BNL-NUREG-23000

CONF-770708--3

THE EFFECT OF STEAM OXIDATION ON THE TENSILE STRENGTH OF HTGR STRUCTURAL GRAPHITES*

A. J. Romano and J. G. Y. Chow
Brookhaven National Laboratory
Upton, New York, United States of America

ABSTRACT

The core support system of the General Atomic Company design High Temperature Gas-Cooled Reactor (HTGR) contains type PGX graphite as core support blocks. The change in ultimate tensile strength of PGX graphite specimens with oxidation (burnoff) has been determined in a safety-related experimental program at Brookhaven National Laboratory (BNL). It is shown that Fe, an impurity in PGX graphite, plays a key role in the rate of oxidation. The subsequent failure of the graphite specimens is dependent upon the total weight loss due to oxidation. The results indicate that the loss in tensile strength is exponentially related to the percent burnoff (weight loss), and that grain orientation of the specimen has a significant effect.

I. INTRODUCTION

The core support structure of High Temperature Gas-Cooled Reactors (HTGRs) will be exposed to certain oxidizing and reducing species during the forty year life expectancy. In the General Atomic Company conceptual design, each seven-column assembly of graphite fuel elements rests on a graphite core support block, which in turn is supported by three graphite support posts.[1] The core support system is shown schematically in Figure 1. The reference graphites under consideration for each of these core support components are Union Carbide Company type PGX graphite for the support blocks and either Stackpole 2020 or Union Carbide Company type ATJ graphite for the support

*Work carried out under the auspices of the U. S. Nuclear Regulatory Commission.

posts. The core support system, which will be exposed to He at hot streak temperatures up to 780°C, is not designed to be replaced. Therefore, a failure of a portion of the core support system could lead to a safety-related consequence.

Accidental ingress of air, water or steam will lead to exposure of the graphite components to oxidizing impurities in He at high temperature, which in turn will result in decreases in weight and strength. It has been shown that the presence of metallic impurities such as Fe in impure graphites will accelerate the rate of oxidation.[2] Type PGX graphite nominally contains as high as 0.1% Fe.

An experimental program to measure the steam oxidation rates of several HTGR reference graphites and the subsequent effect of oxidation on the tensile strength of PGX graphite is part of the BNL HTGR safety evaluation program. Specially prepared graphite tensile specimens were exposed to He in a recirculating loop containing ~ 100 ppmV H_2O and concomitant impurities such as CO, H_2, CO_2 and CH_4, at temperatures to 750°C and times to 1974 hours. Post-exposure examinations of the PGX specimens included weight change measurements (oxidation rate), density profile estimates, tensile strength determinations, chemical analysis for metallic impurities concentrations and metallographic investigations. Oxidation rate measurements were made on the aforementioned structural graphites and type H451 graphite (Great Lakes Carbon Co.), which is under consideration as the core graphite. In this paper, the discussion of the results on the graphites other than PGX shall be limited in scope.

II. EXPERIMENTAL TECHNIQUE

A. HELIUM IMPURITIES LOOP

Other work at BNL shows that although H_2 in the gas may inhibit the oxidation of pure graphites, it effectively enhances the oxidation rate of Fe containing graphites by maintaining the Fe in a reduced chemical form.[3] Because both the reactants and the oxidation products in the gas are important in determining the oxidation rate and presumably the associated strength changes, it is important to run oxidation tests in closed loop type systems in addition to the simpler once through equipment.

A helium (impurities) recirculation loop (HIL) was used to expose these graphite specimens to He containing water and other impurities. A schematic representation of the loop is shown in Figure 2. The loop essentially consists of five circuits; (1) the main flow circuit containing the pump, graphite bed, test retorts and heat exchanger, (2) a bypass circuit around the graphite bed, (3) a purification circuit, (4) impurity injection systems, and (5) an impurity monitoring system. The gas circulating pump can supply a high volume flow of He (at low pressure) with the capability of achieving very high velocities in the test retorts.

The circuit used with graphite samples in the retorts was the bypass

heater circuit. Thus, the only graphites coming in contact with the He gas were the specimen graphites. The maximum temperature of the loop occurs at the outlet of the test section region. The HIL test section region consists of three vertical parallel tubes, each of which is approximately 5.1 cm inside diameter and 76.2 cm long. A high-temperature flange at the top of each tube permits easy access to the specimens located below.

During the experiment, the impurity concentrations in the loop varied due to the mode of operation. For graphite specimen exposure, the mode of operation was as follows: (1) water was continuously injected and controlled at ~ 100 ppmV, (2) impurities such as CO, H_2, CO_2 and CH_4 were allowed to increase in concentration and achieve a maximum allowable level (control of the gas concentration by purification without simultaneously removing H_2O was difficult), (3) when an allowable maximum limit in the concentration of CO or H_2 was attained, complete purification of the gas was performed by bypassing some gas through the purification system. A summary of the operation of the loop is given in Table I. In terms of operating time, water injection and impurity buildup occurred for ~ 2-3 days and complete purification was accomplished in 0.5 - 1 hour. Following the complete purification of the gas, the cycle was repeated.

Two gas chromatographs were used to monitor the He stream at several points around the loop. The chromatographs have the capability of measuring H_2, CO, CO_2, CH_4, O_2 and N_2 using combinations of separation columns and thermal conductivity detectors. A dew point meter with several detectors located around the loop was used to monitor H_2O concentration. In addition, ZrO_2-Y_2O_3 electrolytic oxygen activity meters were used to determine the oxygen activity of the gas.[4]

B. PREPARATION AND EXPOSURE OF SAMPLES

The samples were prepared from a single log of each of the respective graphites. For example, cylindrical tensile specimens were machined from a single log of PGX graphite (Union Carbide Co. log #2V4-1). Specimens were prepared from material taken with and against the grain orientation. The samples were taken from one end of the log and their locations mapped. The PGX samples were of one size, 1.27 cm diameter x 7.62 cm long. The 2020 samples were the same size. The other graphites tested (ATJ and H451) were prepared in a similar manner, except that two sizes were used, 0.63 cm diameter x 7.62 cm long, and 1.27 cm diameter x 7.62 cm long. The ends of each sample were machined to give a close fitting pin and socket arrangement by which specimens were connected together for insertion into the retorts.

A schematic representation of a typical test section is shown in Figure 3. Each specimen is fixed to the end of another to form a column of 7 samples (A through G) approximately 53.3 cm long. Eight columns, supported at the top and bottom by graphite spacers, make up each of three test sections. Helium enters the test retort at the top at about 600°C, is heated as it passes through the section, and exits at the bottom at about 750°C. Detailed temperature profiles were determined with thermocouple probes in each test section.

III. RESULTS

A. OXIDATION RATE MEASUREMENTS

At the conclusion of the exposure of specimens, each sample was weighed and dimensioned. Mean oxidation rate measurements for all of the graphites tested are shown in Table II. The mean temperature associated with these results (calculated from temperature profile measurements) was ~ 675°C. Detailed analysis of the ATJ, 2020 and H451 graphite results are given in progress reports.[5,6] From the data summarized here, several trends are observed. Graphites of higher purity (lower metallic content) have lower weight losses. For example, the average of the measurements of Fe concentration in all samples analyzed at BNL were as follows: type H451 = 5 ppm, type 2020 = 12 ppm, type ATJ = 40 ppm and type PGX = 480 ppm. The oxidation rates measured here are in fair agreement with the data in the literature for graphites tested under similar conditions.[7-9] A comparison of the results of the 0.64 cm and 1.27 cm diameter samples indicates that there is closer self agreement for a particular type of graphite when the data are reported as mg/cm^2, suggesting a size effect. Results obtained in another test on 2.54 cm diameter PGX compression samples confirm these size effect observations.[6]

The weight change data for the individual PGX graphite samples are shown in Figure 4. Included in the data are samples with only 669 hours of exposure. The data, although showing considerable scatter, indicate a strong temperature dependence. The overall weight losses are about two orders of magnitude higher than the H451 core graphite, which approximately corresponds to the ratio of average Fe concentrations for these graphites. The highest weight loss measured on an individual sample is equal to 6.6×10^{-2} mg/g hr, or 12.8%.

B. CHEMISTRY OF GRAPHITE

Several of the PGX tensile specimens were analyzed by emission spectroscopic methods for the following metallic impurities: Ca, Al, Si and Fe. Some of the scatter in the weight change data can be attributed to the Fe concentration of the respective specimen, as shown in Figure 5. The sample discussed previously, which had the highest observed weight loss, also had the highest Fe concentration of those measured. The other three impurities seem to have little effect on oxidation. Of interest to note is the range of Fe concentrations measured, i.e., 5 to 1300 ppm. In comparing the analytical results with the original location of the sample in the graphite log, it was found that most of the low Fe samples were taken near the edge whereas most of the high Fe samples were toward the center.

Work is continuing at BNL on catalytic oxidation of graphite.[3] Emphasis is being placed on studying the role of iron in catalyzing the oxidation of PGX graphite. The study involves analyzing the chemical form of iron in the graphite using Mössbauer spectroscopy. In general, the results indicate that the catalytic effect depends upon the chemical (and perhaps physical) form of the iron and the form of iron in the graphite also depends on the experimental conditions. As a part of this study, several PGX samples which had been exposed in HIL were examined. Most of the iron in the tensile

samples examined was in the form of metallic Fe. In separate tests, most of the iron in PGX samples exposed in air was in the form of iron oxides. The results of this work strongly indicate that the hydrogen in the He in the HIL plays a key role in determining the form of Fe in the graphite and that metallic Fe is the stronger catalyzing agent.

C. MECHANICAL PROPERTY MEASUREMENTS

Since the highest weight losses were measured on the PGX samples, it was anticipated that the largest changes in tensile strength would also be observed on those samples. Therefore, several PGX samples having high burnoffs were tested.

Tensile tests were performed on unexposed samples and on specimens that were oxidized in the loop. The unexposed samples used in the strength determination were straight sided specimens, 1.27 cm in diameter and 7.62 cm long. Both groups of specimens were taken from the same PGX graphite log.

The tensile specimens were cemented to aluminum socket grips with epoxy cement. A fixture that was recommended by ASTM Tentative Specification C815 (Proposed Method of Test for Tensile Properties of Nuclear Graphite, June 18, 1975) was used for aligning the grips to the specimen. Roller chain load train with swivel fixtures were used for proper alignment. The specimens were pulled at a strain rate of 0.005 inch per minute.

A review of the literature regarding the loss in strength of nuclear grade graphite with loss in weight due to oxidation indicates that most of the data in the literature fits a relationship of the type:

$$\frac{S}{S_o} = \left(\frac{\rho}{\rho_o}\right)^{\alpha} \qquad (1)$$

where S and ρ are rupture stress (compression, tensile, etc.) and density, respectively, and α an empirically determined constant.[10] The equation can be reduced to:

$$S = S_o\,(1 - W_L)^{\alpha} \qquad (2)$$

where W_L is the fractional burnoff of the graphite. However, most of the data available in the literature are for pile grade graphite (low Fe).[11] Some compression strength data exists for Type CS graphite, a commercial grade similar to ATJ.[12] In addition, much of the data is for air and CO_2 oxidation and at temperatures ranging from 200 to 950°C. There are apparently no data in the literature for PGX graphite. The review indicates that values of α for tensile strength data range from 8.0 to 13.5 with most of the data close to 8.0.

The results of the tensile strength measurements of the PGX samples are given in Table III. Contrary to expected results, the controls taken with

the grain averaged 1000 ± 43 psi, slightly lower than controls taken against the grain which averaged 1159 ± 86 psi in strength. Similarly, for the same burnoff, oxidized samples taken with the grain showed lower strengths than those taken against the grain. As expected, the higher burnoff samples showed lower strengths. Specimens with the grain decreased in strength by a factor of one-half after only 7% burnoff while samples against the grain show the same decrease after 13%.

The results for PGX are plotted in Figure 6 as log tensile strength vs. % burnoff. The results for samples taken with the grain and those taken against the grain are clearly separable into two curves. The slopes of these curves (α) are 5.1 and 9.2 for against grain and with grain, respectively, indicating that for PGX the relationship of loss of strength with loss of weight is similar to pile grade graphites. The implication of this data needs to be emphasized. Although the Fe in PGX graphite accelerates the rate of oxidation as compared to nuclear graphite, the failure mechanism of the PGX appears to be independent of the Fe content but instead is a function only of overall weight loss, i.e., at present no effect of catastrophic strength loss with small weight loss has been observed.

Low magnification examination of the fracture surface did not show a pronounced difference between the oxidized and unoxidized specimens. However, a more detailed scanning electron microscopic study of the fracture surface to determine the effect of oxidization is being carried out by the Aerospace Corporation under a subcontract with BNL.[13]

D. DENSITY PROFILE MEASUREMENTS

Density profile measurements were made on some of the samples exposed to He and compared with unexposed standards. Several exposed samples showed complex density profiles, but the majority of those examined showed either flat profiles or only slight changes near the surface. There does not appear to be a strong correlation with any single parameter such as exposure time, temperature, position or grain orientation, but there does appear to be a correlation with overall weight loss. The high weight loss samples show the deepest penetration from the surface. This is evident in Figure 7, where the density profiles of samples of various weight losses are plotted. In reading the plot, one must recall the original density of each sample was of the order of 1.7 - 1.75 g/cm^3.

IV. DISCUSSION

The results of oxidation rate measurements made on several HTGR candidate graphites show that the rate is dependent upon the Fe concentration in the graphite. The rate of oxidation for type PGX graphite containing about 1000 ppm Fe (nominal content of commercial grade) is about 6.6×10^{-2} mg/g-hr or 12.79% at 750°C. The data reported here suggests that quality control of the PGX graphite used in HTGRs regarding Fe chemistry may be needed.

The results from the tensile test measurements of PGX graphite specimens clearly indicate that the relationship between loss of strength and

loss of weight due to oxidation is exponential. Although there appears to be an effect due to grain orientation, the results for PGX graphite are in agreement with the data in the literature for pile grade graphites when the results are presented in a traditional exponential form relating reduction in strength to loss in weight.

There are several factors that must be considered before conclusions may be drawn from this data. The first is the effect of size. These data (as well as most data available in the literature) are for small diameter specimens, in this case 1.27 cm. The depth of oxidation in a small specimen may represent a large proportion of the overall diameter, whereas in the HTGR support blocks, the depth will have to be considerable to have an effect. The second factor is the effect of impurity level in the He. In HIL the impurity levels were not controlled, except for H_2O. The multiple effects of H_2, CO_2, CO and CH_4 on graphite oxidation are uncertain. However, if one considers that the loop operates at $\sim$ 1 atm, whereas an HTGR would operate at 50 atm, 100 ppmV H_2O in HIL would be equivalent to $\sim$ 2 ppmV H_2O in an HTGR. The Technical Specification Limits for oxidants in Fort St. Vrain is $\sim$ 10 ppmV. If CO_2 and H_2O are considered the only oxidants, the HIL atmosphere was within the operating range. Another factor to consider is exposure time. The PGX specimens were exposed for only $\sim$ 2000 hours, whereas an HTGR is expected to operate for $\sim$ 280,000 hours (40 years). Still another factor is the effect of imposed stress on the rate of oxidation. Krefeld et al. found the effect of stress on oxidation and strength to be considerable, i.e. the addition of small loads increased the rate of oxidation by a factor of five.[14]

In conclusion, the parameters of greatest significance are oxidation rate and the effect of Fe on the rate. It has been shown that of all the graphites in an HTGR, the PGX graphite (due to its high metallic impurity concentration) is oxidized at a sufficiently high rate indicating that some further consideration is required. The complex nature of PGX oxidation suggests a need for further tests to determine the effect of size, applied stress and long time exposures. There is a strong indication that the loss of strength of PGX graphite is dependent on the overall weight loss. This suggests that data regarding loss of strength vs. burnoff for nuclear graphite can be extrapolated to high burnoffs to determine similar relationships for PGX.

REFERENCES:

1. "General Atomic Standard Safety Analysis Report", GASSAR - Vol. 2, GA-A13200, 1974.

2. POINTUD, M. L., KARCHER, W., POLLITT, N. (Dragon Project) and LOTHE, J., (CIIR, Oslo), "Catalytic Influence of Different Metals on Corrosion Rate of Graphite", Dragon Project Report 332.

3. SKALYO, J. et al., "Reactor Safety Research Programs Quarterly Progress Report", BNL-NUREG 50624, pp. 69-75, October - December, 1976.

4. ISAACS, H. S., "Kinetic Dependence of Iron Catalyzed Graphite Oxidation on Oxygen Potential", 13th Carbon Conference, UCI, Irvine, California, July 18-22, 1977.

5. ROMANO, A. J., "HTGR Safety Evaluation Division Quarterly Progress Report", BNL-NUREG 50599, pp. 28-37, April-June 1976.

6. ROMANO, A. J., "HTGR Safety Evaluation Division Quarterly Progress Report", BNL-NUREG 50645, pp. 97-115, July-September 1976.

7. BLAKELY, J. P. and OVERHOLSER, L. G., "Oxidation of Graphite by Low Concentrations of Water Vapor and Carbon Dioxide in Helium", Carbon, 2, pp. 385-394, 1965.

8. BLAKELY, J. P. and OVERHOLSER, L. G., "Oxidation of ATJ Graphite by Low Concentrations of Water Vapor and Carbon Dioxide in Helium", Carbon, 3, pp. 269-275, 1965.

9. HTGR Fuels and Core Development Program Quarterly Progress Report", GA-A14298, February 1977.

10. MORGAN, W. C. and BECKER, F. L., "In-Service Monitoring of the Strength of HTGR Core Support Structure", BNWL-B-359, June 1974.

11. ROUNTHWAITE, C., LYONS, G. A. and SNOWDON, R. A., "Influence of Thermal Corrosion on the Strength, Permeability, and Frictional Properties of Nuclear Graphite", Second Conference on Industrial Carbon and Graphite, Society of Chemical Industry, London, 299-319.

12. GRIGGS, B., "The Effect of Oxidation on the Compression Strength of CS-GBF Graphite", HW-42498, April, 1956.

13. ZIMMER, J. et al., "Reactor Safety Research Programs Quarterly Progress Report", BNL-NUREG 50661, pp. 33-39, January-March 1977.

14. KREFELD, R., LINKENHEIL, G. and KARCHER, W., "The Effect of Stress on Graphite in Water Vapor Atmosphere", 11th Biennial Conference on Carbon, CONF-730601, USAEC, 88-89, 1973.

TABLE I

SUMMARY OF OPERATION OF HELIUM IMPURITIES LOOP

Main Flow Circuit

Maximum Gas Circulating Pump Flow	=	1350 std. ℓ/min
Mean Loop Pressure	=	1.2 atmosphere

Test Retort Circuit

Maximum Flow per Retort	=	240 ℓ/min
Average Velocity in Retort	=	292 cm/sec (9.6 ft/sec)
Mean Temperature Gradient	=	600 to 750°C

Impurity Monitoring

Water Concentration, mean	=	100 ppmV
CO_2 Concentration, mean	=	250 ppmV
Ratios of Impurities: $\frac{H_2}{H_2O}$	=	20 mean
$\frac{CO}{CO_2}$	=	10 mean
Methane Concentration, mean	=	100 ppmV

TABLE II

SUMMARY OF OXIDATION RATE MEASUREMENTS

Type of Graphite	Number of Specimens	Diameter (cm)	Mean Oxidation Rate, mg/g-hr	Mean Oxidation Rate, mg/cm^2
H451	21	1.27	1.27×10^{-4}	0.13
H451	35	0.64	1.93×10^{-4}	0.10
ATJ	30	1.27	2.96×10^{-4}	0.32
ATJ	49	0.64	9.64×10^{-4}	0.52
2020	7	1.27	2.17×10^{-4}	0.24
PGX	39	1.27	1.04×10^{-2}	11.22

TABLE III

RESULTS OF TENSILE STRENGTH MEASUREMENTS OF PGX GRAPHITE

Standards Unexposed Sample No.	Grain Orientation	Stress, psi
G-5	With Grain	960
G-6	"	1010
G-7	"	1070
G-8	"	960
G-10	"	975
G-11	"	1025
Average		1000 ± 43
G-13	Against Grain	1070
G-14	"	1230
G-15	"	(540)*
G-16	"	1100
G-17	"	1235
Average		1159 ± 86

Samples Exposed in HIL Sample No.	Grain Orientation	Burnoff, %	Stress, psi
1-3A	With Grain	0.13	970
1-4A	"	0.17	810
2-4B	"	0.73	852
1-4B	"	0.97	906
1-3B	"	1.02	925
1-1D	"	1.03	760
2-3E	"	1.62	865
1-1E	"	2.60	805
2-3F	"	2.73	765
3-3E	"	2.88	815
1-3G	"	4.28	685
1-3F	"	5.21	500
1-3E	"	6.47	565
2-3D	Against Grain	0.58	1005
1-3C	"	2.08	995
2-4G	"	2.10	1150
1-4F	"	4.91	745
3-4F	"	6.57	840
1-4G	"	10.21	656
1-3D	"	12.79	645

*Not included in average.

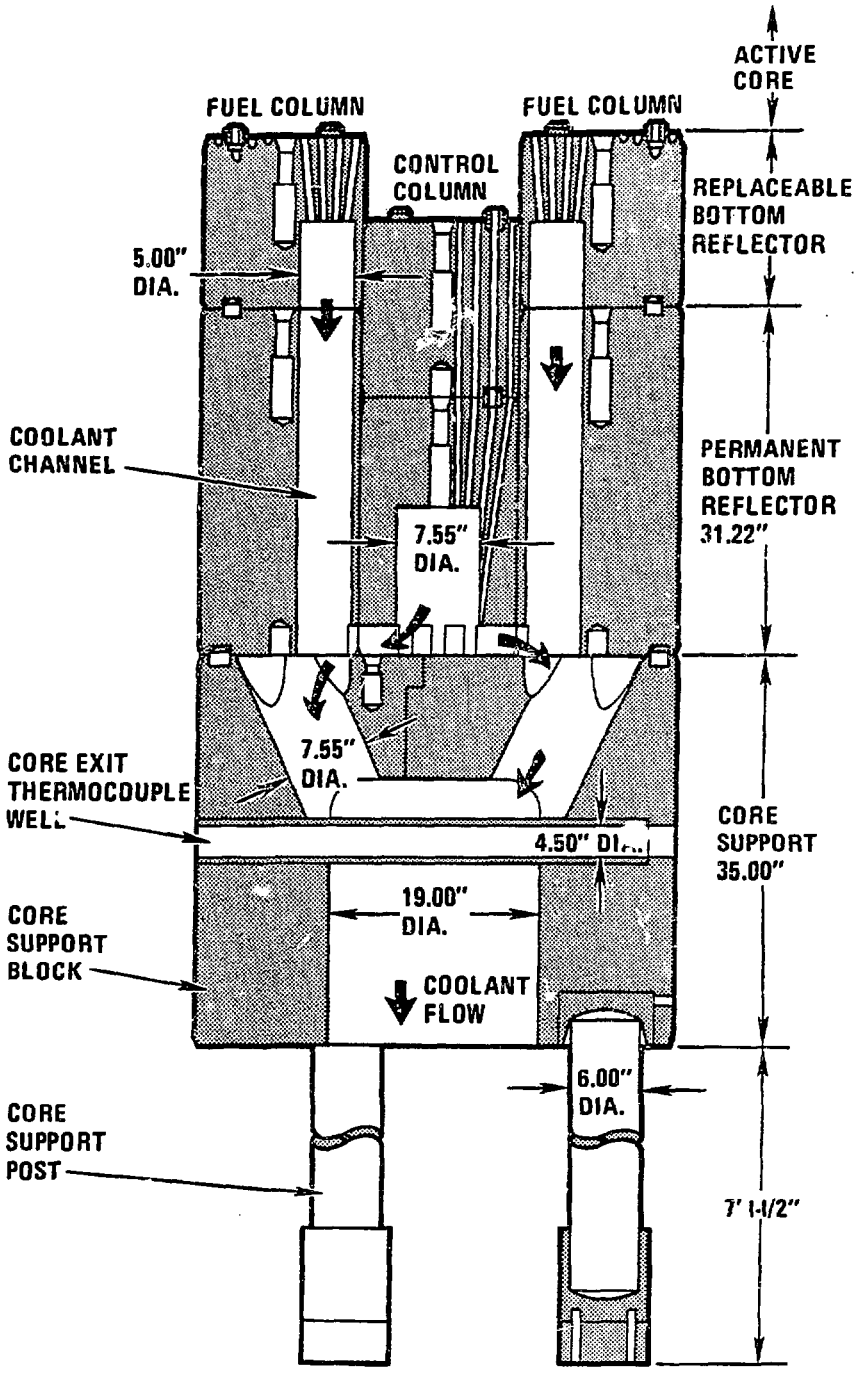

Figure 1. Section of high temperature gas-cooled reactor core and support structure.

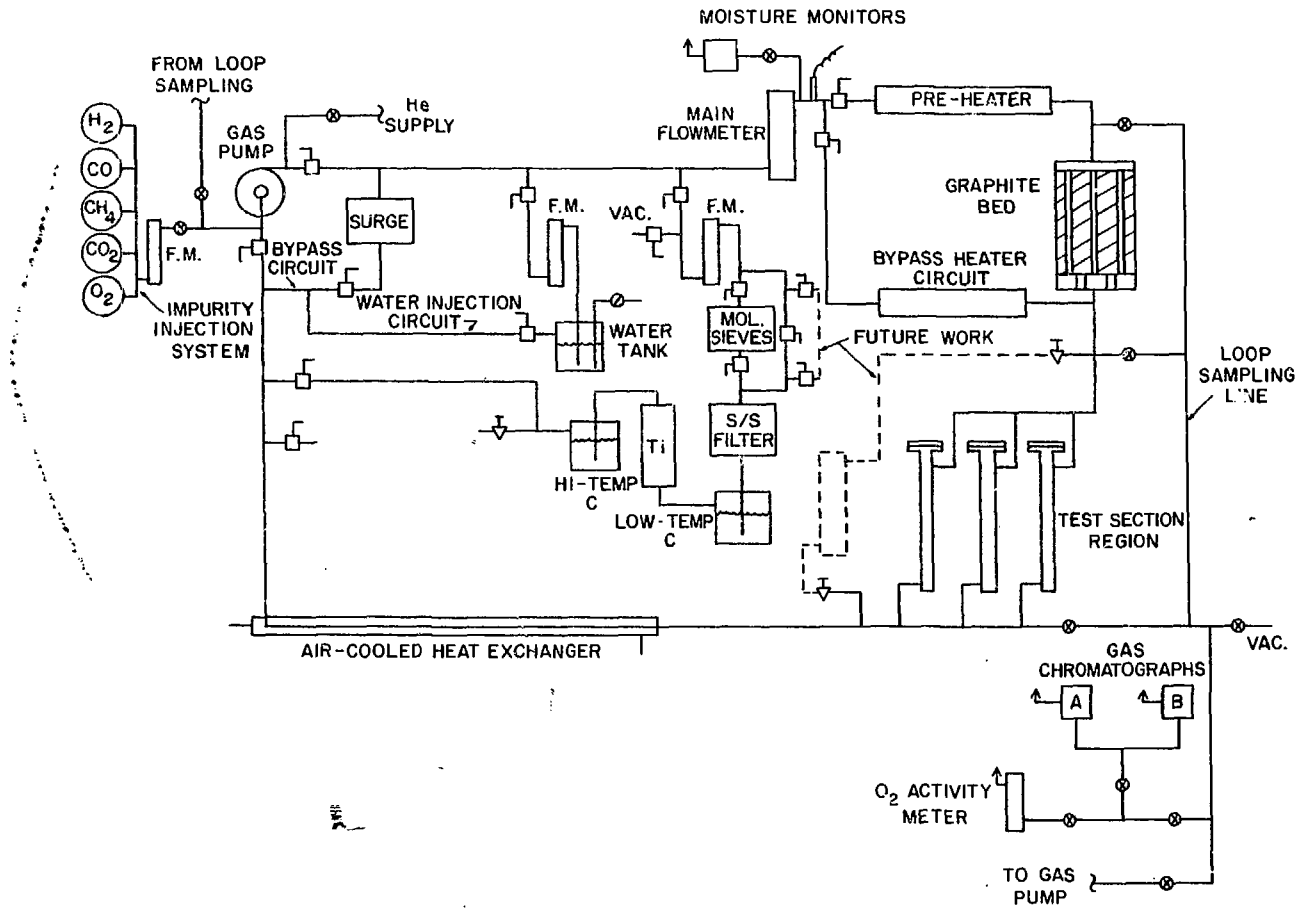

Figure 2. Helium impurities loop (schematic flow sheet).

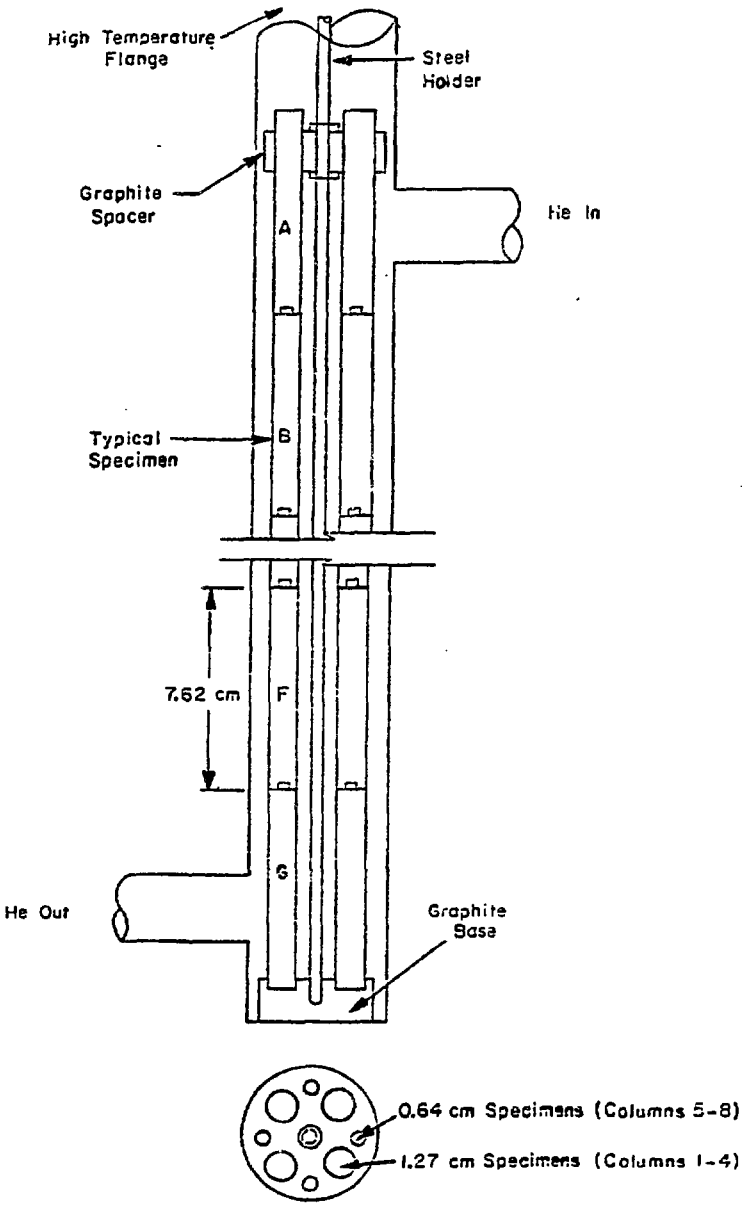

Figure 3. Graphite tensile specimen test section.

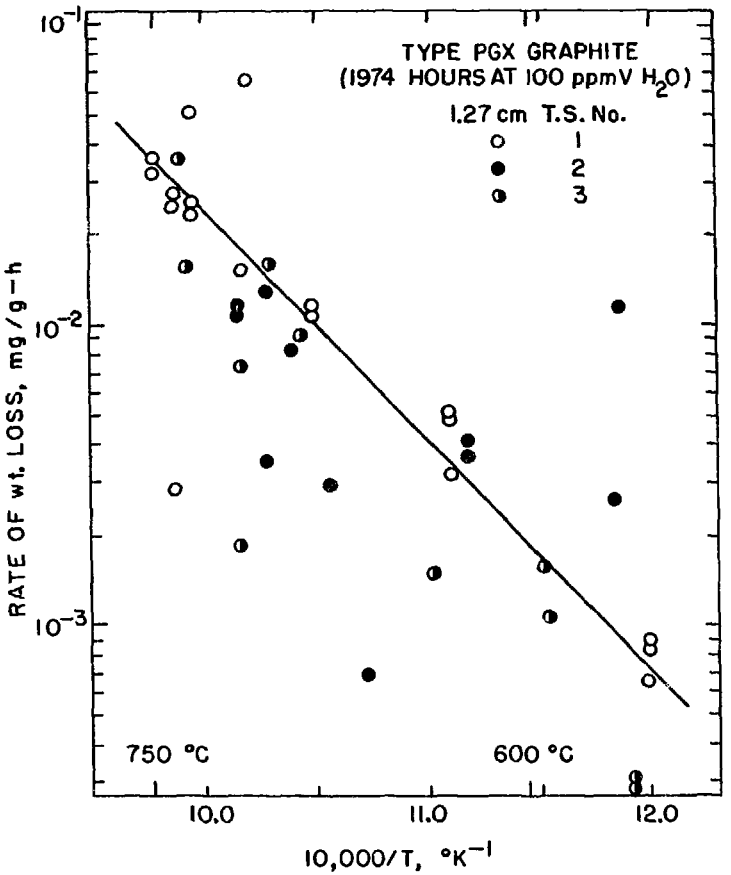

Figure 4. Plot of weight loss of PGX specimens vs. reciprocal temperature.

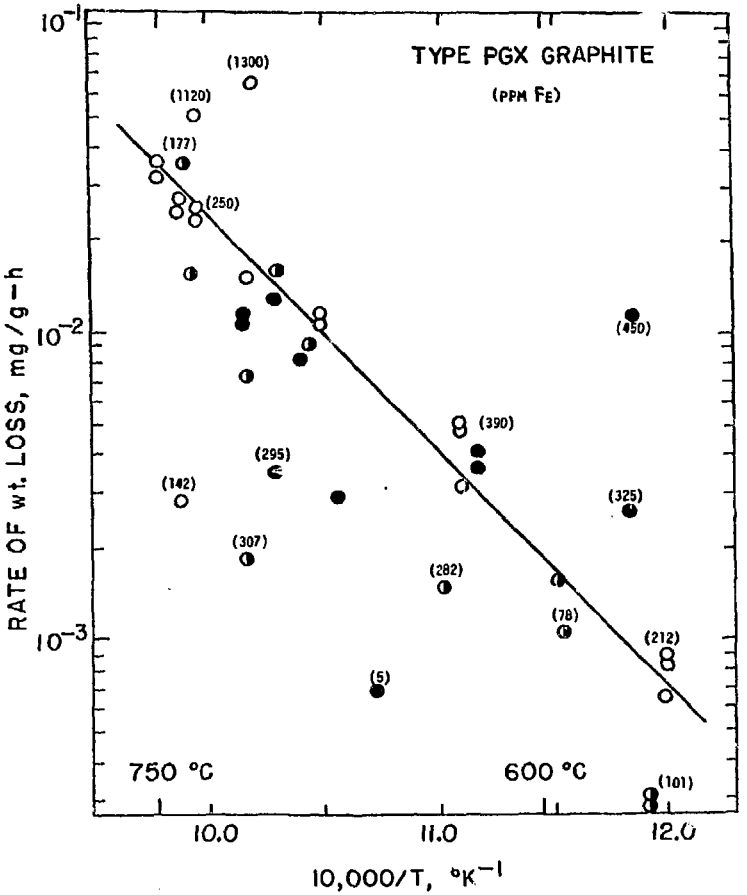

Figure 5. Concentration of Fe in PGX specimens analyzed.

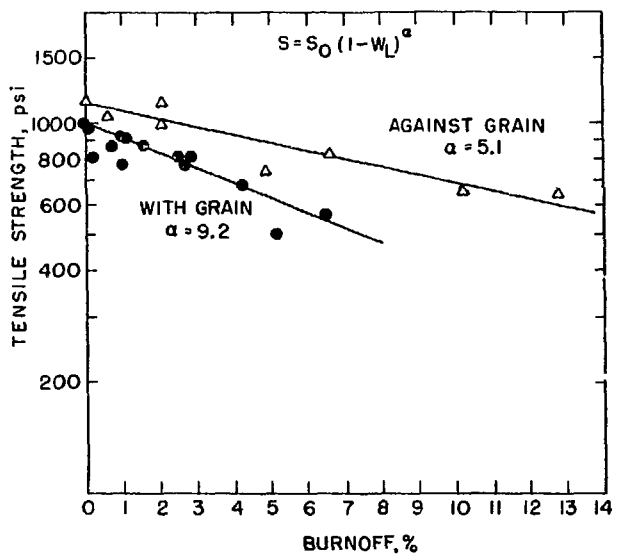

Figure 6. Tensile strength of PGX graphite as a function of extent of oxidation.

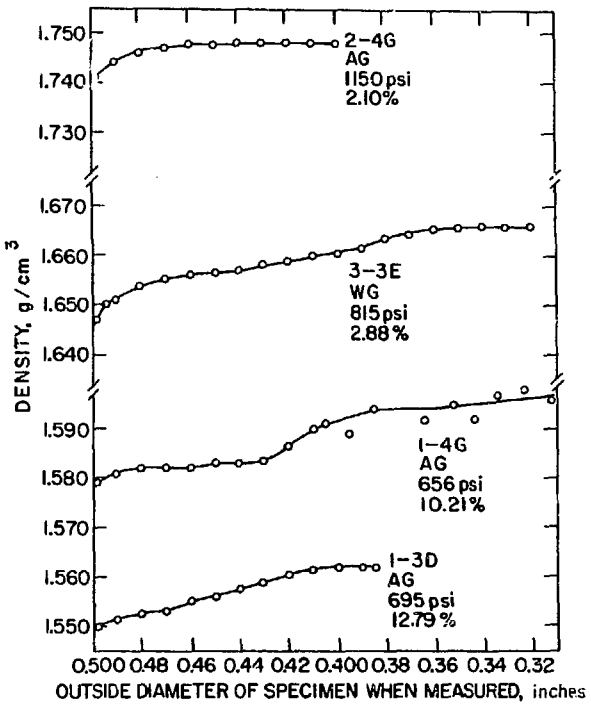

Figure 7. PGX graphite density profiles after oxidation.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the help and guidance received from D. G. Schweitzer, H. Isaacs, C. Sastre and the rest of the HTGR Safety Evaluation Division Staff. In particular, they would like to thank D. Wales, C. Brewster and A. Muscarella for their efforts in carrying out the experimental investigations.