COO-2712-2

STUDIES OF MECHANICAL PROPERTIES AND IRRADIATION DAMAGE NUCLEATION OF HTGR GRAPHITES

MASTER

PROGRESS REPORT

FEBRUARY 1, 1976 - JANUARY 31, 1977

P. A. THROWER

The Pennsylvania State University
University Park, Pennsylvania 16802

February 1977

PREPARED FOR

The U. S. Energy Research and Development Administration

Under Contract No. EY-76-S-02-2712*000

DISCLAIMER

ABSTRACT

Sample preparation for irradiation studies has been completed but irradiations are unlikely to commence until late 1977.

The effect of compressive stresses up to 650 p.s.i. on the reaction rate of Stackpole 2020 graphite with helium containing small amounts of either H_2O or CO_2 has been investigated. In no case has any effect been found.

Relationships between the compressive strengths of 2020 and Great Lakes H440 graphites and air oxidation burn-off show that a 10% burn-off results in a 50% strength reduction. Sample external dimensions were unchanged even with a 50% burn-off. Strain to failure was relatively independent of burn-off except for 2020 graphite with burn-offs in excess of $\sim$28% when strains increased rapidly. Scanning electron microscope examination reveals preferential removal of binder material over filler particles.

The effect of flow rate of He/H_2O and He/CO_2 gas mixtures over the graphite sample during oxidation has shown a decrease in oxidation rate with increasing flow rate in the flow rate range 13.8 to 15.3 ml/sec.

1. Irradiation Damage Studies

The purpose of the irradiation damage study part of this program has been fully discussed in the proposal. At the time of writing the last progress report[1] single crystals of natural graphite and two samples of pyrolytic graphite had been doped with different concentrations of boron (B^{11}). During the early part of the period covered by this report the crystals were carefully photographed and placed in graphite capsules for irradiation.

At the time of writing, the specimens are still awaiting irradiation. This situation has arisen because of the inoperative state of the Oak Ridge Reactor. It now appears that irradiation could take place in ORR using General Atomic Capsule OG-5 beginning in October 1977 at the earliest. This would provide irradiation temperatures in the range 600-1350°C with a fast fluence of around 2×10^{21} n/cm^2. An alternative possibility is irradiation in HFIR later in 1977 with temperatures of 1500°C and 1900°C to the same fluence. In the latter case the temperatures are known only to $\pm$ 100°C but the higher available temperature is attractive. If possible both facilities will be used.

2. Effect of Compressive Stress on Oxidation Rate

A. Apparatus

A full description of the apparatus used in this investigation was given in last years progress report. Some important modifications have subsequently been made. The top and bottom plates of the reaction vessel have been extensively redesigned so that they are now both water cooled. A smaller bellows configuration has been fitted to the top plate in order to allow compressive stresses to be more easily transmitted to the sample and to give longer bellows life. These changes have resulted in a better seal to the reaction vessel and increased gasket life, which in turn also makes for a better seal to the system.

A transducer load cell (Tyco Instrument Division) has been incorporated into the dead-weight loading apparatus. Loads of up to 1000 pounds may now be measured with an accuracy of <1% and fed directly to the one remaining input of the six-point recorder which is already adjusted to measure furnace and sample temperatures and H_2O, CO and CO_2 concentrations in the gas stream entering or leaving the reaction chamber.

B. Experimental Procedure

The cylindrical graphite sample, 0.75" diameter (ϕ)x1.5" long (ℓ), is carefully positioned between the alumina anvil and ram and the furnace closed and checked for leaks while a small helium positive pressure is maintained.

In order to obtain reproducible data it has been found necessary to perform a preliminary sample burn-off by passing oxygen over the sample at a rate of 10 cm^3/sec at a temperature of 900°C. This is presumably due to graphite debris from the machining process being dislodged from the sample at the commencement of oxidation and hence producing a larger surface area and higher reaction rate. The system is then purged by flushing with dry helium until the effluent gas contains less than 20 ppm of oxygen obtained by summing the measured CO and CO_2 concentrations.

Stackpole grade 2020 graphite has been used exclusively for the investigations reported here. Reactions with He/CO_2 and He/H_2O gas mixtures have been examined. The He/CO_2 gas mixture was obtained by mixing gases from cylinders of pure He and a He/1000 ppm CO_2 mixture at a constant total flow rate. He/H_2O mixtures were obtained by passing He over a refrigerated ice bath at an appropriate temperature.

C. Results

In no case investigated so far has there been any instance of increased activity when a compressive stress was applied to the sample. A summary of some of the data obtained is given in Table I.

The gas concentrations are given to the nearest 5 ppm but the accuracy of measurement is generally slightly better than that. In all cases where the C-CO_2 reaction was studied it can be seen that

$$X_{CO_2}^{out} + \frac{1}{2} X_{CO}^{out} = X_{CO_2}^{in} ,$$

i.e., there is conservation of oxygen.

The compressive strength (σ_c) of the Stackpole 2020 graphite is around 12,000 p.s.i. (see Section 3) so that the loads applied here are $\leq \sigma_c/20$, however even when the experimenter applied his own weight to the apparatus pushing the stress to over 1000 p.s.i. there was still no effect on the reaction rate! A typical data output from a run is shown in Figure 1.

D. Discussion

The original Euratom Petten work on this effect by Krefeld et al.[5] differed from our investigations in that tensile stresses were used.

Effects were observed at 1000°C with only 20 ppm H_2O present and stresses of 350 p.s.i. were sufficient to produce the maximum effect, which consisted of a 2-7 fold increase in the concentrations of reaction products. No model which can even qualitatively explain these results (viz. pore opening or impurity migration due to the stress field) would predict zero effect of compressive stress.

G. B. Engle of General Atomic Co. spoke with Krefeld about his work last year. He reported:

"Krefeld claims his results were reproducible and the effect is real.

Krefeld's experimental system was operated at a flow rate of 200 ml/hr. at 780 mm Hg which is almost a static condition. They purged the system with argon (not helium) then bubbled argon through boiling water in a separate line to form a mixture of 1000 ppm H_2O in argon."

Our results are obviously inconsistent with those of Krefeld. Major differences are in the mode of stress (compressive vs tensile) and the flow rates (33,000-55,000 ml/hr vs 200 ml/hr). We are unable to use much lower flow rates for the infrared gas analyzers, but with a 2 ppm accuracy on CO and CO_2 concentration measurements it would certainly appear that if there were any change in oxidation rate due to the stress it would be measureable.

During the year workers at KFA Jülich, W. Germany, have been in contact concerning this work both by letter and telephone. They have duplicated Krefeld's experiments using an identical apparatus and the same graphite material as that for which Krefeld found the largest effect, in addition to other materials. In no case was any effect of tensile stress on oxidation rate found. A copy of a preliminary report (in German) has been received. Correspondence relative to this matter is attached as an appendix to this report.

Table I

Sample Temperature (°C)	Compressive Stress (p.s.i.)	$X_{CO_2}^{in}$ (ppm)	$X_{H_2O}^{in}$ (ppm)	$X_{CO_2}^{out}$ (ppm)	X_{CO}^{out} (ppm)
888	0	85	-	60	45
	267	85	-	60	45
	362	85	-	60	45
888	0	175	-	135	80
	267	175	-	135	80
	362	175	-	135	80
893	0	-	885	75	125
	267	-	885	75	125
	362	-	885	75	125
	456	-	885	75	125
908	0	115	-	85	60
	456	115	-	85	60
	650	115	-	85	60
908	0	-	125	15	30
	362	-	125	15	30
	456	-	125	15	30

3. Effect of Oxidation on Compressive Strength

A. Experimental

There is very little data on the effect of oxidation in various atmospheres on compressive strength. This study was undertaken in an attempt to obtain a better understanding of some of the factors involved. Graphites chosen for investigation were Stackpole 2020 grade and Great Lakes H440 grade, both possible candidates for HTGR core support posts.

Initially, work was aimed at specifying test conditions. Strain rates were varied between 0.1"/min and 0.002"/min and no significant variation in fracture stress and strain to failure was found. Samples of dimensions 0.25" diameter (ϕ)x0.5" length (ℓ) and 0.75" ϕ x 1.5" ℓ were also examined and the average fracture stress was the same in each case. It was therefore decided to use samples of 0.25" ϕ x 0.5" ℓ and a strain rate of 0.01"/min. The choice of the smaller sample size allowed for most testing to be performed using a table model Instron machine available in the laboratory. It was found that frictional effects between sample and machine could be eliminated by placing thin pieces of Teflon tape between the ends of the sample and the machine anvils.

Oxidations reported here were performed in air at atmospheric pressure using an open quartz vessel in a muffle furnace.. Each sample was held in a pair of Pyrex tongs which masked the sample end faces thus allowing them to be used for subsequent compressive testing.

B. Results

A comparison of the fracture conditions determined experimentally and those given in manufacturers' data sheets is given in Table II. The data for the fracture stresses is in reasonable agreement but it is surprising that the measured strains to failure are approximately double those expected.

Table II

Graphite	Fracture Stress (σ_c) PSI		% Strain to Failure	
	Given	Expt.	Given	Expt.
H440	7,800	8,100	∿2	4.4
2020	13,000	11,000	1.9	4.3

The effect of oxidation on the compressive strength (σ_c) of the two graphites is shown in Figures 2 and 3. It can be seen that in both cases a burn-off of 8-9% is sufficient to produce a 50% loss in strength. There is also no apparent effect of temperature on the data. Both these results are in agreement with the data of Board and Squires[(2)] on the effect of CO_2 oxidation on British PGA graphite.

A surprising result that came out of this work was the inability to visually estimate the amount of burn-off. Samples oxidized to as much as 40-50% burn-off were not significantly decreased in size although they were quite fragile and measurement was restricted to using a mm rule. It was also surprising that the sample integrity was maintained after such high amounts of oxidation.

C. Microscopic Examination

Oxidized samples examined in the scanning electron microscope showed no outer reacted zone but rather it appeared that oxidation had occurred fairly uniformly throughout the sample. Figure 4 shows a sample of H440 graphite oxidized to 15% burn-off. The binder is obviously the more reactive constituent being rapidly transformed into a spongy material while surrounding filler particles were relatively untouched.

The photographs show that attack occurs preferentially on specific sites indicative of possible catalytic effects, there being much more activity in the binder. In Figure 4a binder material surrounded by filler particles has obviously suffered a larger weight loss. The binder (Fig. 4b) has a basic layer structure but attack has occurred at points within the layers in addition to the layer edges. A similar case is shown in Figure 4c where attack at the edges of filler particles is clearly evident while the nearby binder seems ragged by comparison.

D. Discussion

It was decided to test the data in Figures 2 and 3 for exponential decay by plotting $\log_{10} \sigma_c$ versus burn-off as shown in Figures 5 and 6. Data for Stackpole 2020 grade does in fact fall on a straight line with an apparent jog to a lower parallel line at around 28% burn-off. This would of itself perhaps not appear to be significant but a similar discontinuity is obtained if one plots strain to failure vs burn-off (Figure 7). Both Board and Squires[2] and Rounthwaite et al.[3] indicate that the strain to failure for tensile fracture of corroded graphites is approximately constant and this certainly appears to be the case here up to ∿28% burn-off, but beyond this the strain to failure increases markedly.

For the Great Lakes H440 graphite however, the plot of $\log_{10} \sigma_c$ vs % burn-off has much more scatter but appears to be linear throughout the whole burn-off range. Similarly, strain to failure data is very scattered but shows no tendency to increase at higher burn-offs. The correlation between a discontinuity in the $\log_{10} \sigma_c$ curve and an increase in strain to failure must obviously be examined further.

It is tempting to hypothesize that in the 2020 grade material a burn-off of ∿28% corresponds to elimination of rigidity contributed by the binder phase at which point larger strains are possible and oxidation rates are reduced because oxidation is now confined to the more crystalline filler particles. The burn-off at this point would probably be in excess of the % binder in the material since filler is also being oxidized.

4. Effect of Gas Flow Rate on Oxidation

Using the apparatus designed for examining oxidation under stress it has been possible to commence investigations into the effect of gas flow rate on oxidation rate. As mentioned earlier the flow rate was between 33 and 55 litres/hr. The exact flow rates used were 9.2, 13.8 and 15.3 ml/sec corresponding to velocities of 2.1, 3.2 and 3.6 mm/sec past the sample.

Reaction rates are calculated using the first order rate equation given by Hedden and Löwe[4] for their "open circuit" oxidation experiments. For the graphite - CO_2 reaction the rate is given by

$$-\frac{dr_c}{dt} = V_{in}(X^{in}_{CO_2} - X^{out}_{CO_2}) \frac{P_{total}}{82.05\ T_{room}\ (K)}$$

where $-dr_c/dt$ is the number of moles of carbon consumed per second, V_{in} is the gas flow rate in cm^3/sec and $X^{in}_{CO_2}$ and $X^{out}_{CO_2}$ are the inlet and outlet mole fractions of CO_2. P_{total} is one atmosphere.

For the graphite $-H_2O$ reaction the rate is

$$-\frac{dr_c}{dt} = V_{in}(X^{out}_{CO_2} + X^{out}_{CO}) \frac{P_{total}}{82.05\ T_{room}\ (K)}$$

where X^{out}_{CO} is the mole fraction of CO in the outlet gas.

Reaction rates as defined in the above equations are plotted as functions of the inlet CO_2 and H_2O partial pressures (mm Hg) in Figures 8 and 9. The three curves on each figure correspond to the three flow rates used. It can be seen that for any given partial pressure the rates increase on increasing the flow rate from 9.2 ml/sec to 13.8 ml/sec but decrease when the flow rate is further increased to 15.3 ml/sec. These results are somewhat mysterious and further investigation is necessary. However the same effect is found for both the C-H_2O and C-CO_2 reactions and there is no reason to doubt its validity at present.

5. Personnel

P. A. Thrower (principal investigator) has devoted 20% of his time to the project during the period reported here and is expected to do so during the remainder of the current contract period.

D. Marx (graduate assistant) 50% time for 12 months.

J. Bognet (graduate assistant) 50% time for 12 months.

6. References

1. P. A. Thrower, Progress Report COO2712-1 (1976).

2. J. A. Board and R. L. Squires, Proc. 2nd Conf. on Ind. Carbon and Graphite, Society of Chemical Industry, London, 1966, p. 289.

3. C. Rounthwaite, G. A. Lyons and R. A. Snowdon, ibid., p. 299.

4. K. Hedden and A. Löwe, Dragon Project Report #205 (1963).

5. R. Krefeld, G. Linkenheil and W. Karcher, ORNL-CONF-730601, p. 88.

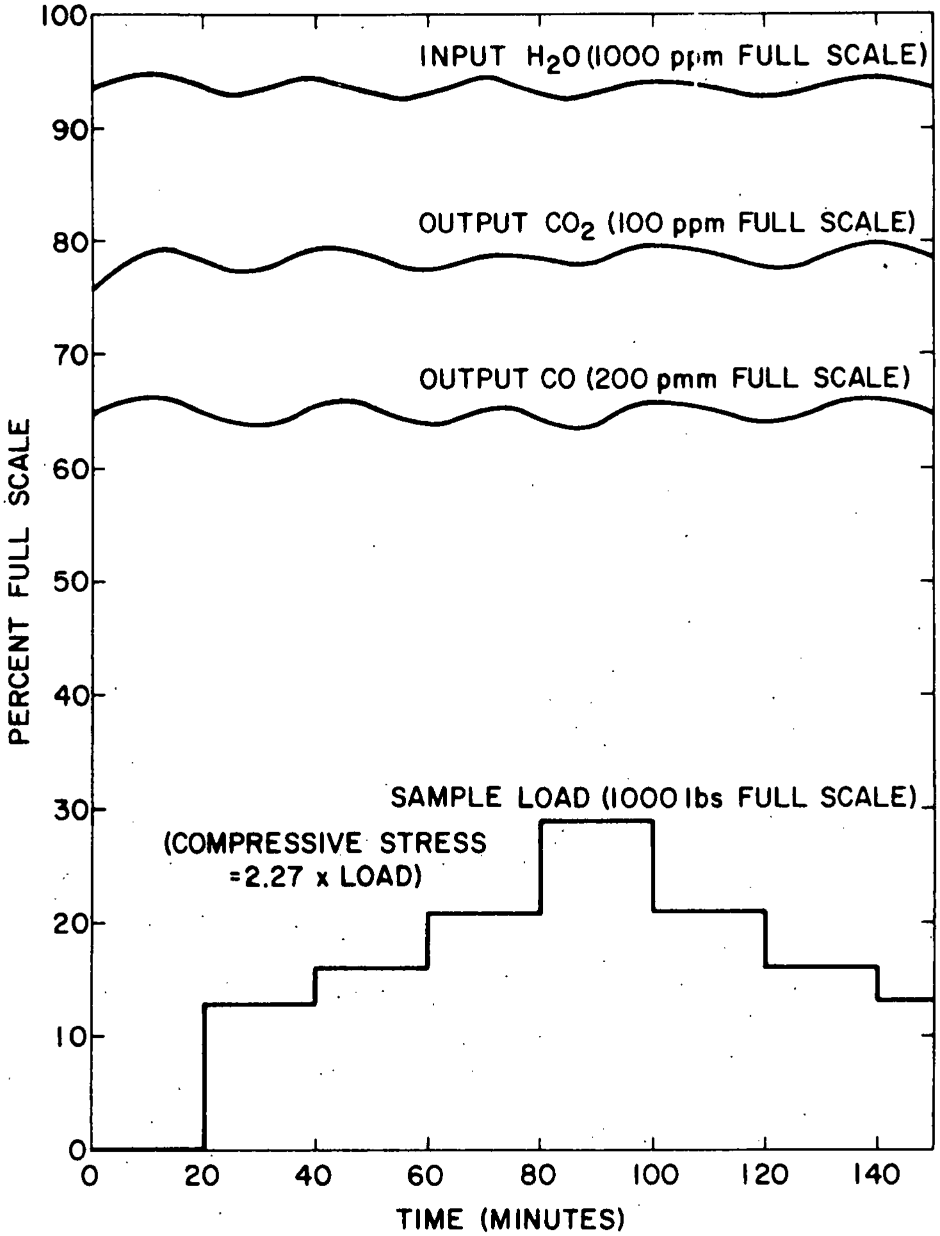


Figure 1. Typical data output for Stackpole 2020 graphite oxidized in helium containing 930 p.p.m. H_2O under different compressive loads.

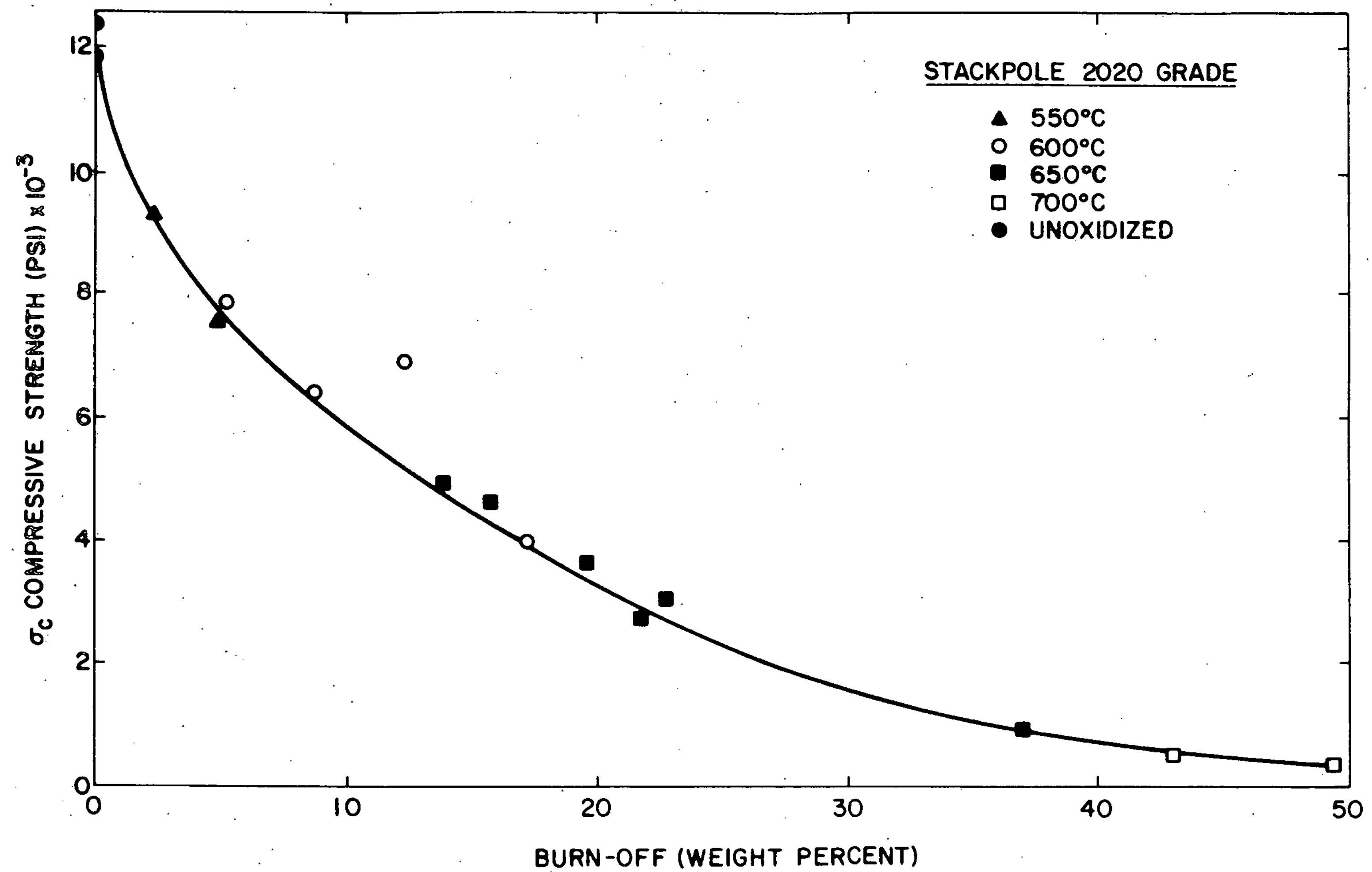


Figure 2. Compressive strength of Stackpole 2020 graphite as a function of burn-off in air.

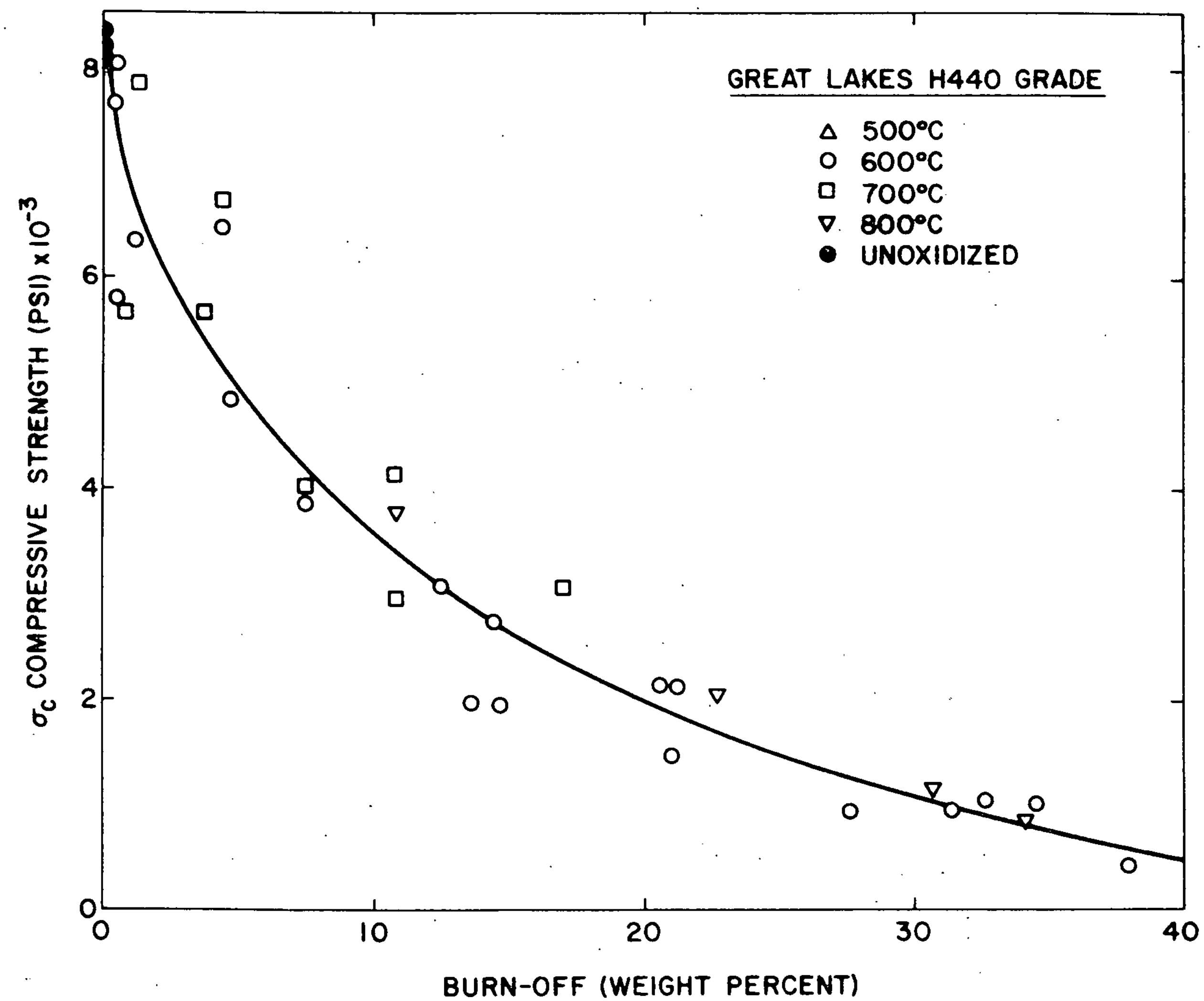
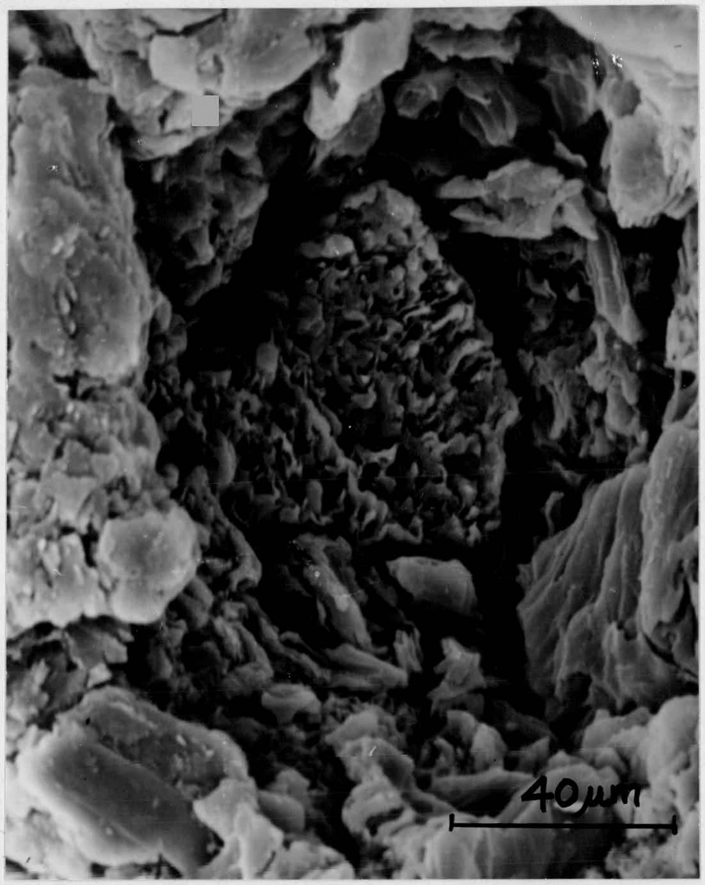
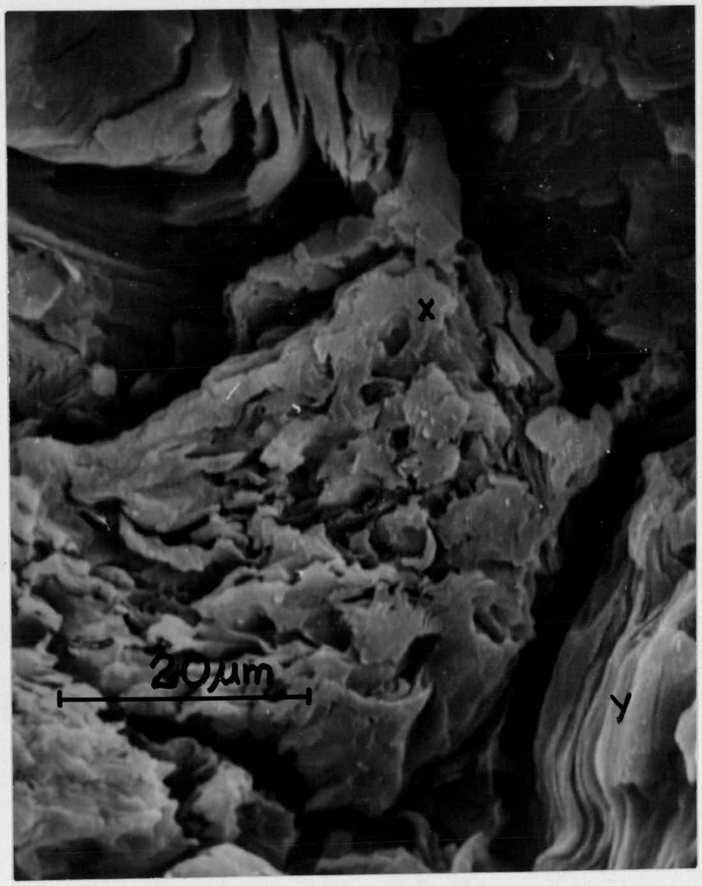


Figure 3. Compressive strength of Great Lakes H440 graphite as a function of burn-off in air.



(a)

(b)



(c)

Figure 4. H440 graphite oxidized to 14% burn-off.

(a) area near edge of specimen showing binder surrounded by filler.
(b) higher mag. of binder in (a) showing large number of reaction sites.
(c) binder and filler half way to centre of specimen. Note reactive sites in binder at (x) and smooth edge of reacted filler particle at (y)

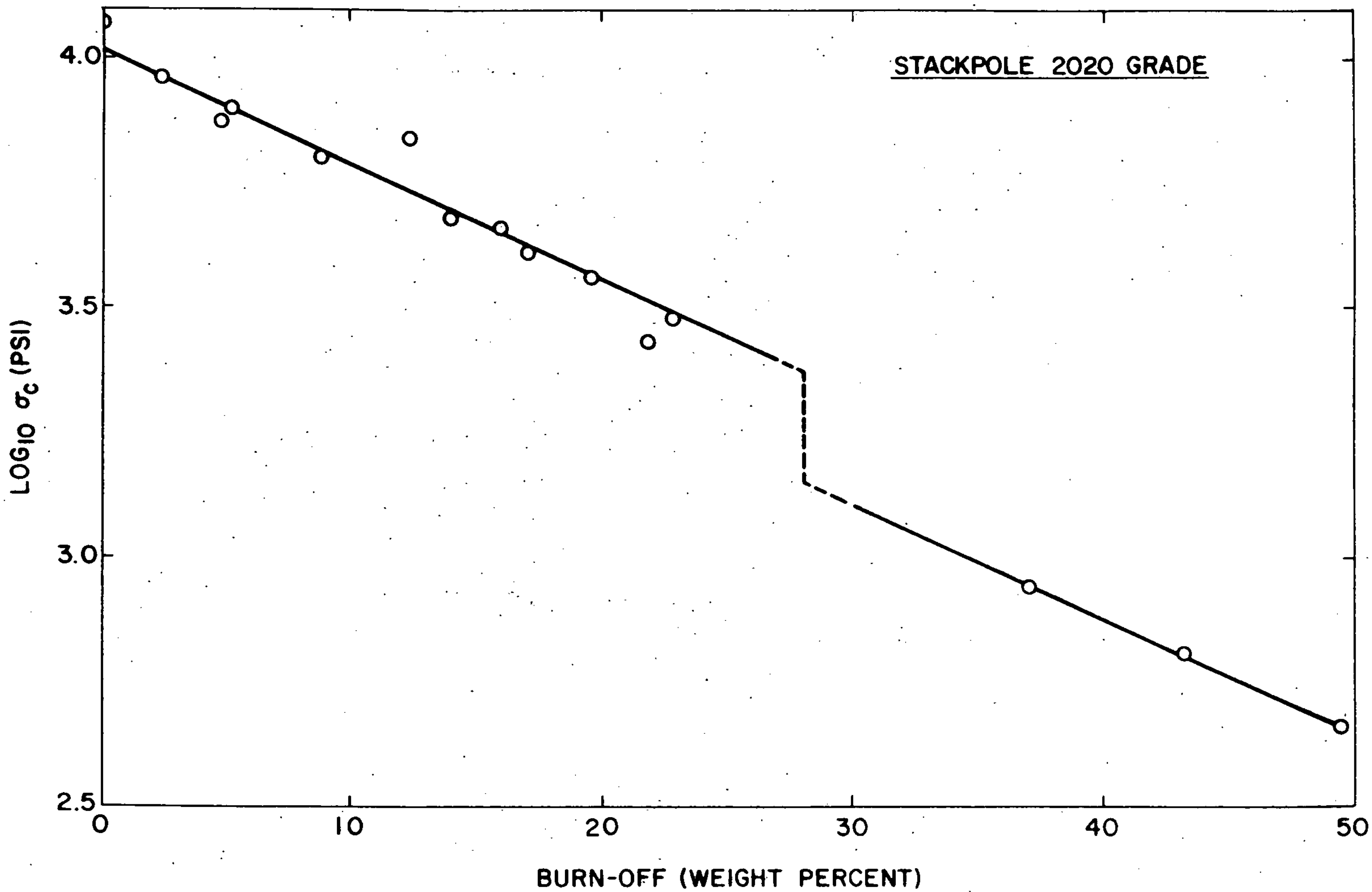


Figure 5. Logarithm of compressive strength of Stackpole 2020 graphite as a function of burn-off in air.

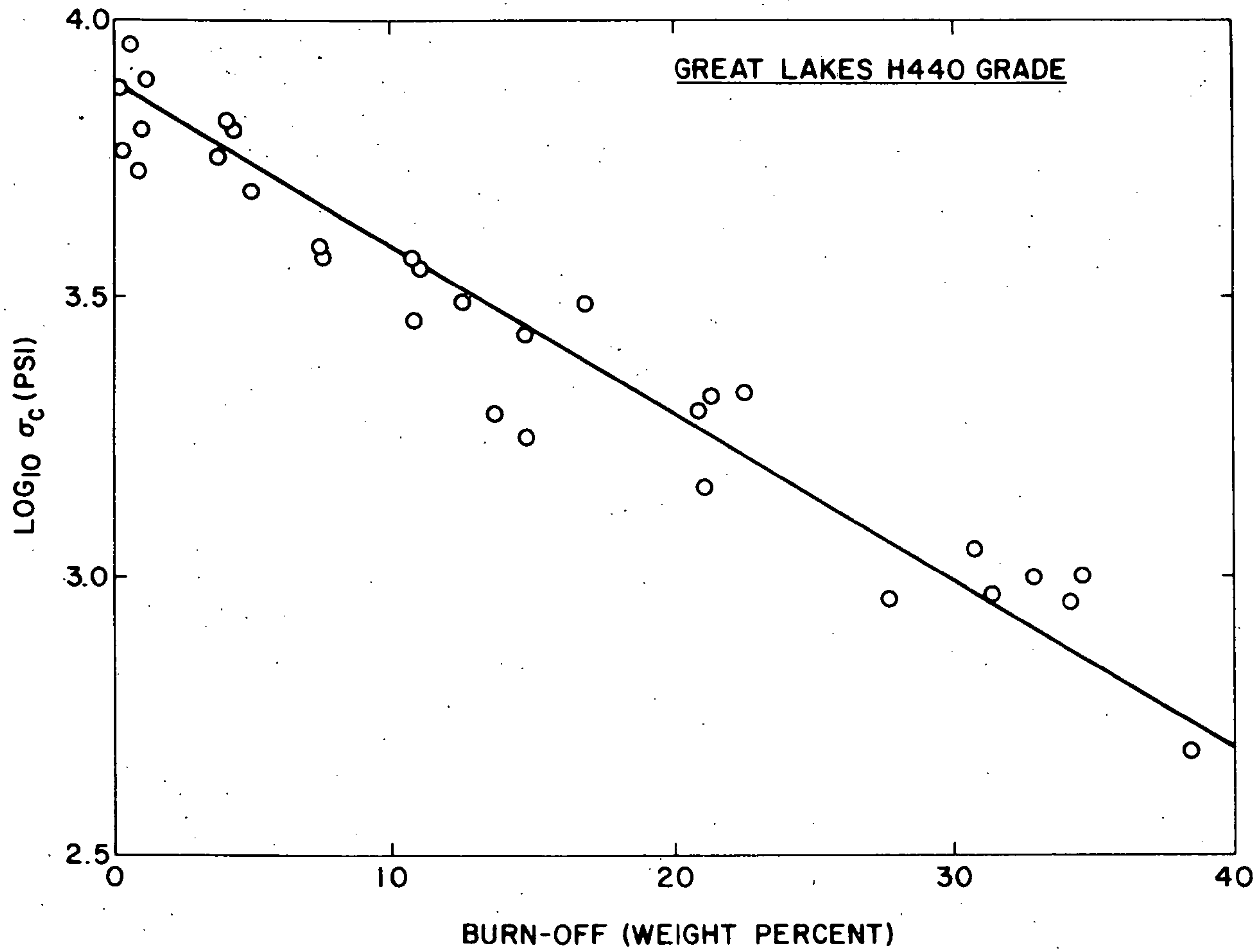


Figure 6. Logarithm of compressive strength of Great Lakes H440 graphite as a function of burn-off in air.

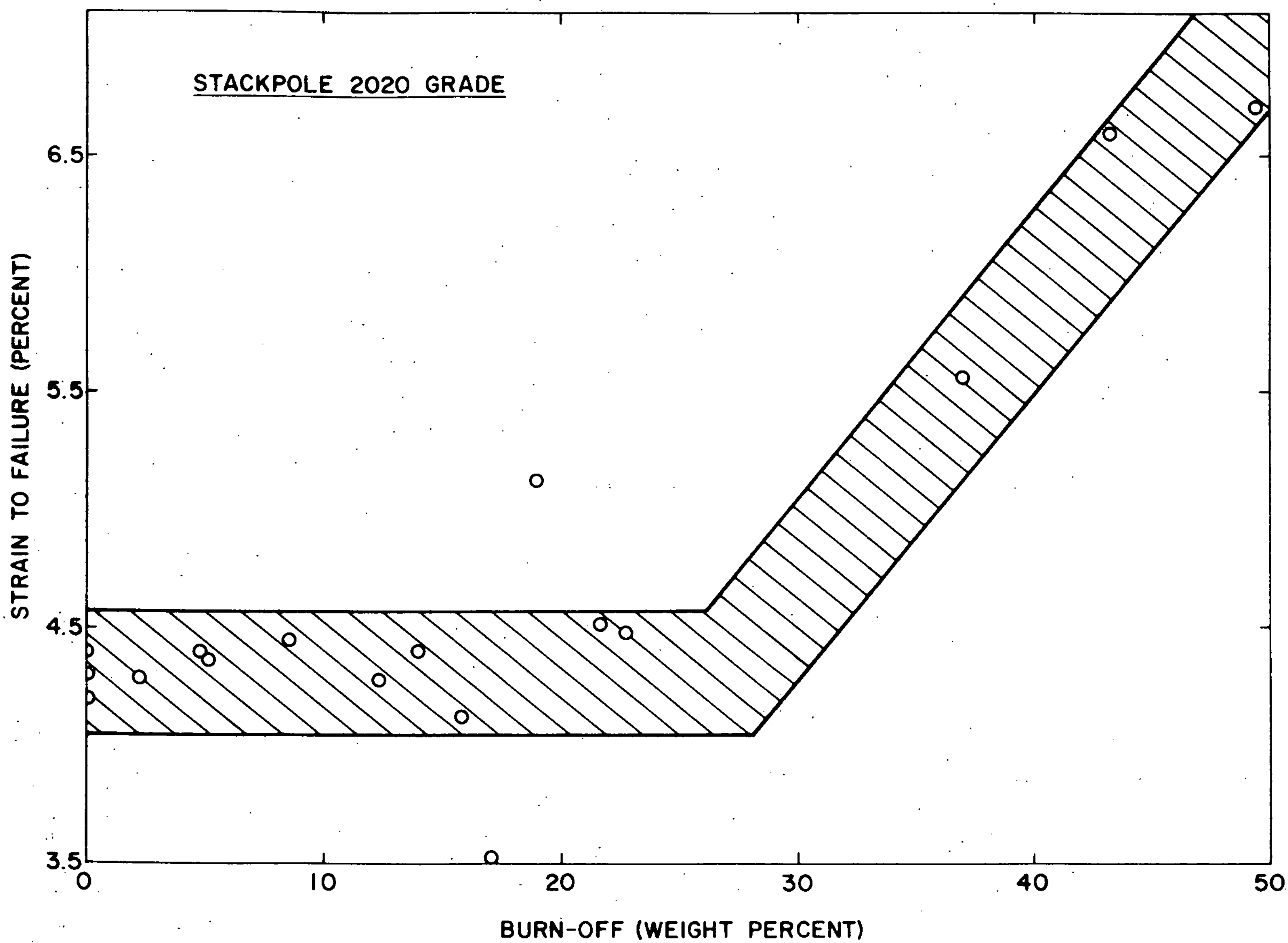


Figure 7. Strain to failure versus burn-off in air for Stackpole 2020 graphite.

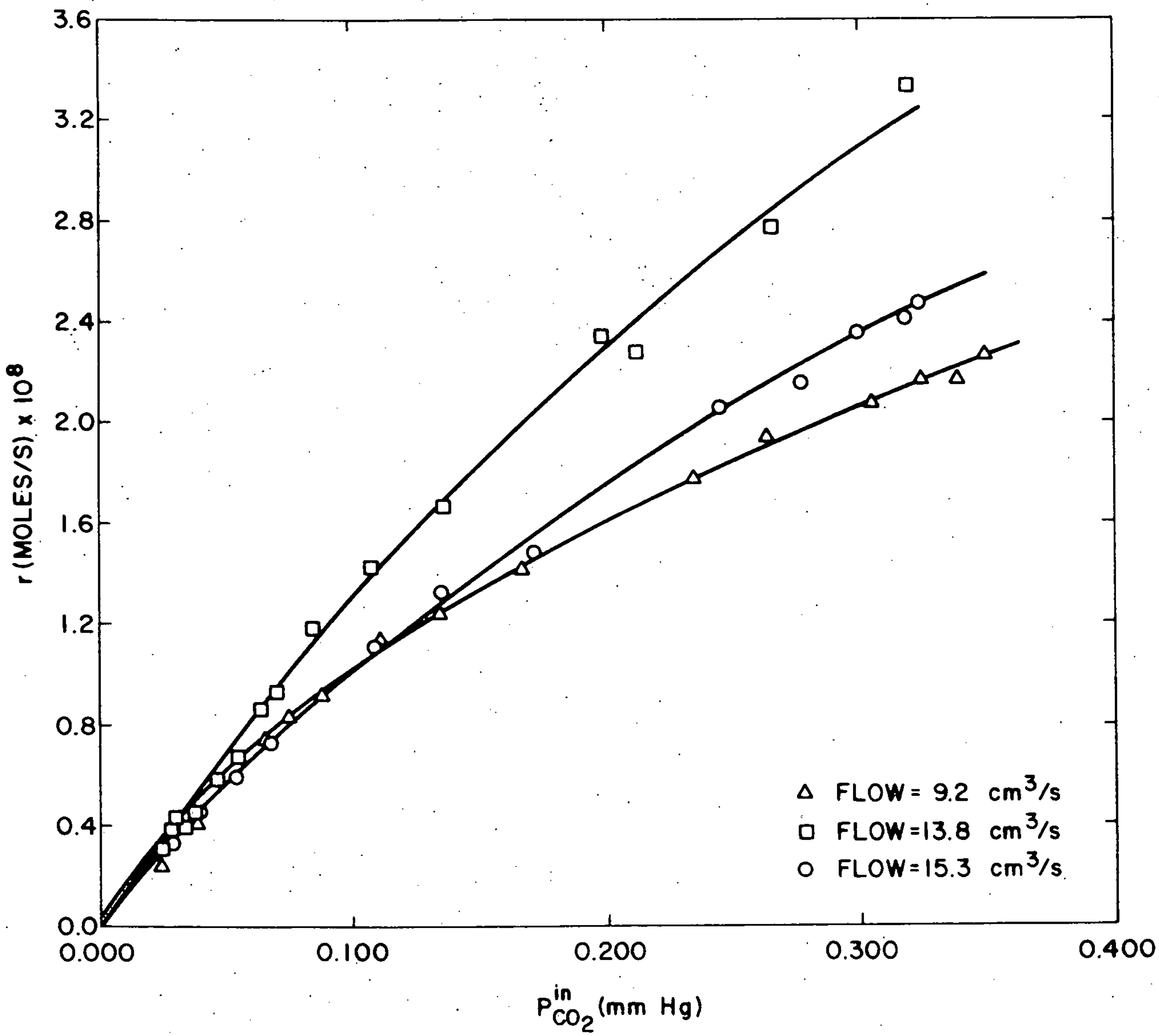


Figure 8. Reaction rate of Stackpole 2020 graphite versus partial pressure of CO_2 in the inlet gas at 893°C for different flow rates.

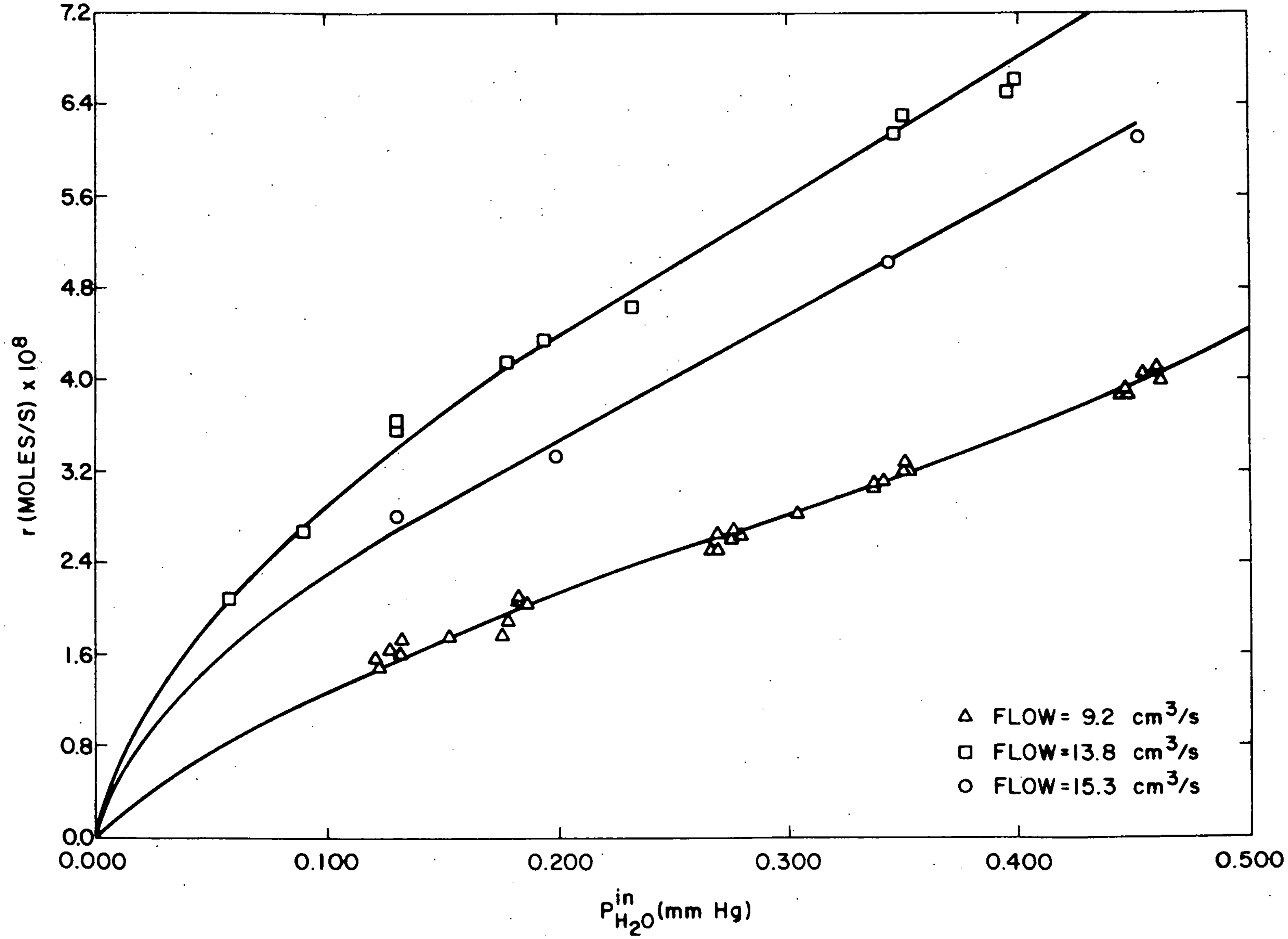


Figure 9. Reaction rate of Stackpole 2020 graphite versus partial pressure of H_2O in the inlet gas at 893°C for different flow rates.

HOCHTEMPERATUR-REAKTORBAU GMBH

HRB

Sitz der Gesellschaft
5000 Köln, Zeppelinstraße 15
Techn. und kaufm. Abteilungen
6800 Mannheim 1, Gottlieb-Daimler-Str. 8
Postfach 5360
Versuchsabteilung
5170 Jülich, Kernforschungsanlage
Postfach 2080
Baustellenleitung
4701 Uentrop, Industriestraße
Kernkraftwerk

Dr. Peter Thrower
Department of Materials Science
The Pennsylvania State University
University Park

Pennsylvania 16802

U.S.A.

Ort/Datum Mannheim, Oct.6, 1976

Bearbeiter Dr.Kubaschewski

Durchwahl 0621-451-489

Ihre Zeichen	Ihre Nachricht vom	Unsere Nachricht vom	Unsere Zeichen (In Antwort bitte wiederholen)
-	-	-	771-107.14 Dr.Kub/fb

Dear Dr. Thrower,

we and a gentleman from the nuclear licensing authority were hoping to meet you at the Carbon Conference in Baden-Baden and to listen to your presentation about graphite corrosion under stress.

In the meantime we have rebuilt our apparatus for such measurements and Karcher and Krefeld have sent us a piece of their graphite on which they claimed to have found a sixfold enhancement of the corrosion rate when stress was applied. So far, the first results obtained in our lab on this graphite haven't shown the slightest stress effect under the following conditions:

temperature	800 and 1000 ^{o}C
H_2O partial press.	a) 0.01 bar b) 0.001 bar
H_2 partial press	a) - b) 0.01 bar
sample geometry	8 mm diam., 75 mm long + screw connections to ceramic grips
graphite sorts examined	1) not very isotrope, extruded pitch coke; ash content $\leq$ 500 ppm 2) extruded gilsonite; ash content $\leq$ 600 ppm 3) Karcher's graphite
binder of graphites examined	for 1) and 2) coal tar pitch

- 2 -

HRB

Blatt 2 zu Brief vom Oct. 6. 1976 Zeichen 771-107.14 Dr.Kub/fb

an Dr. Peter Thrower, Department of Materials Science
The Pennsylvania State University, Pennsylvania 16802

Now the licensing authority wants us again to explain the contradicting measurements and there fore we would be very grateful to you if you would write us shortly about your first results.

Yours sincerely

i.V. [signature] i.A. [signature]

University of Bath

Claverton Down
Bath BA2 7AY

Telephone Bath 6941
Telex 449097

School of
Materials Science

Professor Bryan Harris

Dr P A Thrower
The Pennsylvania State University
College of Earth and Mineral Sciences
101 Mineral Industries Building
University Park
Pennsylvania 16802
U S A

BMcE/akh

4th August 1976

Dear Dr Thrower

I would be most interested to have details of the work that you have done on the effects of stress on graphite corrosion. I was looking forward to hearing your contribution on this subject to the Carbon 76 meeting in Germany was disappointed to learn that you were unable to be present. We have been considering starting some work on effects of stress on graphite corrosion here in Bath in collaboration with Dr C J Wood's group at CEGB Berkeley Nuclear Laboratories. We would therefore appreciate any details you may have of your work on stress corrosion on graphite.

Yours sincerely

Brian McEnaney

Dr Brian McEnaney