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PRODUCTION TEST IP-725

INCREASED GRAPHITE TEMPERATURE LIMIT, F REACTO

FINAL REPORT

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PRODUCTION TEST IP-725
INCREASED GRAPHITE TEMPERATURE LIMIT, F REACTOR
FINAL REPORT

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PRODUCTION TEST IP-725
INCREASED GRAPHITE TEMPERATURE LIMIT, F REACTOR
FINAL REPORT

INTRODUCTION

This report presents the results of a high graphite temperature test conducted at F Reactor from January through June, 1965.^{1, 2} Since the reactor was soon to be permanently shut down, this was believed to be a good opportunity to investigate the effect of increased graphite temperature on graphite stack oxidation with CO₂. During the first phase of the test, the graphite temperature limit was increased from 650 C to 700 C for a period of approximately 3 1/2 months. During this phase of the test the actual maximum operating graphite temperature was maintained near the 700 C limit. During the second phase of the test the temperature limit was further increased to 750 C for approximately 2 months. Unfortunately, the actual graphite operating temperature was maintained at the desired temperature level for only several weeks and thus complicated interpretation of the test results. Throughout the 6 month test period, stack oxidation was monitored with graphite samples inserted in 2 bare process tube channels and by measurement of CO (reaction product of graphite and CO₂) in the reactor gas atmosphere.

SUMMARY AND CONCLUSIONS

During the first phase of the test, the graphite temperature was increased from 650 C to 700 C by reducing the helium concentration in the reactor atmosphere from approximately 75% to approximately 50%. The helium loss rate was reduced by about a factor of 2. Stack oxidation rate, as indicated by the formation of CO in the gas atmosphere, increased by less than a factor of 2. During the second phase of the test, the graphite temperature was further increased to approximately 750 C by reducing the helium concentration to essentially 0%. The lack of direct proportionality of helium reduction with temperature increase resulted from the fact that during the second phase of the test the power level was being reduced because of increasing river temperature. Stack oxidation rate, again as indicated by the formation of CO, increased by a factor of approximately 5 as compared to the rate at 650 C. Biological shield temperatures increased from approximately 80 C prior to the test to approximately 95 C when the graphite temperature was 700 C and to 160-170 C when the graphite temperature was 750 C. Shield temperatures are, therefore, an important parameter in determining the permissible amount of helium reduction.

Oxidation of the stack graphite with CO₂ results from two mechanisms; radiation and temperature. At temperatures below approximately 650 C the oxidation rate is controlled primarily by a radiation induced reaction and is essentially proportional to radiation level. At temperatures above approximately 650 C the reaction is controlled predominantly by temperature and increases exponentially with temperature. Since both radiation and temperature are present in reactor, it would be expected that the stack oxidation rate

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with CO₂ would increase relatively uniformly with reactor power level until the graphite temperature reached approximately 650 C, at which point any further increase in temperature would result in a relatively rapid increase in oxidation rate. These expectations were borne out by this test and support the contention that to date the principle cause of oxidation with CO₂ in all reactors using a He-CO₂ atmosphere has been the result of radiation rather than graphite temperature. The data from this test suggest that even though the thermally controlled reaction mechanism makes a significant contribution to the overall stack oxidation rate, an increase in the graphite temperature limit from 650 C to 700 C would increase the stack oxidation rate with CO₂ by less than a factor of 2 and would still be within the currently accepted criteria that the graphite stack oxidation rate be no more than 2% weight loss per 1000 operating days.

DISCUSSION

A. Background

The fundamental objective of the graphite temperature limit is to prevent excessive oxidation of the graphite moderator blocks with CO₂ and water vapor in the reactor atmosphere. Laboratory tests have shown that 10 per cent uniform oxidation of graphite results in a loss in strength of approximately 50 per cent.³ This value of a strength loss of 50 per cent has been arbitrarily established as the limit to graphite oxidation over the lifetime of the reactor stack. This limit has been further arbitrarily interpreted as an oxidation rate of not more than two per cent per thousand days of reactor operation (2%/KOD). At this rate limit, the reactor stack could be operated for 15-20 years before the graphite strength was reduced 50 per cent.⁴

As with any chemical reaction, the rate of reaction of graphite with oxygen, CO₂ and water vapor increases with increasing temperature. While all three oxidants are present to some degree in the reactor gas system, the reaction between graphite and oxygen at the present temperatures is so rapid that all practical precautions must be taken to exclude it from the gas system. In addition, reaction with water vapor is sufficiently low at present temperatures and concentrations that it does not significantly contribute to the overall stack oxidation. The graphite temperature limits presently in effect at the smaller reactors were therefore primarily established to hold the reaction rate between graphite and CO₂ to not more than 2% per thousand operating days.

Since it is not practical to routinely remove samples of graphite directly from the moderator stack blocks to monitor compliance with the oxidation criteria, small preweighed graphite samples are instead placed in one or more bare (untubed) process tube channels. These samples are then periodically removed and weighed. In the past it has been the policy to assume that if these samples showed less than 2 % weight loss per thousand operating days, the stack graphite could also be assumed to be oxidizing at less than 2%/KOD. This is a reasonable assumption since the monitor

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samples are in uncooled channels which operate at temperatures 10-15% higher than the stack graphite and therefore oxidize more rapidly.

B. Actual Temperature vs Temperature Limit

During the first phase of the test, the graphite temperature limit was increased from 650 C to 700 C corresponding to an increase in the stringer temperature limit from 735 C to 790 C. This temperature increase was accomplished without difficulty by reducing the helium concentration from ~75% to ~50%. As seen from the data summary in Appendix A, the actual maximum stringer temperature at equilibrium operation was generally within 10-15 degrees of the limit. The temperature plotted is the maximum temperature observed of all seven thermocouple stringers in the reactor. At any one time, however, there may be as much as 50-100 C spread in the maximum temperature on each stringer. An example of this spread during a typical period is illustrated in Figure 1. These temperature differences observed between stringers and the corresponding fluctuations in stack temperature complicate interpretation of oxidation monitoring samples and analysis of oxidation products in the reactor gas atmosphere.

During the second phase of the test, the graphite temperature limit was increased from 700 C to 750 C, corresponding to an increase in the stringer temperature limit from 790 C to 850 C. This was accomplished by further reducing the helium concentration from ~50% to ~0%. During the temperature rise period, it was noted that the biological shield temperature was also increasing. The graphite temperature increase was therefore temporarily halted to authorize approval to increase the shield temperature limit beyond that already provided by the test procedure.⁵ As seen from the data summary in Appendix A, the desired graphite stringer temperature of 850 C was approached but never achieved. Increasing river temperature which necessitated reduced power levels and higher than anticipated shield temperatures which necessitated some helium addition, prevented reaching the desired temperature. In addition, a management decision to operate at a lower power level during the final operating period further reduced the operating graphite temperature. While the desired stringer temperature of 850 C could not be held throughout the second phase of the test, good data was obtained during a 3 week period when temperatures were 830-840 C.

C. Helium Percentage vs Helium Loss Rate

The helium percentages and corresponding helium loss rates throughout the test are shown in the data summary in Appendix A and plotted in Figure 2. As expected, the helium loss rate was found to be an exponential function of helium percentage. This occurs for two reasons. First, the greater the percentage of helium in the gas, the greater will be the quantity of helium lost for each cubic foot of reactor gas which leaks out of the system and secondly, the greater the helium percentage, the less dense will be the gas mixture and the greater will be the gas loss rate for any given size hole in a gas seal.

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FIGURE 1 - TYPICAL VARIATION IN GRAPHITE STRINGER TEMPERATURE

- x Stringer 3466
- Stringer 1284
- △ Stringer 3773
- Stringer 3484

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FIGURE 2 - HELIUM LOSS RATE VS HELIUM PERCENTAGE

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D. Gas Pressure

Maintenance of a positive pressure within the reactor gas system with respect to outside air is necessary to keep air out of the gas system. Because of leaks which have developed in gas system seals, excessive pressurization would result in significant gas losses, therefore, the system is maintained at just sufficient positive pressure to exclude air. Gas system pressure was measured in the front plenum chamber at the bottom of the reactor by a gauge measuring the ΔP between the front plenum and front face atmospheric pressure. This gauge, however, measured the ΔP only at grade level or 0 elevation and the pressure will vary with elevation. For example, with a gas whose density is the same as air, the ΔP at the top of the reactor would be the same as that measured at the bottom of the reactor since both the gas in the plenum and the outside air decrease in pressure uniformly with increasing elevation. With a gas whose density is less than air, e.g., 100% Helium, the pressure in the plenum does not decrease as rapidly with elevation as does the outside air. Therefore, if a slight positive pressure were measured at the bottom of the reactor, the ΔP between plenum pressure and outside air pressure would become even more positive with increasing elevation and air exclusion would be maintained since leakage would be out, not in. If the gas were more dense than air, e.g., 100% CO₂, the plenum pressure would decrease more rapidly with elevation than would the outside air pressure. Thus a slight positive pressure at the bottom of the reactor would reverse to a negative pressure at the top of the reactor. An increase in gas pressure would then be necessary to counteract the effect of elevation to prevent air from leaking in at the top of the reactor. These effects are illustrated in Figure 3. Note that if the ΔP were 0 or just slightly positive at the bottom of the reactor with a 100% CO₂ gas atmosphere, the outside air pressure would have decreased by .61 inches of water at the top of the reactor. The plenum pressure, however, would have decreased by .93 inches of water, i.e., there would be a negative ΔP of .32 inches of water and air would leak into the gas system. To prevent air in-leakage would then require that the ΔP at the bottom of the reactor be maintained at at least .31 inches.

Prior to the test and during the first phase of the test when the helium percentage was greater than 37%, the ΔP at the bottom of the reactor was maintained at .05-.10 inches and was sufficient to exclude air from the gas system. When the helium percentage was reduced to less than ~40% it was necessary to constantly increase gas pressure as the helium percentage was reduced. When 100% CO₂ was finally reached, the gas pressure was increased to .25-.30 inches of water which is in reasonable agreement with the values predicted from Figure 3.

E. Oxidation Rate of Graphite Monitor Samples

Prewighed graphite samples were placed in empty process tube channels 3580 and 1067 to monitor stack oxidation before and during the test. Oxidation rate profiles plotted as rate vs position in the stack are shown in Figure 10, 11, 12, and 13 in Appendix A. Each charge contained two different grades of graphite, designated KS and TSGBF. KS graphite is typical of the type

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used in the F stack while TSGBF is the type of graphite used in the K Reactor stacks. The maximum oxidation rate of each type of graphite used in the two monitor channels, expressed in terms of per cent oxidation per 1000 operating days (%/KOD), is summarized in the following table:

<u>Residence period of Samples</u>	<u>Stringer Temperature Limit in Effect</u>	<u>Channel 3580</u>		<u>Channel 1067</u>	
		<u>KS</u>	<u>TSGBF</u>	<u>KS</u>	<u>TSGBF</u>
7/7/64 - 11/20/64	735 C	.7-.8%/KOD	.3%/KOD	.2-.3%/KOD	.2-.3%/KOD
11/20/64 - 2/3/65	735 C from 11/20 to 1/5 790 C from 1/6 to 2/3	—	.6-.7	—	.4
2/3/65 - 3/30/65	790 C	4.8	.7-.8	1.2	.3
3/30/65 - 7/6/65	790 C from 3/30 to 4/12 850 C from 4/12 to 7/6	26	.6-.7	4	.3

Note that the KS graphite showed a significant increase in oxidation rate, particularly in channel 3580 while the TSGBF graphite showed little change in either channel even though the temperature was increased in the order of 100 C. The difference in oxidation rate of the KS graphite between the two channels may be explained by the fact that throughout the test period the graphite temperature in the upper region of the reactor was consistently higher than in the lower region. The lack of change in oxidation rate of the TSGBF material in either channel was not expected and is difficult to explain. It should be expected that the TSGBF graphite samples should have shown lower oxidation rates than the KS graphite since it is a purer graphite and therefore less reactive, but it is surprising that so little change was observed.

F. Biological Shield Temperature

Heat generated within the biological shield by neutron moderation and gamma attenuation is transferred to the cooled cast iron thermal shield. Since the primary heat transfer mechanism is conduction, the biological shield temperature is sensitive to reactor gas composition as well as reactor power. Figure 4 shows the maximum temperature observed in the top and side biological shields over the range of gas compositions used during the test. Note that the top shield was consistently hotter and more sensitive to gas composition than the side shield. While the shield temperatures were in the range of 160-170 C, a distinct odor of masonite was noted in the front face work area.

Since the Process Standards recommends a maximum temperature of 110 C to insure prolonged shield life, it is unlikely that the helium percentage could have been reduced to less than 40% on a continuing basis regardless of the effect of such a change on graphite oxidation. The apparent limit to helium reduction of ~40% at F would not necessarily apply to B and D Reactors which have a different shield poison configuration.

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FIGURE 4 - MAXIMUM TOP & SIDE BIOLOGICAL SHIELD TEMPERATURES VS HELIUM PERCENTAGE

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INTERPRETATION OF RESULTS

As shown in the following illustration, the oxidation of graphite with CO_2 is activated by two mechanisms; temperature and radiation:

The radiation induced reaction results from the dissociation of a portion of the CO_2 in a radiation field into CO and O with subsequent attack of the graphite by oxygen. Relatively little is known about the kinetics of this reaction other than the reaction rate is relatively low and only slightly temperature dependent. The thermally induced reaction, however, is an exponential function of temperature. At low temperatures the thermal reaction is insignificantly low in comparison to the radiation induced reaction but increases with temperature until some crossover region is reached at which point the thermally induced reaction predominates. The crossover point at which the thermal reaction becomes more predominate than the radiation reaction is not known exactly but is thought to be in the order of 650°C . Thus, a given increase in graphite temperature below this crossover region has relatively little effect on oxidation rate because the rate is controlled primarily by the radiation level rather than temperature. Above this crossover region, however, the same increase in temperature has a much more pronounced effect and the observed oxidation rate increases exponentially with temperature.

In addition to temperature, this reaction is also influenced by a number of factors such as 1) the type of graphite, 2) the amount of prior oxidation of the graphite which effects its surface area, 3) whether oxidation takes place uniformly throughout the graphite as occurs when the reaction rate is relatively low or whether oxidation becomes "diffusion limited", i.e., the reaction on the surface takes place so rapidly that some or all the CO_2 is converted to CO before it ever reaches the graphite interior. This "diffusional control" occurs at relatively high temperatures, in the order of 900°C or above. While the graphite in reactor has not been appreciably effected by items 2 or 3 to date, a fourth parameter, the concentration of CO in the reactor gas has a measurable effect on the oxidation rate with CO_2 . As seen in the following conceptual illustration, CO acts as an inhibiting agent to reduce the graphite- CO_2 oxidation rate.

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In a recirculating gas system, the graphite is continually re-exposed to the same atmosphere. Thus, the CO which is continuously formed as the reaction product, builds up in the recirculating system until some equilibrium condition is established. If the initial operating graphite temperature were high enough to be in the range where the thermally controlled reaction was the predominant oxidation mechanism, the reaction between graphite and CO₂ at that temperature would generate CO and an equilibrium would eventually be established between the amount of CO being generated (a measure of the oxidation rate) and the amount of CO being lost by gas leakage. If the temperature were increased 50 C, for example, with no change in the CO concentration, the reaction rate would be expected to increase approximately 8-10 fold. In practice, however, the additional CO which would be generated by the increased reaction rate at the higher temperature would further inhibit the reaction and something less than an 8-10 fold increase would be observed. The exact magnitude of the increase would, of course, depend upon the value of the new equilibrium or more correctly, steady state CO concentration⁶ would depend upon the rate of CO generation and the rate of CO loss through gas leakage.

The reaction of TSX graphite (N Reactor graphite) as a function of CO₂, CO and temperature has been described by Woodley⁶ and Giberson⁷ by the following equation:

$$R = \frac{k_1 P_{CO_2}}{1 + k_2 P_{CO} + k_3 P_{CO_2}}$$

Where R = Graphite oxidation rate, %/KOD

P_{CO₂} = Partial pressure of CO₂, atmospheres

P_{CO} = Partial pressure of CO, atmospheres

$$k_1 = 1.52 \times 10^{16} e^{-\frac{66.83 \times 10^3}{RT}}, \% / \text{KOD} / \text{atmosphere}$$

$$k_2 = 3.15 \times 10^{-4} e^{-\frac{29.5 \times 10^3}{RT}}, \text{atmosphere}^{-1}$$

$$k_3 = 2.66, \text{atmosphere}^{-1}$$

This equation is shown in graphical form in Figures 5 and 6 as the oxidation rate of TSX graphite vs temperature at 50% and 100% CO₂ with parameters of CO concentration. Unfortunately, similar data are not available for the KS and KC graphites used in the B, D, and F Reactors. While the magnitude of the KS and KC graphite reaction rates are likely higher than for TSX under comparable conditions because they are less pure, the change in rate with changes in temperature and CO concentration are probably of the same order.

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FIGURE 5 - REACTION RATE OF TSX GRAPHITE WITH 50% CO₂

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FIGURE 6 - REACTION RATE OF TSA GRAVITY WITH 100% CO₂

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Assuming the reaction rate data for KS and KC graphite to be approximately comparable to the data shown for TSX, the oxidation taking place throughout the whole reactor block may be estimated. Sample calculations are presented in Appendix B. From these calculations it is possible to estimate the generation rate of CO. Since the rate of formation of CO in the gas atmosphere is a reasonably good measure of stack oxidation rate, the calculations described in Appendix B have been used to estimate the CO generation rate as a function of maximum graphite temperature for the thermally induced graphite-CO₂ reaction. This is shown in Figure 7 as the expected generation rate of CO, in cubic feet per day, vs maximum graphite temperature. It should be noted that these curves represent an in-reactor condition in which a balanced or steady state condition is established between oxidation rate, graphite temperature, CO concentration, CO generation rate, and CO loss rate by gas leakage. The CO generation rate is a convenient analytical tool which can be measured from reactor data and can be used to estimate stack oxidation rate.

A review of previous reactor operating data reveals the interesting observation that up to the present graphite temperature limit of 650 C, the generation rate of CO has been directly proportional to reactor power level. Figure 8 is a plot of reactor power level vs CO generation rate. The CO generation rate is calculated by measuring CO concentration in the gas atmosphere when the reactor is at equilibrium and the CO concentration has reached a steady state value. The rate of CO generation is then equal to the rate of CO loss by gas leakage, i.e.,

CO generation rate, ft³/day = CO loss rate, ft³/day = [CO] x daily gas loss rate, ft³/day.

While graphite temperature has increased with power level, the direct proportionality of CO generation rate with power level indicates that radiation intensity, rather than temperature, has been the major contributor to graphite oxidation with CO₂, at least up to the present graphite temperature limit. This is consistent with the radiolytic reaction between graphite and CO₂.⁸

Since the radiation induced reaction is relatively insensitive to temperature, the CO generation rate from the radiation induced reaction at current power levels is plotted in Figure 7 as essentially a straight line at ~130 ft³/day (admittedly the radiation induced reaction is not independent of temperature, however, since the temperature dependency is small it has been neglected). Note that the crossover region, i.e., the point at which the thermal reaction becomes more predominate than the radiation reaction appears to be in the order of 675 C. Presumably then, above the crossover point the CO generation rate should increase rapidly with temperature. Note from the test data in Appendix A that the observed CO generation rate was ~200 ft³/day at 700 C and ~700 ft³/day at 750 C, both of which are in reasonably good agreement with the values predicted from Figure 7.

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FIGURE 7 - RATE OF CO GENERATION IN RECIRCULATING SYSTEM WITH 100% CO₂

FIGURE 8 - OBSERVED GENERATION RATE OF CO IN REACTOR

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The maximum oxidation rate which would be expected in a steady state reactor system is shown in Figure 9 and has been prepared by assuming a gas loss rate of 20,000 ft³/day, selecting a CO generation rate from Figure 7, calculating the CO concentration and from Figure 6 determining the oxidation rate at that temperature and CO concentration. Repeating for various temperatures gives the curve shown in Figure 9 for the thermally induced graphite-CO₂ reaction. Also shown is the calculated maximum oxidation rate resulting from the radiation induced reaction and was calculated by assuming that the total CO generation rate of ~130 ft³/day which is observed at the present graphite temperature limit of 650 C results from the radiation induced reaction and occurs within the fueled region of the stack, a volume of ~2.55 x 10⁶ lbs. It is further assumed that the oxidation rate distribution follows the usual cosine distribution in which case the ratio of maximum oxidation rate to average oxidation rate is 4.43/3.13, the same as the ratio of maximum fuel power to average fuel power. The maximum rate is then calculated as:

1. 130 ft³ CO/day is formed by oxidation of 2.17 lbs graphite/day
2. average oxidation rate = $\frac{2.17 \text{ lbs}}{2.55 \times 10^6 \text{ lbs}} = 8.53 \times 10^{-7} \text{ lbs/lb/day} = .0853\%/KOD$
3. maximum rate = $.0853 \times \frac{4.43}{3.13} = .12\%/KOD$

The radiation induced rate intersects the thermal rate at ~625 C and at first glance would appear to be in disagreement with Figure 7 which predicts no increase in CO generation, i.e., no increase in oxidation rate until a temperature of ~675 C is reached. It must be remembered, however, that in reactor there is a considerable variation in maximum temperature from one part of the reactor to another. Thus, even though the oxidation rate may indeed begin to increase when the local temperature reaches ~625 C, only a relatively small amount of graphite may be affected with little or no apparent increase in the total CO generation rate. As the temperature is further increased, the increase in rate eventually effects a sufficiently large volume of graphite that an increase in total CO generation results. Thus, to imply that no increase in oxidation rate has occurred because no increase in CO is observed is not strictly correct.

Interpretation of the behavior of the graphite monitor samples and correlation with the gross reactor data cited previously is somewhat difficult because the sample operating conditions of temperature and CO inhibition are not well known. Since the samples are placed in uncooled channels, they probably operate at about the same temperature and experience the same magnitude of temperature fluctuations as the graphite stringers. Because the samples operate at temperatures which are well up into the thermally controlled range and therefore are very sensitive to temperature, oxidation rates can vary by orders of magnitude throughout the sample residence time in reactor. In addition, the higher oxidation rates of the samples, sample holder and adjacent tube block probably results in a locally higher CO concentration in the samples. Thus any attempt to correlate what happens in the stack on the basis of before and after weight loss measurements of samples with a varying temperature history gives results which are only approximate at best, particularly if the oxidation rate of the samples is controlled primarily by temperature while the oxidation in the rest of the stack is controlled primarily by radiation. So long as the samples show a maximum weight loss of 2%/KOD or

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FIGURE 9 - RADIATION AND THERMAL OXIDATION RATE IN RECIRCULATING GAS SYSTEM

less, however, it can be assumed that the maximum oxidation rate in the stack is also less than 2%/KOD. Such is the condition which now exists at the current graphite temperature limit of 650 C. When the samples show greater than 2%/KOD, however, this is no longer a valid assumption. Thus, one of the difficulties associated with increasing the graphite temperature limit is the loss of ability to insure, with monitor samples alone, that the stack oxidation rate is less than 2%/KOD.

While the oxidation rate of the stack cannot be directly inferred from the weight loss measurements of the monitor samples, the rapid increase in sample oxidation rate during the test indicates that the samples operated in a temperature range where the thermal reaction was definitely the predominant mechanism. The oxidation rate of the KS graphite samples for example, increased by a factor of ~ 7 with the first 50 C increase in temperature limit and by a factor of ~ 40 with the second 50 C increase. This would undoubtedly have been even greater if the reactor had been operated at the desired temperature throughout the second 50 C increase phase of the test.

Despite the incorrectness of using the monitor samples as a direct measure of stack oxidate rate, it is interesting to compare the KS sample results with the calculated reactor oxidation rate.

Two data points from the KS samples are also shown in Figure 9. The monitor sample data point at .7%/KOD was measured prior to the test when the graphite temperature limit was 650 C. From the graphite stringer temperatures, it is estimated that the maximum temperature in the samples averaged ~ 725 C during their residence. The data point at 5%/KOD was measured when the graphite temperature limit had been increased to 700 C. Again from the graphite stringer temperatures, it is estimated that the maximum temperature in the samples averaged ~ 775 C during their residence. Considering the uncertainty of the estimated sample operating temperatures, the two data points appear in reasonable agreement with the calculated rates. The measured sample oxidation rate of 26%/KOD obtained when the graphite temperature limit was increased to 750 C is not shown since the graphite temperatures varied so greatly during the sample residence that any attempted correlation of rate with temperature is not really meaningful.

CONCLUSIONS

1. An analysis of the results from this test and previous reactor data indicate that up to the present graphite temperature limit of 650 C, the principle cause of oxidation of the stack graphite with CO_2 has been reactor radiation rather than graphite temperature. This implies that some increase in the graphite temperature limit (in the order of 50 C) is technically feasible within the existing criteria of maintaining the stack oxidation rate below 2%/KOD. Any significant additional increase does not appear feasible because of the high oxidation rates associated with the temperature controlled oxidation mechanism.

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2. At current power levels and with current shield poison configuration, biological shield temperature, rather than graphite temperature, could be a controlling factor in helium reduction, particularly during the summer months.
3. As expected, there was an exponential reduction in helium loss rate with reduced helium percentage.
4. As expected, it was necessary to increase gas pressure to prevent air in-leakage when the helium percentage was reduced to less than ~40%.
5. Oxidation monitoring samples showed significant differences in oxidation rate between the two types of graphite used.

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Reactor Engineering Unit
Process and Reactor Development

AR:alj

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REFERENCES

1. Russell, A. Production Test IP-725, Increased Graphite Temperature Limit - F Reactor, RL-REA-14. December 1, 1964. (SECRET).
2. Russell, A. Production Test IP-725, Supplement A, Increased Graphite Temperature Limit - F Reactor, RL-REA-14 Sup A. March 19, 1965. (SECRET).
3. Griggs, B. Effect of Oxidation on Compression Strength of CSGBF Graphite, HW-42498. April, 1956. (SECRET).
4. Curtiss, D. H. Basis for Graphite Limits, HW-45154. August, 1956. (SECRET).
5. Russell, A. Production Test IP-725, Supplement B, Increased Graphite Temperature Limit - F Reactor, RL-REA-14 Sup B. June 18, 1965. (SECRET).
6. Woodley, R. E. A Review of the Reaction of Nuclear Graphite with Carbon Dioxide, HW-74663. August 17, 1962.
7. Personal Communication with R. C. Giberson.
8. Nightingale, R. E. Nuclear Graphite. Academic Press, 1962.

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APPENDIX A - DATA SUMMARY

Power Level, MW	1935	1945	1980	2000	2005	2010	2015	2010	2010	2010	2000	2005	2010	2005	2005	2005	1995
Fe%	62	63	56	53	53	50	53	51	50	51	52	51	52	51	52	53	50
He loss rate, ft ³ /day	11000	11400	11200	7500	0800	7500	8200	6000	6600	7800	8700	7900	8600	8100	8600	8100	7505
CO%	.7	.7	.9	1.3	1.3	1.3	1.4	1.3	1.3	1.3	1.4	1.3	1.1	1.2	1.1	1.0	.9
CO generation rate, ft ³ /day	<div> <div> <div>130-140</div> <div>220-230</div> </div> </div>																
Lbs. graphite oxidized/day	<div> <div>2.2</div> <div>3.8</div> </div>																
B shield temperature	80	80	75	81	85	89	89	91	93	94	94	94	93	93	94	92	90

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DATA SUMMARY (CONTD)

Power Level, MW 1995 2025 2030 2040 2010

He% 50 51 52 23 54

He loss rate, ft³/day 9500 10600 10200 10700 9000

CO% .9 1.0 .9 .9 .9

CO generation ft³/day <-----210-220----->

lbs graphite oxidized/day <-----3.6----->

B Shield Temperature 90 94 94 95 95

1920 1965 2025 2035 2040

61 60 56 53 52

13800 11700 11000 10600 10600

.5 .6 .6 1.0 1.0

72 78 83 91 91

1990 2015 2020 2025 2030

52 50 50 43 52

10100 9600 8700 7900 6700

.7 1.0 1.0 .8 .9

76 86 91 95 96

2025 2025 2025 2025 2030

50 50 50 49 49

5500 5500 5500 5500 5500

.9 .9 .9 .9 .9

99 99 99 99 99

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DATA SUMMARY (CONTD.)

Power Level, MW	1950	1980	2010	1975	1900	1930	1960	1975	1975	1975	1955	1955	1955	1745	1950	1955	1950
He%	51	51	52	43	40	31	19	18	7	10	6	14	36	19	8	0	0
He loss rate, ft ³ /day	11200	10800	—	7100	7900	4200	2800	3000	1200	1200	2800	2400	8300	3500	1000	0	0
CO%	.8	.5	.8	.9	.8	1.2	1.9	1.8	2.4	2.4	2.5	1.7	.5	1.3	1.9	2.7	2.7
CO generation rate ft ³ /day	(---500-600---)																
Lbs graphite oxidized/day	(---10---)																
B Shield Temperature	60	73	79	.8	73	94	113	126	135	143	153	149	94	106	128	147	147

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DATA SUMMARY (CONTD.)

Power Level, MW	1750	1930	1930	1930	1810	1850	1880	1880	1880	1880	1880	1835	1825	1810	1790	1790	1790	1790
He%	0	0	0	2	0	5	3	6	6	2	2	1	5	3	9	8	8	8
He loss rate, ft ³ /day	0	0	0	-	0	1000	1300	1200	2700	1500	1500	1100	1000	1500	2200	1000	2000	2000
CO%	3.7	3.1	2.7	2.5	1.5	1.6	1.8	1.9	1.9	1.7	1.7	1.6	1.3	1.4	1.4	1.4	1.3	1.3
CO generation rate ft ³ /day	600-700	600-700	600-700	600-700	1.5	1.6	1.8	1.9	1.9	1.7	1.7	1.6	1.3	1.4	1.4	1.4	1.3	1.3
lbs graphite oxidized/day	11.6	11.6	11.6	11.6	1.5	1.6	1.8	1.9	1.9	1.7	1.7	1.6	1.3	1.4	1.4	1.4	1.3	1.3
B Shield Temperature	167	160	167	172	161	171	172	171	172	168	172	172	171	171	170	169	170	167

FIGURE 10

Oxidation Rate Distribution in
Channel 3580 F, 8/7/64-11/20/64
Graphite Temperature Limit 650 C
X KS Graphite
O TSGBF Graphite

FIGURE 11

Oxidation Rate Distribution in
Channel 3580 F 2/3/65-3/30/65
Graphite Temperature Limit 700 C
X KS Graphite
O TSGBF Graphite

FIGURE 12

Oxidation Rate Distribution in
Channel 3580 F, 3/30/65-7/6/65
Graphite Temperature Limit, 750 C
X KS Graphite
O TSGBF Graphite

Oxidation Rate %/KOD

30

25

20

15

10

5

0

40

80

120

160

200

240

280

320

Distance from front of stack, inches

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FIGURE 13

Oxidation Rate Distribution in
Channel 1067 F, 3/30/65-7/6/65
Graphite Temperature Limit 750 C
X KS Graphite
O TSGBF Graphite

Oxidation Rate, %/KOD

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APPENDIX B

The intent of these calculations is to estimate the stack oxidation rate from the rate data for the thermally induced graphite-CO₂ reaction shown in Figure 6. It is immediately apparent that even if the temperature distribution in the reactor stack is known, the corresponding oxidation rate cannot be directly read from Figure 6 because the CO concentration is not known. These calculational procedures are therefore intended to estimate the steady state balance which exists in the reactor between oxidation rate, CO concentration, CO generation rate and CO loss rate at various temperatures.

Rather than attempting a trial and error process of selecting a temperature and CO concentration from Figure 6 to give an oxidation rate which forms a certain quantity of CO per unit time which in turn just balances with the CO loss rate, the approach has been to use the reverse procedure of determining the number of pounds of graphite which must be oxidized per day to give a certain quantity of CO generated per day. This quantity of CO, when coupled with the reactor gas loss rate, defines a certain concentration of CO in the reactor gas atmosphere. The temperature at which this occurs may then be determined from Figure 6.

To illustrate the use of this procedure, the assumption has been made that the volume of graphite effected by the thermally induced graphite-CO₂ reaction is confined within the process tube pattern and within a zone of about 11 feet near the center of the stack. Figure 14 shows the front to rear graphite temperature distribution for two cases in which the maximum graphite temperature is 700 and 750 C. Also shown is the corresponding front to rear oxidation rate distribution for the two temperatures, calculated from Figure 6 with 100% CO₂ and 0% CO. Note that since the oxidation rate is so strongly dependant on temperature, oxidation occurs to a significant degree only between ~80" and 220", a width of approximately 11 feet. The total volume of graphite within this zone is $\sim 1.15 \times 10^6$ lbs. Since essentially all the oxidation is occurring within this zone, all the CO which is formed is also generated within this region. The total quantity of CO being generated per unit time is therefore proportional to the total integrated area under the rate curve. It will be noted that the shape of the rate distribution curves, while different in magnitude between the two temperatures, are essentially triangular in shape having a base of ~11 feet. Calculation of the rate distribution at other temperatures and concentrations of CO show the same triangular distribution with a base of ~11 feet. Calculation of the rate at which CO is being generated within this region is, however, cumbersome because the abscissa is in units of feet while the ordinate is in units of reaction rate per unit time. If the oxidation could be considered as occurring uniformly throughout the 11 foot region rather than varying within the region, the oxidation rate per unit time would lead directly to the total volume of CO being generated per unit time. For example, a uniform oxidation rate within the 1.15×10^6 lb. zone of 1%/KOD would result in the formation of 690 ft³ of CO per day.

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FIGURE 14
Front to Rear Oxidation Distribution -
Thermally Induced Reaction With Pure
CO₂

Since the quantity of CO formed is proportional to the area within the triangular shaped rate distribution curve, a uniform rate which gives the same area should also generate the same quantity of CO. As seen in the following illustration, a uniform rate whose magnitude is one half the maximum rate of the triangle forms the same area:

i.e., the area of the rectangle with base b and height $\frac{h}{2}$ forms the same area as the triangle with base b and height h . Thus by assuming a uniform oxidation rate of one half the actual maximum oxidation rate, the quantity of CO generated per unit time may be easily calculated. This technique considerably simplifies the calculations in that now the total volume of CO being generated per unit time can be calculated by assuming the oxidation occurs uniformly throughout the 1.15×10^6 lb. volume.

Construction of the curves shown in Figure 7 is illustrated by the following example:

Let volume of graphite reacting = 1.15×10^6 lbs.

Let total volume of gas loss from reactor = 20,000 ft³/day

Let CO concentration = .1%

Then at steady state reactor conditions:

1) Oxidation of 1 lb of graphite with CO₂ → 60 ft³ CO

2) generation rate of CO, ft³/day = loss rate of CO, ft³/day = 20,000 x .001 = 20 ft³ CO/day

3) 20 ft³ CO/day is formed by oxidation of .333 lbs graphite/day

4) average oxidation rate = $\frac{.333 \text{ lbs}}{1.15 \times 10^6 \text{ lb.}} = .29 \times 10^{-6} \text{ lbs./lb./day}$

5) Since $.29 \times 10^{-6} \text{ lbs./lb./day}$ represents the average rate over the entire reacting volume of $1.15 \times 10^6 \text{ lbs.}$ the maximum rate is $2 \times .29 \times 10^{-6} \text{ lbs./lb./day}$.

6) $.58 \times 10^{-6} \text{ lbs./lb./day} = .058\%/KOD$

7) From Figure 6 this rate of .058%/KOD occurs with .1% CO at a graphite temperature of 615 C.

8) Locate the CO generation rate of 20 ft³/day at 615 C on the 20,000 ft³/day gas loss parameter in Figure 7.

Repeating the above calculations for other concentrations of CO and gas loss leads to the generation of the curves shown in Figure 7.

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