HW-23720

**Cover Sheet for a Hanford
Historical Document
Released for Public Availability**

Released 1994

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

**RECEIVED
DEC 13 1994
OSTI**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DECLASSIFIED

RECORD CENTER FILE

AEC RESEARCH AND DEVELOPMENT REPORT

HW-23720

Technology - Hanford Processes
Special Distribution

This document consists of 27
pages. Copy No. 44 of
74 copies. Series A
FIG. 4.5.6
Plus 3 unclassified attachments

COPY 1 OF 1, SERIES MA

WARNING - PRELIMINARY REPORT
THIS REPORT CONTAINS INFORMATION OF
A PRELIMINARY NATURE AND IS PREPARED
PRIMARILY FOR THE USE OF PERSONNEL WHO WORKS
TECHNICAL SECTION. THIS RE-
PORT IS SUBJECT TO REVISION ON FURTHER
CHECKING OR COLLECTION OF ADDITIONAL DATA.

TECHNICAL ACTIVITIES REPORT

GRAPHITE STUDIES GROUP

Classification Cancelled and Changed To

DECLASSIFIED

By Authority of CG-PR-2

C H HANAGER 3-23-92

By T J KEATON 6-22-94

Verified By PM Eick 6-22-94

By

L. P. Bupp
Pile Engineering Sub-Unit
Pile Technology Unit

RECEIVED

JUN 19 1956

300 AREA
CLASSIFIED FILES

March 6, 1952

This document is classified
in accordance with the provisions of the Atomic Energy Act
or the disclosure of its contents to the public is prohibited.

NUCLEONICS DIVISION
RICHLAND, WASHINGTON

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DECLASSIFIED

REFERENCE COPY

DECLASSIFIED

-2-

HW-23720

Technology - Hanford Processes

INTERNAL DISTRIBUTION

1. O. H. Greager
2. R. H. Beaton
3. W. K. Woods
4. V. D. Nixon - R. T. Jaske
5. E. P. Lee - J. H. Warren
6. R. O. Mehann
7. T. W. Hauff
8. G. E. McCullough
9. W. R. Lewis - J. A. Ayres
10. P. H. Reinker
11. W. K. Alexander
12. M. W. Carbon
13. R. M. Fryar
14. P. F. Gast
15. W. J. Ozeroff - A. B. Carson
16. R. L. Dickeman
17. G. E. Duvall
18. F. E. Kruesi
19. D. E. Davenport
20. E. B. Montgomery
21. E. C. Wood
22. H. L. Henry
23. J. C. Chatlen
24. H. F. Zuhr - R. A. Rohrbacher
25. R. Ward - W. T. Kattner
26. H. L. Mars - W. L. Schalliol
27. L. D. Turner
28. O. J. Wick
29. E. C. Pitzer
30. D. H. Gurtiss - E. M. Carr
31. B. B. Lavett - J. C. Bellinger
32. H. H. Burton - C. N. Spalaris
33. J. M. Wright - E. E. Woodley
34. J. F. Muzio - J. M. Davidson
35. D. M. Knott
36. K. J. Tauer - A. M. Corners
37. W. C. Riley
38. J. R. Townsend
39. H. H. Greenfield
40. L. P. Bupp
41. 700 File
42. 300 File
43. Pink Copy
44. Yellow Copy

DECLASSIFIED

DECLASSIFIED

-3-

HW-23720

Technology - Hanford Processes

EXTERNAL DISTRIBUTION

45. Argonne National Laboratory, Attn: O. C. Simpson
46 - 48. Atomic Energy Commission, Washington
49. Atomic Energy Commission, Washington, Attn: J. F. White
50. Battelle Memorial Institute, Attn: H. Z. Schofield
51. Brookhaven National Laboratory, Attn: D. H. Gurinsky
52. Chicago Patent Group
53 - 56. duPont Company
57. Hanford Operations Office
58. Hanford Operations Office for F. Seitz, University of Illinois
59 - 60. Knolls Atomic Power Laboratory
61. Knolls Atomic Power Laboratory, Attn: H. Hurwitz
62. Knolls Atomic Power Laboratory, Attn: J. P. Howe
63. Knolls Atomic Power Laboratory, Attn: K. H. Kingdon
64. Knolls Atomic Power Laboratory, Attn: C. Manna
65. North American Aviation, Inc., Attn: C. Starr
66. North American Aviation, Inc., Attn: S. Siegel
67. Patent Branch, Washington
68. Savannah River Operations Office
69 - 73. Technical Information Service, Oak Ridge
74. University of California Radiation Laboratory, Attn: R. H. Ball

DECLASSIFIED

DECLASSIFIED

-4-

HW-23720

TECHNICAL ACTIVITIES REPORT - FEBRUARY 1952

GRAPHITE STUDIES GROUP

CONTENTS

SUMMARY AND DISCUSSION.....	5
FILE GRAPHITE MONITORING	
X-Ray Studies of Pile Graphite: PT 105-477-P.....	8
Stored Energy - B Pile Graphite Stringer.....	11
GRAPHITE BURNOUT AND CHEMICAL STUDIES	
Graphite-Carbon Dioxide Reaction.....	11
F Pile Burnout Samples: PT 105-391-P.....	13
A Proposed In-Pile Experiment.....	13
Graphite-Carbon Dioxide-Carbon Monoxide Kinetics.....	17
High Temperature Burnout.....	17
In-Pile Controlled Atmosphere Experiment: Project C-410.....	18
GRAPHITE PHYSICAL PROPERTIES STUDIES	
X-Ray Diffraction Studies.....	18
Dependence of Graphite Damage on Neutron Energies.....	19
Surface Studies.....	20
Stored Energy: PT 105-403-P.....	20
Heat Generation in Graphite.....	22
Thermal Conductivity Measurements.....	22
CONTROLLED TEMPERATURE EXPOSURE: PT 105-403-P.....	23
THERMAL CONDUCTIVITY OF GASES.....	24
DAMAGE MECHANISM STUDY.....	24
SPECIAL EXPOSURES: PT 105-269-P.....	24
EXPERIMENTAL GRAPHITE PROGRAM	
The TS Graphite Program.....	25
Experimental Graphites from BMI.....	25
Physical Property Correlations.....	27

DECLASSIFIED

DECLASSIFIED

-5-

HW-23720

SUMMARY AND DISCUSSION

The crystal expansion of graphite samples removed from a process tube channel in the central region of the D Pile indicates some recovery in graphite damage over the last year and a half. The trends in the damage profile shown by these data are similar to those observed recently for the B and F Piles. Principal recovery in the year and a half period since the last sampling has been in the fringe region, two to four feet in from the reflector graphite. Bore graphite in the center of the pile appears to be in a steady state of damage with very little recovery indicated. Continuing crystal expansion occurs in the tube blocks in the extreme fringe zone, between the reflector and two feet in from the reflector.

Two process tube channels in a lower corner of the F Pile were mined, and crystal expansion data from these fringe locations have a pattern similar to fringe graphite damage profiles observed at the H Pile. Tube bore graphite from a process tube channel two lattice units in from the edge of the active zone of the pile showed comparable crystal damage all along its length. The second channel, six lattice units in from the pile edge, showed less damage in the center of the channel in spite of considerably greater exposure. The fringe regions of this latter channel showed the greatest damage with the overall profile of the channel being symmetrical. This double hump in damage is characteristic of central process channel graphite conditions; however, usually the downstream damage is less than damage near the front face because of warmer temperatures in the rear of the pile. The reason for the symmetrical damage contour in this case is not known, but may be caused by unsymmetrical flux in this region of the pile.

The total stored energy of samples from a stringer of graphite removed from the C test hole at the B Pile shows a damage profile similar to X-ray crystal expansion and thermal conductivity data collected earlier. The maximum stored energy of these samples, which are representative of filler block conditions, was reported to be 138 cal/gm for a position about one foot into the active zone of the pile from the far side reflector. The total stored energy in the center of the pile was 100 cal/gm. After receiving a 1000°C thermal anneal, a similar set of samples had less than 15 cal/gm total stored energy remaining. These data indicate that about 90 percent of the damage along the stringer has a low activation energy of annealing. This would be expected for samples in the pile fringe where the exposures are low and the temperature is also low, but it is surprising to find such a large amount of low activation energy damage in the central region where exposures have been great and the temperature has been hot -- of the order of 350°C. These data were compiled for only four samples along the stringer length. More samples will be measured to confirm this information.

The rate of reaction between graphite and carbon dioxide at 854°C has been determined for a static system containing an initial pressure of 0.5 atmosphere. Previous experiments of a similar nature have been completed for 903°C and 955°C. For the lower two temperature runs, the initial reaction rate appears to be second order with respect to the carbon dioxide pressure. Initial reaction rates at 955°C were too rapid to measure. An activation energy based only on these two temperatures was found to be 52 Kcal per gram mole, compared with 76 Kcal per gram mole reported earlier from studies utilizing a flow system. This

DECLASSIFIED

DECLASSIFIED

-6-

HW-23720

discrepancy will be examined more closely as more data become available. In all three cases, the reaction shifts to follow a first order expression as moderate amounts of carbon monoxide forms in the system.

Apparatus utilizing a flow system has been modified to obtain the rate of reaction between reactor grade graphite and a mixture containing about 3.5 percent carbon monoxide in a carbon dioxide atmosphere. These data at several temperatures will augment the studies mentioned above and will show the effects of small amounts of carbon monoxide on the reaction rate and activation energy of a system similar to the pile gas. This study is in progress.

Exposure conditions for the last series of graphite specimens, charged as part of the F Pile burnout production test, have been very good. In both process tube locations containing the previously weighed graphite samples, the temperatures of central specimens have been between 420°C and 450°C for a period of about three weeks. In view of this desirable history, the samples exposed to the pile atmosphere will be discharged as soon as possible. The remaining specimens, which are being exposed under several controlled atmospheres, will be discharged at the following shutdown.

A heater assembly, designed to maintain graphite specimens at controlled temperatures as high as 550°C, has been assembled and tested in the laboratory under simulated pile conditions. Following successful operation for a period of about ten days, the entire assembly has been disassembled for study. A production test will be initiated shortly to install a similar heater in a process tube channel to obtain burnout data in the pile atmosphere at higher temperatures.

A special goniometer has been constructed to complement existing X-ray equipment and allow the crystal orientation of various manufactured graphites to be obtained by measurement of the intensity of reflected X-rays. The method is independent of the absorption coefficient of graphite, and should allow rapid evaluation of orientation.

Theoretical studies relating the intensity of various X-ray reflections from graphite, with the area of the reflecting atomic planes in crystallites, has indicated that the standard expression for angular dependence may not apply for most reactor grade graphites. Studies will continue in an effort to place relative intensity measurements on a more significant basis and relate such observations with structural changes in irradiated graphite.

Careful studies of the surface characteristics of two virgin KC graphite specimens have been completed following outgassing procedures at 500°C and 1000°C. The samples were placed in quartz ampules, outgassed thoroughly at the same respective temperatures, and sealed in high vacuum. Irradiation of these and similar samples are planned as soon as test hole space is available. This experiment is designed to obtain the effect of irradiation on the surface characteristics of graphites and also to explore graphite irradiation damage in the absence of a gas atmosphere.

The stored energy spectra for graphite samples exposed for 193 MD/CT, equivalent cold test hole exposure, at average temperatures of 111°C, 139°C, and 164°C, has been determined for annealing temperatures up to 600°C. The total stored energy

DECLASSIFIED

DECLASSIFIED

HW-23720

-7-

released during annealing was 25, 16, and 10 calories per gram, respectively. A high rate of release of energy near 250°C annealing temperature was noted for the sample exposed in the pile at 111°C. This behavior is similar to the stored energy spectra of graphites exposed in a cold test hole. The rate of heat energy released near 250°C for the sample exposed in the pile at 139°C was materially less and the rate of release of heat in this region of annealing temperature was virtually zero for the sample exposed in the pile at 164°C. These data agree qualitatively with other annealing studies which indicate that the effective in-pile temperature is much greater than the observed temperature as far as it affects the properties of graphite.

Calculations have been made to establish the feasibility of an in-pile experiment to determine the amount of heat generated in graphite during pile exposure. A system comprised of a graphite cylinder with thermocouples to measure radial temperature differentials appears to have promise. Principal difficulties with this system would be changes in the thermal conductivity of the graphite with exposure and the dependability of thermocouples in the pile. Studies are being continued.

Graphite samples, exposed for about 500 MD/CT equivalent cold test hole exposure at four temperature intervals between 100°C and 250°C, have been discharged for property measurements. Simultaneous with the discharge of these series II samples, a similar facility containing series IV samples was charged and the controlling temperature set at 135°C. The other heaters reached initial equilibrium at 115°C, 90°C, and 85°C. Series III samples and heaters are in the instrument shop being modified so that it will be possible to control each temperature individually.

Irradiation damage studies on special graphites made at the Battelle Memorial Institute have begun. The first series of irradiations contain samples of resin bonded graphites having two filler particle sizes and two graphitizing temperatures. For each set of similar samples, the thermal conductivity has been shown to be twice as great for graphitization at about 2500°C as at about 1400°C.

The casings of special TS graphite scheduled for test hole irradiation have not as yet been charged because of adverse conditions at the DR Pile D Hole. The loading is scheduled for early March and in the meantime the capsule and papoose irradiations are continuing.

DECLASSIFIED

DECLASSIFIED

-8-

HW-23720

FILE GRAPHITE MONITORING

X-Ray Studies of Pile Graphite - JR Townsend, CA Lund

Tubes 0284-F and 1290-F were mined on 12/16/51 during a shutdown caused by tubes in F Pile which had been leaking water. Data from X-ray diffraction studies are shown in Figure 1. All data are from powder samples except for three bore ends of cores from channel 0284 indicated in the figure. Tube 2167-F, a more central tube mined 12/5/52, is shown for comparison.

Tube channel 0284-F has a total exposure since startup of 125 MWD or 1400 MD/CT in the central region -- all of it as a normal metal tube. This exposure compares between tubes 2766-H and 2970-H reported in the December Technical Activities Report⁽¹⁾. A pronounced shoulder toward high angles of diffraction in both the 10 ft. and 12 ft. samples agree with line shapes from the H Pile traverses. In the central portions, however, 0284-F samples show rounded and symmetrical peaks as opposed to the double peaks found in the central portions of 2970-H. Note the three bore ends of cores from 0284-F are appreciably lower in crystallite expansion than are the powders. This may arise from the small amount of bowing expected in this tube, and hence the process tube would be on the bottom of the process tube channel. Hence, the cores would be taken from the hottest region of the channel and thus have a reduced crystallite expansion.

Tube 1290-F has a tube exposure of 275 MWD or a central specific exposure of 3080 MD/CT. All diffraction peaks were well rounded in shape. The crystallite expansion near 32 feet is very similar to that around the 10-foot region. This is quite contrary to the usual situation as illustrated by the 2167-F traverse in the same Figure. It strongly suggests a very small temperature rise across the tube, thus making both temperature and flux conditions similar. This, however, is not the case, as a number of temperature maps showed 1290-F to have outlet temperatures very similar to central zone tubes. The generally lower flux in this near fringe tube would lead to less heat generation in the graphite, and hence to a lower bore graphite temperature in both front and rear regions. It may be the tube water rise is less effective in determining bore graphite damage under those conditions than in more centralized tubes. The symmetrical form of this traverse is, in general, difficult to understand. Data from other near fringe tubes would be desirable to determine whether present data were typical.

Tube 1585-D was mined on December 31, 1951, with a tube exposure of 441 MWD or a specific exposure of 4940 MD/CT, as part of the regular monitoring program. Its crystallite expansion profile is shown in Figure 2, along with earlier data available from D Pile. In the 11 to 13-foot region, annealing is continuing, while near 9 feet, crystallite damage appears to continue building up. The

(1) "Technical Activities Report, Graphite Studies Group, December 1951," HW-23169.

DECLASSIFIED

DECLASSIFIED

-9-

HM-23720

FIGURE 1

DECLASSIFIED

FIGURE 2

DECLASSIFIED

-11-

HW-23720

double peak, apparently due to a mixture in the mined sample, does not appear in the 1585-D 10-foot sample, though this may be due to increased peak widths resulting in a merging of the double peaks.

Stored Energy - B Pile Graphite Stringer - JC Ballinger

Preliminary results have been obtained from the National Bureau of Standards on samples taken from the C test hole stringer at B Pile. The samples studied were selected from four positions along the stringer. These positions were previously determined from studies of crystal lattice damage⁽²⁾ and thermal conductivity measurements,⁽³⁾ to provide as complete and accurate a picture of the filler layer condition as possible. Prior to shipment of the samples, a portion of each was annealed at 1000°C to provide information on the amount of energy remaining above this temperature. A comparison of the results is given in Figure 3.

The total stored energy gradient along the stringer agrees very closely with the crystal lattice damage gradient.⁽²⁾ A very rapid increase in energy content is observed across the innermost portion of the reflector, rising to a maximum of 138 cal/gm at approximately one foot from its inside surface. From there it tapers off to about 100 cal/gm at the center of the pile. It may be noted that the 1000°C annealing removes about 90 percent of the total stored energy. In addition, the energy remaining above 1000°C appears to be very uniform throughout the pile, dropping off in the fringe zone at the same point as the total stored energy.

Included in the same figure, for comparison, is the total stored energy gradient for the A test hole filler layer at D Pile. The greater amount of stored energy here is undoubtedly the result of higher total exposure combined with the fact that the D Pile has operated for a shorter period of time at higher temperatures.⁽²⁾

GRAPHITE BURNOUT AND CHEMICAL STUDIES

Graphite-Carbon Dioxide Reaction - JM Wright, RE Woodley

One-fourth of the month was spent at Downey and Berkeley, California, discussing with the North American Group their cyclotron irradiations and our proposed irradiations. A trip report has been written on this visit and will be documented soon.

A third run has been made on the carbon dioxide-graphite reaction kinetics study. The same apparatus and static system described in HW-22891⁽⁴⁾ was used for this

-
- (2) "Technical Activities Report, Physical Chemistry Group, February 1951," HW-20494.
 - (3) "Technical Activities Report, Graphite Studies Group, March 1951," HW-20799.
 - (4) "Technical Activities Report, Graphite Studies Group, November 1951," HW-22891.

DECLASSIFIED

DECLASSIFIED

FIGURE 3

DECLASSIFIED

DECLASSIFIED

-13-

HW-23720

determination. The temperature of the system was maintained at 854°C; 0.5 atmosphere of carbon dioxide was admitted into the system and the rate of the reaction followed by the increases in pressure with time. An analysis of the data shows that the rate of decrease of the pressure of carbon dioxide with time follows the same equation as was found to follow the reaction rates at the temperature 903°C and 955°C for pressures of carbon monoxide of 3.3 percent through 8 percent; pressure changes were not recorded beyond 8 percent carbon monoxide formed. This equation is:

$$\frac{dP}{dt} = \frac{-kP}{\log P^0/P}$$

in which P^0 is the initial pressure of the carbon dioxide in cm; P is the pressure of carbon dioxide in cm at any time t (min.), and k is a constant (min^{-1}).

It was also found that for the reactions run at 903°C and 854°C, the initial rate of reaction can be expressed as:

$$\frac{dP}{dt} = -bP^2$$

in which P is the pressure in cm. of carbon dioxide at any time t (minutes) and b is a constant ($\text{cm}^{-1} - \text{min}^{-1}$). The rate of reaction appears to follow this equation for the first 15 minutes of reaction in both instances; however, for the run made at 955°C this equation does not appear to be a valid expression for the initial rate.

A calculation of the initial rate constant based on just the two points at 903°C and 854°C indicates that the energy of activation is about 52 Kcal per gram mole, which is 20 Kcal lower than that reported by H. H. Burton.⁽¹⁾ These data and the plots showing the initial rate and the rate from 3-17 percent carbon monoxide formed are shown in Figures 4, 5, and 6.

Duplicate runs at the above temperatures were started; however, the quartz reaction vessel developed a leak upon removal of the thermocouple and has been under repair since that time.

F File Bur at Samples: PT 105-391-P - JM Wright, RE Woodley, HH Burton

The samples discharged at F File on January 18, 1952, have been taken to the hot shop in the 300 Area and most of the samples have been removed and weighed. A complete report of the data taken from this discharge will be given next month.

A Proposed In-Pile Experiment - JM Wright, RE Woodley

The rough draft of the production test to study in-pile radiation induced reactions, as described in HW-23145,⁽⁴⁾ has been written by John Fox of Special Irradiations. The equipment necessary for performing this production test has been received and the samples should be ready for installation by the middle of April.

DECLASSIFIED

DECLASSIFIED

DECLASSIFIED UNCLASSIFIED

-15-

HR-23720

FIGURE 5

UNCLASSIFIED

DECLASSIFIED

UNCLASSIFIED

DECLASSIFIED

FIGURE 6

UNCLASSIFIED

DECLASSIFIED

DECLASSIFIED

-17-

HW-23720

Graphite-Carbon Dioxide-Carbon Monoxide Kinetics - HH Burton

The construction of apparatus for the laboratory study of graphite oxidation rates in a CO₂-CO mixture has been completed. In trial tests the CO₂-CO proportioning apparatus yielded a mixture containing 3.5 percent CO by volume and appeared to be quite stable.

The study of one sample has been started with the intent to simultaneously determine oxidation rates in both CO₂ and CO₂-CO atmospheres at temperatures from 850°C to 1025°C in 25° increments. The CSF transverse cut sample (61-23-3, cylinder 0.426 in. diameter x 1 in. long) selected for the experiment is identical to the sample (61-23-2) used in a burnout study in CO₂ reported in HW-23169, (1) "December Technical Activities Report, Graphite Studies Group." Reaction rates in CO₂ are measured by the analysis of CO in the effluent gas stream with the weight loss of the sample serving as a direct check on the analyses. Reaction rates in the CO₂-CO mixture are determined solely by the sample weight loss incurred during a measured time interval at a fixed temperature. The CO₂-CO mixture composition is determined for each run by withdrawing into evacuated flasks two samples from the gas stream -- one near the start and another near the completion of the run. Analysis is effected by sweeping the flask contents through a tared CO₂ absorber, a heated copper oxide column and a second tared CO₂ absorber.

Since weight changes are of prime importance in the determination with a CO₂-CO atmosphere, the sample was first brought to a constant weight by successive one-hour heatings in a helium stream at 1000°C. Some difficulty was encountered here, making it necessary to scrub the helium for water, CO₂, and O₂ before weight changes were reduced to .01 percent (.0004 gms.) between heatings. The first rate study at 850°C has been completed with the following results:

- (1) In CO₂ the sample weight loss was 0.00083 grams/gram of sample present/day.
- (2) In CO₂ + 3 percent CO the sample weight loss was 0.00017 grams/gram of sample present/day.

Sample 61-23-2 in CO₂ at 850°C oxidized at a comparable rate of 0.0012 grams per gram of sample per day. These data should not be stressed too heavily since the total weight loss of the 3.5 gram sample during the 850°C run was only 0.0005 grams. More accurate checks at higher temperatures are forthcoming.

High Temperature Burnout - DB Lovett

The heater assembly, designed to maintain graphite samples at an elevated temperature while being exposed to pile radiations and atmosphere, has been completed and tested. It was possible to maintain the inner core of the heater and the graphite samples at 550°C with a power input to the heater of 300 watts. During the test, CO₂ was maintained with a pressure differential of 1 inch of water across the heater in a process tube block. Flow rates in the neighborhood of 1 liter/min. were measured through the heater. The heater unit will be disassembled and examined before the unit to be utilized in the production test is constructed.

DECLASSIFIED

DECLASSIFIED

-18-

RW-23720

In-pile Controlled Atmosphere Experiment: Project C-410 - DM Knott

A literature survey of the reaction kinetics of charcoal and graphite, with oxygen, carbon dioxide, and steam, was continued during the month. As previously mentioned, most of the literature in this field refers to work in the temperature ranges well above 1000°C reached in commercial combustion and water gas production. The comparatively few useful articles found to date are being utilized in planning experiments to be carried out in Project C-410, the In-Pile Controlled Atmosphere Experimental Facilities.

The latest schedule for the installation of Project C-410 calls for installation of the gas analysis equipment on the X-1 level of DR Pile by February 27, and installation of the in-pile heater facility in the C Test Hole of DR Pile by April 15. The in-pile heater facility installation date represents a setback in schedule occasioned by defective heaters on the heater facility. Two short circuits were observed in the heater facility when it was received, and after opening the shell of the unit for a visual inspection, it was considered inadvisable to attempt to install the unit in the DR Pile without replacing all heaters of the facility. The Pile Applications Branch, after discussions with representatives of the Graphite Studies Group, is requesting the Project Engineering Unit to replace all resistance heaters of the in-pile heater facility before installing the unit in the DR Pile.

GRAPHITE PHYSICAL PROPERTIES STUDIESX-Ray Diffraction Studies - JR Townsend, CA Lund

a. Intensity comparisons

In order to compare intensities of various X-ray reflections in a powder photograph from a material with those calculated on the basis of atomic positions, a number of angular corrections are necessary. A study has been made of these corrections in the case of powder diffraction work in an effort to place relative intensity measurements on a more significant basis. It was found that the standard angular dependence, viz.

$$\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

where θ is the Bragg angle, was based on the assumption that the atomic planes had dimensions of the order of $10^5 \text{ \AA}$ which is seldom the case in graphite. Recent calculations, however, show that for smaller atomic planes, up to $10^4 \text{ \AA}$, the dependence on angle should be

$$\frac{1 + \cos^2 2\theta}{\cos \theta}$$

As these two expressions differ by a factor of twenty at the 002 reflection in graphite, it is apparent the discrepancy is a critical one in the

DECLASSIFIED

present work. A further result from the recent calculations is that the intensity is proportional to the square of the area of the planes when smaller than about 10^4 Å in size. Thus, a portion of the observed decrease in diffracting power of graphite when irradiated could be due to a break-up of the crystallites.

b. Photographic studies

Since the intensities of reflections other than the 002 drop off very rapidly with irradiation, an effort will be made to use powder photographs of long exposure. The microphotometer to be used for running off the photographs has been tried on a powder photograph of a virgin natural graphite and found to be very satisfactory. Samples of Kodak fine grain film have been obtained, which should help regarding resolution and photographic background.

c. Preferred orientation studies

An orientation goniometer, described by L. G. Schultz in Jour. App. Phys. 20, 1030, (1949), has been constructed and given some preliminary tests. The relative number of graphite 002 planes with various angular positions is obtained directly by measuring the intensity of the reflected X-rays for various sample positions. The ideal sample for orientation runs is a cube about $5/8$ in. on a side, but it has been found that standard .426 in. diameter samples can also be tested. The method is independent of the graphite's absorption coefficient which is of considerable help since measurement of this is complicated by small angle scattering due to the small particle size in graphite.

Dependence of Graphite Damage on Neutron Energies - JR Townsend

A recent classified report by Sidhu and Henry of Argonne National Laboratory⁽⁵⁾ has given some very interesting data on the results of irradiating graphite at around room temperature with high energy neutrons having an average energy of 3 Mev. From the data given, it is estimated the graphite received a total neutron flux in a time of 10 hours comparable to what occurs in the pile in a matter of a minute or so. The surprising thing is that this exposure appeared to be equivalent in terms of damage done to about 220 MD/CT cold test hole exposure. Thus, the high energy neutrons alone accomplished in an effective time of about 100 seconds what takes the pile about $2\frac{1}{2}$ months. If the quoted flux and other data are correct, two possibilities are present. Either the neutron spectrum in this experiment had an unusual concentration in extremely high energy neutrons, or else the graphite irradiated in the piles is being annealed almost as rapidly as it is being damaged. Taking the latter possibility as more likely, it gives the strong suggestion that high energy neutrons are ineffective in annealing and that pile annealing should be attributed to those neutrons having less than say 100 or 200 electron volts of energy.

(5) "The Proceedings of Irradiation Damage Conference at Westinghouse Atomic Power Division, March 6, 7, 1951," TID 5021.

DECLASSIFIED

These neutrons would be ineffective in causing damage since they cannot transmit the displacement energy of around 25 ev to the carbon atoms. On the other hand, they would be very effective in annealing damage as their effective "temperature" would be very large indeed. It is hoped these results can be checked by means of neutron bugs giving total fluxes of around 10^6 to 10^7 neutrons per sec. and with an appreciable fraction of these neutrons possessing energies of 5 - 9 Mev.

Surface Studies - CN Spalaris

Two samples of virgin KC graphite were prepared for the in-pile experiment proposed in last month's report. Samples #87-90 and 87-93 were outgassed, their surface characteristics determined, outgassed for a second time and finally sealed in a vacuum of 10^{-5} mm. in quartz containers.

The surface area for sample #87-93, outgassed at 500°C for four hours, was found to be $0.44 \text{ m}^2/\text{gm}$. The surface area for #87-90, outgassed at around 1000°C for one hour, was found to be $0.51 \text{ m}^2/\text{gm}$. These values agree with those previously reported for other virgin KC graphites. The value for surface area apparently does not change very much in outgassing beyond 500°C . If this is found to be true for all samples, it will be of extreme value to our experimental work since heating only around 500 to 600°C will be sufficient for most studies. The difficulties arising from high temperature outgassing will thus be eliminated.

The pore-size distribution for sample #87-90 outgassed at 1000°C is found to have about the same micropore structure as reported previously for other KC graphites. It is, however, of interest to note that the principal peak around 20 to 25 Å has expanded toward larger pore-sizes. A secondary peak at around 90 Å has appeared which may be of importance. Another secondary distribution at around 140 Å appears to be similar to the one reported before for this sample. The importance of these secondary peaks remains to be proved after the samples have been exposed to radiation. Pore-size distribution for sample #87-93 outgassed at 500°C is similar to the one reported before for sample #87-90, outgassed at 450°C . The similarity of pore distribution can be observed by the comparison of the desorption isotherms for the two samples.

A progress report is prepared to summarize the work done in surface studies of graphite and outline the program for future work.

Stored Energy: PT 105-403-P - JC Ballinger

Stored energy annealing spectra for three temperature controlled samples of CSF graphite have been obtained for annealing temperatures up to 600°C . These samples were given an exposure of 193 MD/CT in tube 1684 of B Pile and held within reasonable limits to temperatures of 111°C , 139°C , and 164°C .⁽⁶⁾ Comparison of the spectra is presented in Figure 7. The rate of rise of temperature for these studies was $9\frac{1}{2}^{\circ}\text{C}$ per minute.

(6) "Technical Activities Report, Graphite Studies Group, June 1951," HW-21562.

DECLASSIFIED

STORAGE ENERGY RELEASE - IN CAL/GM/°C

FIGURE 7

DECLASSIFIED

DECLASSIFIED

DECLASSIFIED

-22-

HW-23720

These curves represent the first step in the present stored energy spectra program by providing a preliminary relationship between temperature and energy storage under constant conditions of exposure period and graphite type. It may be observed that the 200°C to 300°C stored energy peak, which is so pronounced in cold test hole exposed samples, appears to be entirely absent in samples exposed at approximately 160°C. This effect at higher exposures will be studied in the near future. The integrated energy release for each sample is indicated directly under the curve.

Efforts are being continued to make possible satisfactory energy release curves up to 1000°C. Problems involving the high temperature properties of available insulating materials are currently under investigation.

Heat Generation in Graphite - JR Townsend

A method has been devised for measuring the heat generated per cc per second (called Q in the following) in graphite under irradiation. It consists of a graphite cylinder of outer radius a with an axial hole of radius b with a thermocouple in contact with both the inner and outer surfaces of this cylinder. By equating the heat flow from a given volume to the heat generated there, when temperature equilibrium is reached the temperature distribution is given by the differential equation $\Delta^2 T = -\frac{Q}{k}$ where k is the thermal conductivity. By making

the cylinder long compared with its diameter and using heat insulators at the ends, essentially radial flow of heat will result. Under these conditions one has a temperature difference between surfaces given by $\frac{Q}{4k}(a^2 - b^2)$. If one

takes 6 percent of the fission energy as dissipated uniformly in the pile graphite, Q is about .03 cal/cc/sec. This gives for a virgin graphite cylinder three inches in diameter, a temperature drop of about 0.45°C which should be readily measured by means of a differential thermocouple.

Since ΔT is inversely proportional to k , ΔT will increase as irradiation causes a decrease in k . If the initial thermal conductivity is known, however, our present knowledge of the change of k with exposure might be used to correct for this effect. A further possibility is to heat the entire cylinder to around 380°C at which temperature the change in k is negligibly slow. Then one could measure Q as a function of time independent of changes in k . Following this, the heater current could be lowered and the graphite thermal conductivity measured as a function of time at various temperatures.

Principal experimental difficulties seem to be mounting of thermocouples, reliability of the thermocouples under irradiation, and seeking to assure that heat flow will be radial. These factors will be investigated and an apparatus constructed in the near future.

Thermal Conductivity Measurements - EM Carr and DH Curtiss

The thermal conductivity and electrical resistivity of a number of virgin samples have been determined. The values obtained for CSF and WSF graphite

DECLASSIFIED

are summarized as follows:

Type	No. of Samples	K, cal/cm,sec,°C	R, ohm-cm
CSF	40	0.224	12.54×10^{-4}
WSF	53	0.218	11.96

Data obtained on special graphites received from Battelle Memorial Institute are summarized elsewhere in this report.

A determination of the accuracy of the equipment for measuring thermal conductivity of disc samples has shown the experimental error to be less than 10 percent. Preliminary results of this determination were reported in January Technical Activities Report.⁽⁷⁾ A number of disc samples, approximately 60 mills thick, were cut from a 4 inch sample of KC graphite previously irradiated in the C test hole stringer of B Pile. The thermal conductivity of this 4 inch sample had been measured on the standard routine measurement equipment and found to be 0.321 cal/gcm°C. Four disc samples cut successively from one end of the central 2 inches of the original sample have been measured and the results are as follows:

Sample #	K cal/gcm °C
0	0.0294
1	0.0289
3	0.0311
4	0.0325
2	broken in preparation

CONTROLLED TEMPERATURE EXPOSURE: PT 105-403-P - DB Lovett

The series II samples were discharged from tube 1684 at 100-B on February 6, 1952. These sample slugs were transferred to the underwater opening facility at 100-H where the aluminum sample containers were removed from the individual sample heaters. These containers were then transferred to 300 Area and the graphite samples were removed. These samples have been turned over to the members of the group for the specialized measurements of their physical properties.

At the time of the discharge of series II, the series IV samples were charged into 1684-B. The controlled temperature is 135°C. The other temperatures are 115°C, 90°C and 85°C.

Series III is in the instrument shop being modified so that it will be possible to control each temperature individually.

(7) "Technical Activities Report, January 1952, Graphite Studies Group," J. F. Music to File, HW-23454.

DECLASSIFIED

-24-

HW-23720

THERMAL CONDUCTIVITY OF GASES - JF Music, JM Davidson

As discussed in a previous report, (4) the end caps for the thermal conductivity cell are being sealed on by means of copper plating. The plating must be deposited in the form of small crystals to give the most effective seal. The previously used solution had two disadvantages which made plating difficult. The first was that the current density had to be low in order to prevent the plating out of basic salts and hydrous oxides. Second, the solution introduced corrosion problems. A new plating solution has been developed that gives crystals of the same size as the former solution but enables three times the current density to be used without plating out basic salts or hydrous oxides. Also, the higher current density allowed by the new solution aids in the prevention of corrosion.

It appears that the cell will be sealed by copper plate in the next few days.

Preliminary instrumentation on the specialized bath has been completed, and tests are under way to determine if the temperature is homogeneous. Also, investigation will be made to determine the response characteristics of the heater-controller.

DAMAGE MECHANISM STUDY - A Corners

The in-pile annealing apparatus design, as discussed in last month's report, has been submitted to the Pile Applications Section for approval. A production test to cover the project is being prepared. It is anticipated that some few weeks will be necessary to process the production test and procure pile test hole facilities.

SPECIAL EXPOSURES: PT 105-269-A - DH Curtiss

Samples exposed in standard receptacle slugs in tubes 3470-D and 1568-D under this production test were discharged on November 29, 1952. These samples, after subsequent decanning operations at H Pile, have been measured for physical property changes. The data obtained and exposure history are summarized as follows:

Tube 3470-D - Loaded with 7 pcs of standard HM slugs

TABLE I

RECEPTACLE SLUG EXPOSURE OF GRAPHITE

ΔT of cooling water was 10°C
Exposure - 875 MD/CT capsule

<u>Sample #</u>	<u>%ΔL</u>	<u>Ko/K</u>	<u>R/Ro</u>	<u>Co, $\bar{A}$</u>
91-95	0.41	22.2	3.17	7.00 $\pm$.01
91-125	0.44	21.6	3.03	7.01 $\pm$.01
91-66	0.34	16.1	2.91	7.00 $\pm$.01

DECLASSIFIED

Tube 1568-D - Loaded with 58 pcs of standard HM slugs

ΔT of cooling water was 61°C
Exposure 875 MD/CT capsule

<u>Sample #</u>	<u>% ΔL</u>	<u>Ko/K</u>	<u>R/Ro</u>	<u>Co, Å</u>
91-64	0.79	25.1	3.10	7.16 $\pm$.01
91-140	0.81	24.0	3.08	7.17 $\pm$.01
91-106	0.60	21.1	3.10	7.11 $\pm$.01

The samples were exposed for a period of ten months during which time inlet water temperature varied from 5°C to 22°C. A calculation of capsule exposure indicates an exposure of 87 MD/CT for tube 1568-D. The actual sample temperature was unknown but was estimated to be approximately 125°C for the samples in tube 1568 and somewhat less for those in 3470-D. It was assumed that the fast neutron flux would be the same for the samples in each tube. Thus, the values for physical expansion, thermal conductivity, and X-ray expansion do not indicate the temperature dependence of radiation damage that was expected. This could be explained by a lower exposure for tube 3470-D caused by a decrease in the fast neutron flux as a result of the loading pattern. Therefore, a substantial decrease in exposure would mask the small temperature dependence effect expected.

EXPERIMENTAL GRAPHITE PROGRAM

The TS Graphite Program - WC Riley

Adverse pile conditions at DR Pile have delayed the test hole loading of TS graphite. The loading is now scheduled for about March first.

Capsule and papoose irradiations of TS graphite were continued.

Experimental Graphites Produced at Battelle Memorial Institute - WC Riley

Physical properties of experimental graphites produced at Battelle Memorial Institute have been measured. These graphites were moulded into small bars 1 inch by 1 inch by 6 inches or 1 inch by 1 inch by 7 inches with a one inch transverse direction. A pulverized AGOT graphite filler was used with a Phenol-formaldehyde resin binder. Two different filler particle sizes and two different graphitizing temperatures were used. Papoose irradiations of transverse 1 inch samples for the purpose of determining dimensional stability have begun. Test hole irradiations will begin within a month.

Thermal Conductivity and Electrical Resistivity of Experimental Graphite - DH Curtiss, EC Carr

The samples received from Battelle Memorial Institute have been measured for thermal conductivity and electrical resistivity. Experimental results are presented in Table II. The values of both measurements varied significantly, indicating a lack of uniformity for samples of a given type. Thermal conductivity values agreed with the previously observed trend that lower

DECLASSIFIED

TABLE II

PHYSICAL PROPERTIES OF BMI EXPERIMENTAL GRAPHITES

Filler Material - AGOT Graphite

Binder Material - Phenol-Formaldehyde Resin

Thermal Coefficient of Expansion

Hanford* Designation	BMI Designation	Graphitizing Temperature	Particle Size	α Transverse $\times 10^6$ per °C	α Parallel $\times 10^6$ per °C	Orientation Ratio	Co Spacing Å
F1	33AG	2480°C	-140 mesh	3.63	2.16	1.98	6.71
E2	33G	2480°C	-50 + 140 mesh	3.83	2.60	1.55	6.72
E3	33A	1370°C	-140 mesh	3.73	2.44	1.53	6.72
E4	33	1370°C	-50 + 140 mesh	3.09	2.38	1.35	6.71

		R ₀ ohm - cm (parallel samples)	K ₀ cgs (parallel samples)
E1	33AG	15.39 x 10 ⁻⁴	.193
E2	33G	14.78 x 10 ⁻⁴	.206
E3	33A	16.76 x 10 ⁻⁴	.095
E4	33	16.29 x 10 ⁻⁴	.102

* Some BMI Designations Were Found To Duplicate Previously Employed Hanford Designations

DECLASSIFIED

DECLASSIFIED

-27-

HW-23720

conductivity is observed for graphite graphitized at lower temperatures. Values obtained for both conductivity and resistivity are in general agreement with expected values.

Thermal Expansion of Experimental Graphites - WC Riley

Thermal expansion coefficients have been determined for transverse and parallel cuts of experimental graphites received from Battelle Memorial Institute. The mean values over a temperature range of 25°C to 400°C are given in Table II.

Deviation from the average thermal expansion values was found to be greater for the transverse cuts than for the parallel cuts. The maximum deviation for transverse graphite was 1.05×10^{-6} and 0.11×10^{-6} for parallel graphite. This may be attributed to cutting samples from different bars for transverse graphite samples and from the same bar for parallel graphite samples.

Comparison has shown that the transverse BMI graphites have a thermal expansion similar to that of transverse CSF graphite, while the thermal expansion of parallel BMI graphites is appreciably higher than that of parallel CSF graphite. This was to be expected, however, if the thermal expansion values were to be in accord with the low orientation values.

Measurement of thermal expansion of the BMI experimental graphites will be continued.

Physical Property Correlations - Experimental Graphites - WC Riley

Orientation measurements appear to be similar to the ratio of the transverse thermal expansion to the parallel thermal expansion of artificial graphite. A comparison of these measurements are listed below. The graphites of Table II and TS graphite are included.

Type	Orientation	$\frac{\alpha_{\text{Transverse}}}{\alpha_{\text{Parallel}}}$
E1	1.98	1.68
E2	1.55	1.48
E3	1.53	1.53
E4	1.35	1.30
TS	2.00	1.92

This tentative correlation will be checked on other graphites.

L. P. Bupp

IN CHARGE - GRAPHITE STUDIES
PILE TECHNOLOGY UNIT
ENGINEERING DEPARTMENT

LP Bupp:md

DECLASSIFIED