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D-REACTOR GRAPHITE BURNOUT INTERIM REPORT -
IP-25A(PT-105-532-E)

By

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November 10, 1961

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D-REACTOR GRAPHITE BURNOUT INTERIM REPORT-
IP-25A(PT-105-532-E)

INTRODUCTION

Oxidation of the moderator graphite in the Hanford Reactors is of concern because a relatively small amount of oxidation will greatly decrease the compressive strength of graphite,⁽¹⁾ 10% oxidation causing a reduction in compressive strength of a factor of 2. In order to control the oxidation rate of the graphite, process standards on reactor gas atmosphere and composition and graphite temperature have been established for the purpose of limiting the rate of oxidation to a value of 2%/1000 operating days (%/KOD) or about 10% total burnoff during a nominal lifetime of the reactor. However, it is necessary to continuously monitor the oxidation of the reactors to establish whether changes in operating conditions may have affected burnout rates. Because it is difficult to directly measure the amount of oxidation in the graphite moderator, the oxidation rate is customarily monitored by measuring the weight loss on small samples which have been exposed to the atmosphere within the reactor at the ambient temperature of the moderator. It is realized that the oxidation rate of the small samples is apt to be higher than that of a large block exposed to the same atmosphere; however, in cases where it has been possible to establish a cross correlation the difference in rate between small monitoring samples and full-sized moderator blocks has been found to be only a factor of 3. For a discussion of this factor see Appendix I.

The oxidation rate of the moderator in D-Reactor has been monitored from samples placed along the length of process tube channel 3478. This work has been conducted⁽²⁻⁸⁾ under Production Test 1P-25A(PT-105-532-E).

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SUMMARY

1. Burnout-rate measurements in channel 3478 during the interval from August 8, 1960, to August 10, 1961, were very high, up to 40%/KOD.
2. From the shape of the front-to-rear burnout profile it is deduced that the oxidant was oxygen and/or water.

RESULTS AND DISCUSSION

Prior to August 8, 1960, there was no evidence from the burnout monitoring program that any excessive oxidizing condition had occurred in D-Reactor; however, samples which were in channel 3478 from August 8, 1960, to August 10, 1961, for a period of 294 operating days showed unusually high rates, as seen from the burnout profile in Figure 1. The curve reaches a maximum about one-fourth the distance from the front of the channel. Although they are not included on this curve, the weight of the last ten samples increased slightly (0.02 to 0.06%/KOD), indicating that some disproportionation of the reaction product had occurred in the cooler, downstream regions.

The location and sharpness of the peak is significant because it indicates that the oxidant was not CO₂. Normally, there is enough partial pressure of this constituent in the reactor atmosphere so that there is no depletion of the CO₂ towards the center of the stack. Thus, the burnout profile with CO₂ as the primary oxidant would show a maximum at, or slightly forward, of the moderator center line where the temperature and flux were highest. As an example of this type of curve see the burnout profile in 3066-KE shown in Figure 3.

The sharp-peaked profile shown in Figure 1 reveals: (1) the region in which oxidation proceeded at a faster rate than the Process Standard limit was from about 40" to 145" into the graphite channel; and (2) the reaction occurred

very rapidly and at relatively low temperatures. This is concluded from the very steep slope and from the location of the peak at a distance of only five feet into the stack where the graphite temperature was probably less than 580°C. The rate of the thermal CO₂-C reaction is not significant below approximately 580°C.⁽⁶⁾ Consequently, it is concluded that the oxidant was either O₂ and/or H₂O.

Mass spectrometer analyses of the reactor atmosphere for O₂ and N₂ during the period of this test are shown in Figure 4. Fifty per cent of the analyses were above the allowed O₂ limit of 0.05%, with the remainder lying between 0.02 and 0.05%. The average value for all the analyses was 0.09%. The periods during which the reactor was shutdown for two days or longer are shown⁽⁹⁾ on the figure. The concentration of nitrogen is also shown in Figure 4 since the presence of this gas is taken to be an indication of air in-leakage.

A tabulation of the volume of water collected during the time of this test appears below.

TABLE I*
Water Leak History at 105-D from August 1960 to August 1961

<u>Total H₂O Collected (gal.)</u>	<u>Collection Period</u>	<u>Location and Type of H₂O Leak</u>
537	August 1960	None
761	September	2761-Internal
327	October	None
567	November	0960-Tube; 1366-Rup.; 2582-RVS
59	December	None
0	January 1961	None
49	February	None
225	March	None
614	April	3477, 3261-Tube
270	May	2677 Tube
378	June	2595, 2762-Tube; 1488, 4376-RVS
477	July	1483, 1679, 1953, 2671 3472-Tube; 0373, 1272, 2860-RVS
1085	August	2663, 3983, 3985-Tube

*This table was furnished by E. E. Leitz, Process Standards Operation
Rup. = Rupture; RVS = Rear van Stone (flange)

From Table I the following observations are apparent concerning the total quantity of H_2O collected: (1) the driest month was January 1961, (2) the wettest was August 1961, and (3) the average amount of water collected was approximately 440 gal., typical of July 1961. A daily maximum and minimum inlet dew point for these three months is shown in Figure 5. It is seen that a dew point of $15^{\circ}F$, the limit set in Process Standard B-010, September 1, 1959, was exceeded only on the 13th and 14th during the dry month, while this dew point was exceeded about half the time during the two wet months. The average dew point for the two wet months was $-2^{\circ}F$ ($P_{H_2O} = 0.8$ mm), and $-32^{\circ}F$ ($P_{H_2O} = 0.2$ mm) for the dry month.

It is possible that the burnout rate of the monitor samples could have been influenced by water leaking directly on the samples. This could happen if tube leaks occurred which were adjacent to or slightly above channel 3478. Referring to Figure 6, it is seen that leaks in channels 3477, 3983, and 3985 may have been close enough to the test channel to influence the oxidation of the samples; however, the tube leak in 3477 occurred about 3 to 4 feet from the rear of the graphite stack. Water from the other two tube leaks may have reached the monitoring samples, but the location of the attack in the front one-fourth of the channel supports the hypothesis that the damage resulted from an oxidant in the inlet gas.

COMPARISON OF OBSERVED WITH CALCULATED OXIDATION RATES

Referring to the front-to-rear burnout profile in Figure 2, it can be seen that the curve peaks very sharply with a maximum of $\sim 50\%/KOD$ at a distance of ~ 64 inches into the graphite stack. Based upon results from the burnout samples, almost all (97%) of the oxidation occurred between 35 and 123 inches. If the approximation is made that all oxidizing gases were consumed in this region,

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it is possible to estimate the oxidation rate ^{of the moderator} in this region from the gas consumption. It will be assumed that the O_2 concentration was 0.09%, the average of all the mass spectrometer oxygen analyses for the duration of this test. Three cases will be assumed for the H_2O concentration: (1) $-32^{\circ}F$ ($P_{H_2O} = .2$ mm) for a dry period such as January 1961; (2) $-2^{\circ}F$ ($P_{H_2O} = .8$ mm) for a wet period such as July 1961; and (3) $+10^{\circ}F$ (1.6 mm) for a case in which the gas atmosphere was allowed to remain at high dewpoints. By calculating the amount of graphite removed by the two reactions, $C + H_2O = CO + H_2$ and $C + O_2 = CO_2$, during the duration of this test and comparing this value with the total amount of graphite in the area in which practically all (97%) of the oxidation occurred, the burnout rate has been estimated. The calculations are shown in Appendix II and the results are summarized in Table II.

TABLE II

Estimate of Oxidation in a Section of D-Reactor
Between August 8, 1960 and August 10, 1961

<u>Assumed Reactor Conditions</u>		<u>Estimated Burnout Rate (%/KOD)</u>	<u>Ratio of Measured Rate of Monitors to Estimated Rate</u>
<u>O_2 Concentration (%)</u>	<u>Inlet Dewpoint ($^{\circ}F$)</u>		
0.09	-32 (.2mm)	2.9	5.5
0.09	- 2 (.8mm)	4.8	3.3
0.09	+10 (1.6mm)	7.5	2.1

The average burnout rate of the small graphite monitors in this section of the channel is 16%/KOD. As shown in the table, the ratios of rates from these monitors to the estimated rates of the moderator are close to those predicted from the examples given in Appendix I.

ACKNOWLEDGMENT

Appreciation is extended to A. J. Jervis, Jr., for his preparation and weighing of the monitoring samples.

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BIBLIOGRAPHY

1. GRIGGS, B., Effect of Oxidation on Compression Strength in CS-GBF Graphite, April 1956, HW-42498.
2. WOODLEY, R. E., Production Test 105-532-E; Graphite Burnout Monitoring Program, October 1953, HW-29729 (Secret).
3. WOODLEY, R. E., Production Test 105-532-E, Supplement A, Graphite Burnout Monitoring Program, January 1954, HW-30571 (Secret).
4. WOODLEY, R. E., Graphite Burnout Interim Report on PT-105-532-E; December 1954, HW-34154 (Secret).
5. WOODLEY, R. E., Graphite Burnout Monitoring Interim Report II on Production Test IP-25-A (PT-105-532-E), August 1957, HW-52267 (Secret).
6. RYAN, B. A. and D. R. de Halas, Graphite Burnout Interim Report on IP-25-A (PT-105-532-E), March 1960, HW-62273, Rev. 2 (Secret).
7. RYAN, B. A., C-Reactor Graphite Interim Report IP-25-A (PT-105-532-E) April 5, 1961, HW-69717 (Secret).
8. FERGUSON, W. J., C-Reactor Graphite Burnout, September 7, 1961, HW-70986 (Secret).
9. DeMERS, A. E. Personal communication, _____.
10. WOODLEY, R. E., Personal communication, _____.
11. COWEN, H. C., J. B. Lewis, and E. W. Sharratt, The Rate of Oxidation of Large Blocks of Graphite in Air, Proceedings of US/UK Meeting on the Compatibility Problems of Gas-cooled Reactors, Held at ORNL February 24-26, 1960, pp. 359-373, TID-7597 (Bk. 2), Feb. 1960.

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APPENDIX I

Relationship Between Oxidation Rates of Small Samples
and Large Moderator Bars

The relationship between the oxidation rate of the small monitoring samples and the graphite stack depends on many variables, such as the temperature of oxidation, the amount of previous oxidation that has occurred, and the presence of impurities on the graphite. Thus, the factor of 3 discussed above should not be taken as a universal constant to relate burnout rate of small samples to that of the moderator; however, there are several experiments to suggest that this value is a good approximation. Three examples are cited below.

The experiment most closely related to this subject involved the exposure of six quarter-bars of CSGBF graphite, 4 x 4 x 12 in., in D test hole at C-Reactor from March 14, 1955 to April 22, 1956 (272.4 operating days). The edge of the charge started 24-1/2" beyond the center line of the stack, and the temperature of the experiment was estimated from two graphite filler-block thermocouples; 50% of the readings fell between 475-525°C. Except for the last three months of the irradiation of these quarter-bars, regular burnout monitoring samples were in channel 1960. When burnout rates from those small samples in the same vicinity as the bars were compared with the average burnout rate of the six quarter-bars, a ratio of 3 was obtained.⁽¹⁰⁾

More recently burnout rates from small monitoring samples exposed to the ambient reactor atmosphere were compared with rates from samples protected by a 3/8" wall of graphite through which the gas had to diffuse. Instead of the usual sample carriers (such as those described in HW-62273 Rev. 2, p. 12), a carrier was designed in which two of the four monitoring samples could be placed in a static-compartment which was closed by a tight-fitting, graphite screw. The other two samples were held in the vented end of the carrier in which the

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reactor gas was free to circulate through several 1/2-in. diameter transverse holes. Five of these carriers were placed in channel 3066 at KE-Reactor. The results are shown in Figure 6. It can be seen that the ratios of the burnout rate for the two types of samples in the upstream half of the channel were in the range 3 to 6.

British workers at Culcheth and Harwell have demonstrated the role of diffusion in determining reaction rates during the air oxidation of large blocks of Grade "A" graphite.⁽¹¹⁾ For this purpose, oxidation was studied as a function of specimen size by using cubes which varied in size up to 4 in. The results of the experiments for two series, one conducted at 500°C and a second at 550°C, are shown in Figure 7. It can be seen that the smallest cubes oxidized 3 to 4 times faster than the largest cubes.

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APPENDIX IICalculation of Oxidation in a Section of D-Reactor

1. Assuming one lattice unit 8.4 x 8.4 x 88 in. shown below,

Then:

$$\text{Volume of F.B.} = 4.2 \times 4.2 \times 88 = 1550 \text{ in}^3$$

$$\text{Volume of T.B.} = \text{Vol. of F.B.} - \pi (0.93)^2 \times 88 = 1550 - 239 = 1311 \text{ in}^3$$

$$\text{Volume of S.B.} = 4.2 \times 8.4 \times 88 = 3110 \text{ in}^3$$

$$\text{Total vol. of one lattice unit} = 5971 \text{ in}^3$$

$$\text{Total weight of one lattice unit} = 355 \text{ lbs. (assuming } \rho = 1.65 \text{ g/cm}^3)$$

And since there are 2004 of these lattice units in the reactor, the total amount of graphite = $355 \times 2004 = 7.11 \times 10^5$ lbs.

2. The volume of reactor gas which flowed through the core during the monitoring test, assuming flow rate is 400 cfm;

$$\text{Vol.} = \text{flow rate} \times \text{time} = 1.69 \times 10^8 \text{ ft}^3$$

3. The amount of graphite consumed by an average oxygen content of 0.09% in the reaction, $\text{C} + \text{O}_2 = \text{CO}_2$, and an inlet gas temperature of 27°C.

$$N_{\text{O}_2} = P_{\text{O}_2} \times V (\text{total}) / RT$$

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$$N_{O_2} = 1.74 \times 10^5 \text{ moles} = N_C$$

And, converting from moles of graphite to pounds,

$$Wt_C = 4.60 \times 10^3 \text{ lbs}$$

4. If it is assumed the inlet dew point was -32°F (0.2 mm) and the reaction, $C + H_2O = H_2 + CO$, occurred, then the amount of graphite consumed is

$$N_{H_2O} = 5.10 \times 10^4 \text{ moles} = N_C$$

And

$$Wt_C = 1.35 \times 10^3 \text{ lbs}$$

5. At an inlet dew point of -2°F (0.8 mm) the amount of graphite lost would be 5.40×10^3 lbs, and at an inlet dew point of $+10^\circ\text{F}$ (1.6 mm) 1.08×10^4 lbs would be oxidized.
6. Thus, if it is assumed that the reactor atmosphere contained 0.09% O_2 and either 0.2 mm, 0.8 mm, or 1.6 mm of H_2O during the 294 operating days of the test, the burnout rates of the section of graphite under consideration would have been 2.9, 4.8, or 7.5%/KOD, respectively.

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FIGURE 1

Front-To-Rear Log Profile of Burnout Rates in Channel 3478 at
D-Reactor From August 8, 1960 to August 10, 1961

FIGURE 2
Front-To-Rear Linear Profile of Burnout Rates in Channel 3478 at D-Reactor From August 8, 1960 to August 10, 1961

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FIGURE 3

Front-To-Rear Log Profile of Burnout Rates in Channel 3066 at
KE-Reactor From August 6, 1957 to February 6, 1959

FIGURE 4
Mass Spectrometer Gas Analysis for Oxygen and Nitrogen at 105-D From August 1960 to August 1961

FIGURE 5

Daily Maximum and Minimum Inlet Dewpoints AT ICS-D

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- Rupture
- X Tube Leaks
- Rear Van Stone Flange Leaks

FIGURE 6

End View of Water Leaks in 105-D From August 1960 to August 1961

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FIGURE 7

Front-To-Rear Log Profile of Burnout Rates in Channel 3066 at
KE-Reactor From June 22, 1961 to November 21, 1961

FIGURE 8

Oxidation Rate as a Function of Size
(Reproduced from Reference #11)

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