 in. in o.d. Later, this extra graphite material was replaced with a porous carbon sleeve.

The entire assembly of heater, slip joints, test specimens, copper electrode, etc., was housed in a graphite support tube which extended from one end of the core section to the other. The tube was in turn supported in the center of the pressure vessel by the end caps into which pipes were welded. The graphite tube rested inside the pipe at each end.

The pressure vessel was protected from high temperatures with internal insulation. Most of the core section was insulated with Fiberfrax (aluminum silicate fibers) in bulk form. In some areas where the temperature becomes too high for Fiberfrax, e.g., the gas outlet of the core section, carbon wool or felt was used as insulation.

High-temperature thermocouples, pressure taps, and gas sample tubes penetrated the pressure vessel through pressure glands. The gas sample tubes, made of stainless steel, led to aluminum oxide tubes which penetrated the graphite support tube. This kept the stainless steel in the cooler areas and prevented melting which might have closed off the tubes.

Temperatures were measured with platinum/platinum-rhodium thermocouples swaged in magnesium oxide in a Type 310 stainless steel sheath. The thermocouple junction was left bare but was placed in a molybdenum tube inserted through the wall of the graphite support tube.

The pressure vessel of the core section of the test loop was a 12-in. "X-heavy", mild steel pipe, with a wall thickness of 1/2 in. It had numerous outlets for thermocouples, etc.; these were mostly 1/4-in. holes threaded directly in the wall of the pipe. The safe operating pressure of the vessel was 500 lb/in.²

Because of the nature of the experiments performed in the test loop, the core section had to be opened and resealed many times. The end caps were very unwieldy, because of their size and weight, yet they had to be fitted carefully over the graphite support tube at both ends. To make this possible, each end cap was supported precisely in line with the rest of the core on three 2.2-in. diam pins. The pins were shrink-fitted into ears which were welded to the end flanges of the core section. The pins extended from the core pressure vessel so that the end caps could rest in line with the axis of the core. The end caps could then be pushed axially into position without the danger of breaking any graphite parts.

Heat Exchangers

Before the gas from the core could be recirculated through the loop by the blower, it had to be cooled, as stated earlier, to near room temperature. Two concentric-tube-type heat exchangers placed in series were used for this purpose. They were made of Type 316 stainless steel; the inner tube was 1/2 in. and the outer tube was 1 in. in diameter. The difficulty in the design of this piece of equipment was the transition from internally insulated mild steel pipe to

the water-cooled stainless steel pipe. In the successful design, shown in Fig. 3, the stainless steel immediately adjacent to the insulation was cooled by directing the cooling water along the opposite face. The helium flow was conducted into the heat exchanger through a graphite tube fitted inside a loosely clamped porous carbon tube (or sleeve). Bulk insulation could not enter the gas stream; but movement, to absorb thermal expansion, was possible in the radial direction. Longitudinal freedom was also provided to the graphite tube by permitting it to slide in the porous carbon tube.

Gas Cleanup System

Since the concentration of contaminants in the helium gas is a primary variable in the test loop experiments, it was necessary to provide a method for cleaning the gas. The system used consisted of a hot copper oxide bed, a water-cooled heat exchanger, and a molecular sieve bed. It was situated in parallel with the test loop with gas flowing from the blower outlet, through the cleanup system, and returning to the blower inlet.

The copper oxide bed was a vertical stainless steel cylinder connected to the system with ring-joint flanges. The cylinder was partially filled with cylindrical pellets of copper oxide, about $3/32$ in. in diameter and $3/32$ in. thick, after air sintering. The operating temperature was 1000°F . Such impurities as CO , CH_4 , and H_2 were oxidized to CO_2 and H_2O . The helium and oxidized impurities were cooled to room temperature in the heat exchanger before passing into the molecular sieve bed where the CO_2 and H_2O were absorbed. A second cylinder housed the molecular sieve bed, consisting of pellets supplied by the Linde Company. Wire screens at each end prevented the pellets from flowing out of the tube where they might plug valves and lines.

Fig. 3. TEST LOOP TRANSITION SECTION

INSTRUMENTATION

The instrumentation associated with the test loop had three functions: (a) to provide diagnostic information, (b) to control the operating variables, and (c) to provide safety in operation. Most of the data were printed out by means of strip and circular chart type electronic recorders, but some were obtained by hand from indicators.

Temperature Measurement

Temperature measurements were made at various locations throughout the test loop. Most of the sensing elements were chromel/alumel thermocouples, some being bare wire couples and others being sheathed in stainless steel. The gas temperatures at the core outlet are measured with platinum/platinum-rhodium units. The sheath temperature was quite near the melting range (2500° - 2550° F), but with no external stress applied and enclosed in molybdenum protection tubes they have functioned well in protecting the thermocouples from contamination in the reducing environment. Earlier, bare platinum/platinum-rhodium thermocouples under the same conditions had failed very rapidly. The outputs of the thermocouples were recorded on Minneapolis-Honeywell "Elektronik" recorders, having ranges of 1500 - 3000° F, 0 - 2000° F, and 0 - 750° F.

Pressure Measurement

The pressure of the system was recorded continuously on a Minneapolis-Honeywell circular chart recorder, and was also indicated on a calibrated Heise gage. The ranges of these instruments were 0-1000 psig.

At a flow rate of 7.5 lb/hr of helium, the pressure drop across the entire loop was about 40 in. of water, varying slightly with the admission of miscellaneous specimens which were occasionally introduced into the loop for environmental testing. The differential pressures across the loop, across the core section, and also across the orifice were measured and transmitted as voltage signals to a recorder. The output was modified in an electronic compensating unit which corrected the signal for temperature and pressure variations from normal (150° F, 500 psig). In this manner a continuous record was obtained of the helium mass flow rate.

Water Flow Rate

The rate of water flow through the heat exchanger was measured with Schutte and Koerting rotameters. Other cooling water flow rates were not measured but were checked visually. The total flow rate of cooling water was on the order of 5 gal/min.

Gas Analysis

Two instruments, capable of nearly continuous operation, were used to analyze the gas stream in the test loop; they were a Beckman infrared gas analyzer (Type L/B-21) and a Consolidated Electrodynamics Corporation gas chromatograph (Type 26-212). The Beckman instrument can measure the concentration of CO and CO₂ with two full scale ranges, 0 to 30 ppm and 0 to 500 ppm

by volume, respectively. The chromatograph can determine CO (6 ppm to 60%), CO₂ (4 ppm to 40%), as well as other impurities.

Temperature (Power) Control

The power was supplied to the main heater of the test loop through a "Thermac" temperature controller and power regulator, made by Research, Incorporated, of Minneapolis, Minn. The device is controllable over the entire power range, but it is equipped with a voltage limiter which can be set to establish an upper limit of power. The controller can be operated manually or it can be used to control the temperature by using a platinum/platinum-rhodium thermocouple.

The power to the preheater is controlled by a Minneapolis-Honeywell "Elektronik" proportional controller. This unit operated a Beck control motor which drove a powerstat. Up to 10 kw of power could be supplied to the preheater upon demand from a chromel/alumel thermocouple.

The heaters in the copper oxide bed of the gas cleanup system were controlled with a Minneapolis-Honeywell Pyrovane pyrometer controller. It has a range of 0-2000°F and operates on demand from a chromel/alumel thermocouple.

Pressure Control

The pressure in the test loop was regulated by two Matheson high-pressure gas regulators connected in parallel. These units were mounted on a panel with high-pressure, flexible tubing leading to the high-pressure gas cylinders. Excess pressure was vented automatically through solenoid valves activated by Mercoid pressure switches.

Safety System

Since the test loop operated at high temperatures and pressures, numerous safety devices were installed which would automatically turn off the power to the test loop. The potential causes for automatic shutdown were as follows:

1. Excessive pressure - (over 650 psig)
2. Insufficient pressure - (under 100 psig)
3. Insufficient helium flow - (under 25 in. of water pressure across the blower)
4. Insufficient water flow - (under 3 gal/min)
5. Excessive outlet gas temperature - (over 2550°F)
6. Excessive surface temperature - (over 700° F)
7. Power outage - (over 12 sec duration).

OPERATION

Before insertion into the test loop, the inside diameters of the nominal 1.1-in. holes in the cylindrical graphite test cylinders were measured to ± 0.0005 in., both the maximum and the minimum values being recorded. The weights of the segments were determined to ± 0.0001 g. The graphite heating rod was weighed to ± 0.1 g and the diameter measured to ± 0.0005 in.

When all experimental specimens were installed, the test loop was assembled and sealed. To remove the atmospheric gases, the pressure in the loop was reduced to 22 in. Hg. More effective removal of adsorbed gases was obtained by heating under reduced pressure.

The loop was pressurized with helium and leak tested. Since the repair of some leaks required venting and reopening the loop, preliminary leak testing was conducted at 100 psig. After the large leaks had been repaired the loop was pressurized to 400 psig and retested. Pressurization to 500 psig then occurred automatically when the loop was heated.

After minimizing gas leakage, the blower, the cooling water, and the heaters were turned on. The valves of the gas cleanup system were opened and a fraction of the helium was diverted through it. Loop temperatures were raised until the contamination level (CO_2 from graphite outgassing), as measured with the infrared analyzer, rose to a preset maximum tolerable level. As the

contaminants were removed by the gas cleanup system the temperature was increased toward the temperature of operation. When the outlet gas temperature reached 2400° F the test loop was "operating" by definition. The "operating time" was that period of time in which the outlet gas temperature was 2400°F.

In the experiments, the concentration of CO₂ in the helium gas was the quantity varied. This was generally achieved by controlling the gas flow through the cleanup system. In the copper oxide bed, CO impurity was converted to CO₂. Generally, the latter is removed from the helium stream by passing it through the molecular sieve bed, but by allowing part of the stream to bypass the molecular sieve bed some of the CO₂ was permitted to return to the test loop. The concentration was controlled by the proportion of gas bypassed.

In addition to various maintenance operations, including replacement of the brushes of the blower, it was necessary to regenerate the gas cleanup system by re-oxidizing the copper oxide bed and renewing the molecular sieves. The copper oxide was re-oxidized in place by passing a side stream of air through the bed at 1100° F. The molecular sieves were replaced and the used sieves regenerated under vacuum at 600°F. Regeneration of the cleanup system was performed with no interruption in the operation of the test loop.

When the operating time had reached 720 hours (30 days), the test was considered complete and discontinued. Some tests were terminated short of the goal because a major repair was indicated.

At the completion of the test, the test specimens and the heating rod were again weighed and measured. The inside surfaces of the specimens were photographed and the pieces put into storage.

Specimens from the first test were examined for a density gradient from the inside surface toward the outside diameter. This was accomplished by machining thin layers from the inside surface of the specimen, and subsequently making weight and dimension determinations. Another method used to observe a

density gradient was radiography. A thin disc was sliced from each specimen and x-rayed. No gradient was observed by either technique, and the examination was discontinued.

EXPERIMENTAL RESULTS

Four tests were made to investigate the rate of corrosion of the graphite core channel and the heating rod as a function of CO₂ concentration. The experiments were designed to simulate the conditions expected in a typical UHTREX core channel. The results have provided data indicating the degree of CO₂ contamination of the helium stream which can be tolerated in the UHTREX reactor over a period of time at the maximum design conditions of the system, i. e. , gas outlet temperatures of 2400° F, 500 psig, and 3 Mw power generation.

Table I shows the primary operating conditions and most of the results from each of the four tests made. The CO₂ concentration is a time average of the values determined during the test.

During the course of these tests, the core temperature profile was not measured successfully. However, in a subsequent experiment, modifications to the test loop were made which permitted optical pyrometer temperature observations at high pressure. A profile was recorded which is believed to be typical of the four experiments described here and is shown in Fig. 4.

In tests 2 through 4, the contamination level of CO₂ was maintained by allowing a portion of the gas to bypass the molecular sieve bed, as described earlier. In test 1, however, CO₂ was supplied from a CO₂ cylinder. Without replacement, as it was depleted by the graphite, the concentration of CO₂ quickly

TABLE I
OPERATING CONDITIONS FOR TESTS 1 THROUGH 4

	<u>Test 1</u>	<u>Test 2</u>	<u>Test 3</u>	<u>Test 4</u>
Weight loss, grams				
Heating rod	44.9	25.7	13.7	3.8
Segment No. 1 (gas inlet)	35.136	15.000	9.244	2.204
Segment No. 2	54.213	9.530	5.080	1.877
Segment No. 3	34.344	7.963	4.091	2.185
Segment No. 4	23.528	7.098	3.820	2.051
Segment No. 5 (gas outlet)	28.507	6.800	4.027	1.238
All segments	175.728	46.391	26.262	9.555
Total	220.63	72.09	39.96	13.36
Surface area, cm ² (geometric)				
Heating rod	456	456	456	456
Segment (each)	131	131	131	131
Segments (all 5)	655	655	655	655
Total	1111	1111	1111	1111
CO ₂ concentration, ppm (volume)				
Inlet	70	17	7	2
Outlet, segment No. 1*	64	14.5	5.3	1.5
Outlet, segment No. 2*	55	12.9	4.4	1.1
Outlet, segment No. 3*	49	11.6	3.6	0.7
Outlet, segment No. 4*	45	10.4	2.9	0.2
Outlet, segment No. 5*	40	9.3	2.1	0.0
Operating time, hours	713	703	630	720
Flow rate, lb/hr	7.5	9.7	9.6	7.2

*Computed from inlet concentrations and the measured weight loss from the core.

Fig. 4. CORE TEMPERATURE PROFILE

dropped to less than 1 ppm. The measurement and control of CO_2 was quite poor in experiment number 1, but it improved as operating experience was gained. The variation of the contamination levels with time is shown in Fig. 5.

The profiles of the changes in channel and rod diameters were approximately mirror images of one another as is illustrated in Fig. 6. To compare the effects of the various contamination levels, the change of the core channel diameter with distance from the core inlet for each test was plotted in semi-logarithmic form in Fig. 7. The values of the weight loss in the four tests are listed in Table II.

A comparison was made between the decrease in weight of carbon as determined by weighing and as calculated from the change in volume and the material density. In every case the weight loss determined from a volume decrease was larger than that obtained by direct weighing. The effect was more pronounced for pieces exposed to the lower CO_2 concentration, as shown in Table II. The discrepancy is explained by the fact that micrometer measurements did not include small pits. The use of the term "pits" here requires some explanation. Actually, the appearance of the reacted graphite indicated that binder material was removed from around the particles in the graphite matrix leaving small mounds. This is probably an effect of the lower density rather than of a greater reactivity of the binder material. Initially the surfaces of the specimens were machined smooth, but pits appeared during the corrosion process. In cases of large weight loss (high CO_2 concentration), the pits were small when compared with the total weight loss; whereas in the case of low weight loss, the pits became important.

The rate of reaction is conveniently expressed as the weight in milligrams of carbon removed per hour per square centimeter of the graphite surface as a function of the concentration of CO_2 in the helium gas phase. During the tests, however, the CO_2 concentration measurements were made only at the

Fig. 5. CARBON DIOXIDE CONCENTRATIONS FOR TESTS 1 THROUGH 4

Fig. 6. COMPARISON OF CORROSION RESULTING FROM TESTS 1 THROUGH 4

Fig. 7. COMPARISON OF CHANNEL WALL AND HEATER ROD CORROSION FOR TESTS 1 THROUGH 4

TABLE II
COMPARISON OF ACTUAL WEIGHT LOSS
WITH THAT DETERMINED FROM DIMENSIONAL CHANGES

<u>Test No.</u>	<u>Specimen No.</u>	<u>Actual weight loss, g</u>	<u>Calculated weight loss from dimensional changes, g</u>	<u>Percent deviation of calculated value from actual</u>
1	1 (inlet)	35.136	26.604	75.7
	2	54.213	46.626	86.0
	3	34.344	27.777	80.9
	4	23.528	17.506	74.4
	5	28.507	13.719	48.1
2	1 (inlet)	15.000	4.319	28.8
	2	9.530	5.021	52.7
	3	7.963	3.726	46.8
	4	7.098	3.000	42.3
	5	6.800	1.899	27.9
3	1 (inlet)	9.244	3.375	36.5
	2	5.080	2.080	40.9
	3	4.091	2.069	50.6
	4	3.820	1.294	33.9
	5	4.027	0.871	21.6
4	1 (inlet)	2.204	0.907	41.2
	2	1.877	0.726	38.7
	3	2.185	0.146	6.7
	4	2.051	0.314	15.3
	5	1.238	0.181	14.6

core inlet. The values downstream were therefore calculated on the basis of the weight loss of the graphite. The results of these calculations are given in Fig. 8 in terms of the fraction of the initial CO_2 remaining at various distances along the specimens.

For the area to be used in evaluating the reaction rate, the geometrical surface area seems to be reasonable. However, in the course of the experiment, the surface area increased as the diameter of the channel changed. To take this variation into consideration an average diameter, d_{av} , was used where

$$d_{av} = \frac{1}{2} (d_{\text{initial}} + d_{\text{final}}).$$

The calculated rate of reaction for each segment is shown in Table III, and the values are plotted in Fig. 9 as a function of CO_2 concentration. Photographs of several of the segments after the tests are shown in Fig. 10. These were taken, one from each test, from near the inlet of the test loop core. The increased degree of corrosion with higher concentrations of CO_2 is obvious.

Fig. 8. CARBON DIOXIDE DEPLETION FOR TESTS 1 THROUGH 4

TABLE III
THE EFFECT OF CARBON DIOXIDE CONCENTRATION
ON REACTION RATE OF GRAPHITE

<u>Segment & Test No.</u>	<u>Average CO₂ Concentration, ppm</u>	<u>Reaction Rate, mg/hr-cm²</u>
<u>1</u>		
Inlet	67.0	36.1 x 10 ⁻²
2	59.3	54.0
3	51.6	35.2
4	46.6	24.5
5	42.1	29.8
<u>2</u>		
Inlet	15.7	16.2
2	13.8	10.3
3	12.3	8.6
4	11.0	7.7
5	9.8	7.4
<u>3</u>		
Inlet	6.1	11.2
2	4.8	6.1
3	4.0	4.9
4	3.3	4.6
5	2.5	4.9
<u>4</u>		
Inlet	1.8	2.3
2	1.3	2.0
3	0.9	2.3
4	0.5	2.2
5	0.1	1.3

Fig. 9. EFFECT OF CARBON DIOXIDE ON GRAPHITE REACTION RATE

Fig. 10. PHOTOGRAPHIC COMPARISON OF CORRODED CHANNEL SURFACES

DISCUSSION OF RESULTS AND PRELIMINARY CONCLUSIONS

Prior to the experiments described above, it was thought that the graphite loss rate would be controlled or limited by the rate of in-pore diffusion. It was felt that the primary damage to the core would be the decrease in density of the channel wall. As a result of the experiments, however, mass transport of CO_2 to the channel wall is tentatively proposed as the rate controlling or limiting step in the reaction mechanism. The primary damage to the core is now expected to be a general enlargement of the channel diameters.

There are three conditions which lead to the mechanism of gas diffusion control. 1) The chemical reaction rate is extremely rapid because of the high temperature in the core (over 2500°F). 2) The concentration of CO_2 in the main gas stream is very low (2 to 70 ppm). 3) The CO_2 in the main gas stream is transported to the graphite surface by the relatively slow mechanism of diffusion because of the low velocity of the main gas stream (Reynolds number less than 1000). If any one of these conditions were changed appreciably, the mechanism could be controlled by pore diffusion.

There are other factors which support the mechanism of gas diffusion in addition to the fact that no density gradient was observed in the graphite. Since the curves in Fig. 6 are nearly mirror images, the reaction rates were almost the same although the heating rod was hotter than the core channel wall.

If pore diffusion or chemical reaction rate were the limiting mechanism the rod would have corroded much faster than the wall.

The relative reaction rates of the rods and the channel walls can be determined by integrating and comparing the areas beneath the curves in Fig. 6. Each of these areas represents a volume of graphite removed per centimeter length on the circumference of the rod or channel. Since the rod and channel are the same length, the area is then also a measure of the loss rate per unit of graphite surface. A comparison of these relative reaction rates is made in Table IV.

TABLE IV
RELATIVE REACTION RATES OF CHANNEL WALL AND HEATING ROD

<u>Test Number</u>	<u>Inlet CO₂ Concentration, ppm</u>	<u>Relative Reaction Rate Channel/Rod</u>
1	70	1.11
2	17	0.78
3	7	0.68
4	2	1.06

"Pitting" leads to an important discrepancy in comparing weight loss data with volume loss data as was mentioned earlier. However, the effect of pitting should be similar for both the heating rod and the channel wall in any given test and should not affect the ratio.

There is a fairly large temperature gradient along the channel from the gas inlet to the gas outlet (2200° to 3000° F), yet the reaction rate does not vary greatly, as seen in Table III. This may be partly responsible for the scatter that does exist. The small temperature effect evident in Table III is characteristic of

rates of gas diffusion which vary with temperature approximately to the 0.8 power (this corresponds to an "activation energy" of about 3 kcal/mole). Pore diffusion (activation energy 43-48 kcal/mole) and chemical reactions (activation energy about 93 kcal/mole) are much more sensitive to temperature changes.² For example, if pore diffusion were the controlling mechanism the reaction rates along the core channel would be separated by a factor of 10.

Mass transport by gas diffusion, which operating conditions and test results indicate, is a first order process; however, a linear least squares fit of all the data shown in Fig. 9 leads to:

$$\text{Rate} = 2.6 \times 10^{-2} C^{0.6}$$

Rate is the milligrams of graphite removed per hour
per square centimeter

C is the concentration of CO₂ in the helium expressed
in parts per million by volume.

The experimental curve in Fig. 11 indicates a tendency toward a first order reaction as the CO₂ concentration increases. There are three possible reasons for the deviation from first order at the lower CO₂ concentrations. In the first place, the reliability of measurements below 1 ppm of CO₂ is low. Second, since the estimation of CO₂ concentration beyond the inlet of the core is by material balance, any handling erosion will appear as a depletion of CO₂. The resulting error will be more appreciable at low than at high CO₂ concentrations. Finally, the presence of a small quantity of moisture in the helium gas would have the same effect as erosion. These potential sources of error would all be small at higher rates of reaction, but the two latter would make the apparent reaction rate too high at the low concentrations, thereby implying an order of less than unity for the reaction.

Fig. 11. FICK'S LAW PREDICTION COMPARED WITH TEST LOOP DATA

Considering only the data for CO₂ concentrations in excess of 1 ppm, the results indicate that the first-order equation for the reaction rate is approximately:

$$\text{Rate} = 1.0 \times 10^{-2} C$$

In Fig. 11 the experimental rates of the reaction, as a function of CO₂ concentration, are compared with the rates calculated from the simple form of Fick's law for mass transport by diffusion control. The latter is given by

$$\text{Rate (gmole/sec-cm}^2\text{)} = (D/RT) (\Delta P/\Delta x)$$

where

$$D = \text{diffusivity, cm}^2/\text{sec} \left(\text{as given by:}^6 D = (1.60 \times 10^{-5} T^{1.84}) / (P/P_0) \right)$$

$$R = 82.057 \text{ atm-cm}^3/\text{°K-gmole}$$

ΔP = difference between the average partial pressure of CO₂ in the bulk stream and the partial pressure at the wall, atm.
(Partial pressure of CO₂ at the wall is assumed to be zero.)

Δx = diffusion path (taken at both the average distance between the heater rod and the channel wall), cm

P = test loop pressure (500 psig), atm

P_0 = 1 atm

T = temperature, °K.

The band described by the calculated points is an effect of the temperature range throughout the core channel. The experimental corrosion rate is generally lower than would be expected from consideration of gas film diffusion control; however, the calculated value may be high because the concentration of CO₂ at the wall is not known and is probably greater than zero. The diffusion coefficient used is also larger than that obtained from other methods of determination.⁷

The carbon monoxide had no apparent effect on the reaction rate during these tests. An analysis, using the generally accepted rate equation for the thermal reaction,⁸

$$\text{Rate} = \frac{k_A p_{\text{CO}_2}}{1 + k_B p_{\text{CO}} + k_C p_{\text{CO}_2}}$$

resulted in a negative specific reaction rate for one step in the mechanism.

The CO concentrations were highly variable for each of the four tests, as shown in Table V; and a correlation, if one existed, should have been readily discernible. Carbon monoxide is credited with inhibiting the CO₂-graphite reaction, but this effect has been found to decrease with temperature and to become very small above 1400°C (2550°F).⁹

TABLE V
CARBON MONOXIDE AND DIOXIDE CONCENTRATIONS

Test Number	CO ₂ Concentration, ppm	CO Concentration, ppm
1	70	7000
2	17	150
3	7	150
4	2	20

Based on the results obtained to date, the UHTREX system appears to be properly designed with respect to corrosion resistance and will function for the three years which is the maximum life anticipated. If the maximum loss of graphite from any channel that can be tolerated is 0.1 in. on the diameter of the core channel, a maximum tolerable CO₂ level can be calculated.

Using the equation, $\text{Rate} = 1.0 \times 10^{-2} C$, and assuming a density of 1.6 g/cm³ and a 1-cm length of channel, it was determined that the reactor could operate at full power for one year at a CO₂ concentration of approximately 3 ppm.

One third of this level is attainable with the gas cleanup system currently planned for UHTREX. The principal source of coolant gas contamination is expected to be the graphite, and most of the impurities evolved will be removed while the core temperature is being increased. Above some minimum temperature, yet to be determined, the rate of heatup of the reactor will depend upon the balance of outgassing rate and cleanup rate. Subsequent contamination may, however, result from the insertion of new fuel elements. Another source of contamination is the carbon deposition reaction in which CO decomposes into CO₂ and carbon. This should be small if the CO level is kept low.

Several tests are currently planned to determine the corrosion rate at temperatures from 1500° to 2100° F outlet gas temperature. The results of these tests should indicate the rates of corrosion to be expected during the heatup period. This information is required in order to determine the maximum permissible heatup rate.

A number of changes in the test loop have been proposed for future experiments. Carbon dioxide concentrations will be controlled automatically from the infrared analyzer. Fiberfrax insulation is being replaced with insulating carbon. A moisture analyzer will be installed to determine the moisture content. The blower will be replaced with another requiring no brushes.

Upon completion of these experiments and a few miscellaneous tests, it is hoped that a machine code can be written to keep a running account of the corrosion in each of the 312 core channels and on each of the fuel elements based on the data generated in these tests and operating data from the reactor. In this way the future life of the core should be predictable at any time during the experiment. The results could be checked occasionally by examining the ejected fuel elements.

REFERENCES

1. Proceeding of the US/UK Meeting on the Compatibility Problems of Gas-Cooled Reactors Held at Oak Ridge National Laboratory, February 24-26, 1960, USAEC Report TID-7597, March 1961.
2. Nightingale, R. E., Nuclear Graphite, pp 387-437, Academic Press, New York, 1962.
3. Walker, P. L., Jr., Rusinko, F., Jr., and Austin, L. G., "Gas Reactions of Carbon", Advances in Catalysis, 11, pp 133-221, Academic Press, New York, 1959.
4. Antill, J. E. and Peakall, K. D., "Attack of Graphite by an Oxidizing Gas at Low Partial Pressures and High Temperatures", Journal of Nuclear Materials, 2, No. 1, (1960).
5. "Ultra High Temperature Reactor Experiment (UHTREX) Hazard Report", LA-2689, April, 1962.
6. Saxena, S. C., Mason, E. A., "Thermal Diffusion and the Approach to the Steady State in Gases: II", Molecular Physics, 2, 379, (1959).
7. Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., Molecular Theory of Gases and Liquids, p 539, John Wiley & Sons, Inc., New York (1954).
8. Ergun, S., "Kinetics of the Reaction of Carbon Dioxide with Carbon", Journal of Physical Chemistry, 60, pp 480-485 (1956).
9. Austin, L. G. and Walker, P. L., "Effect of Carbon Monoxide in Causing Gasification of Graphite by Carbon Dioxide", American Institute of Chemical Engineers, Journal, 9, No. 3, pp 303-306, (1963).