



Public Service Company of Colorado

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July 18, 1980
Fort St. Vrain
Unit No. 1
P-80223

Mr. George Kuzmycz, Project Manager
U.S. Nuclear Regulatory Commission
Standardization and Special Projects Branch
Mail Station 228
Washington, DC 20555

Docket No. 50-267

Subject: Inside/Out Oxidation of
Graphite

Dear George:

Enclosed, for your information, is a memorandum written by R.D. Burnette of General Atomic Company. The memo addresses the topic of inside/out oxidation of graphite in relation to the Fort St. Vrain reactor.

Mr. Burnette reports that the test conditions that produced this phenomenon in experiments conducted at Battelle Pacific Northwest Laboratories and Oak Ridge National Laboratory were not the same as FSV reactor conditions. Mr. Burnette concludes that this phenomenon will not occur in the FSV reactor and it has not been observed in oxidation profiles generated in the laboratory under conditions representative of FSV reactor conditions.

If you have any questions concerning this matter, please contact me.

Very truly yours,

F. E. Swart
Nuclear Project Manager

FES/JL:pa

Enclosure

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FROM R. D. Burnette
TO S. Brown/T. Gulden/W. Graul
SUBJECT Inside/Out Oxidation

IN REPLY
REFER TO CCB:480:RDB:254

DATE 6-20-80

SUMMARY

Inside/out oxidation of graphite has been observed by G. Tingey at BNWL and by Eatherly and Wichner at ORNL. The explanation for inside/out oxidation is enhanced catalysis on the inside of large samples due to a decreased oxygen potential as the oxidants (CO_2 or H_2O) diffuse into the sample resulting in chemical reduction of certain impurity catalysts. Impurities such as iron are highly catalytic in the reduced state but relatively non catalytic in the oxidized state. This could result in chemical reactivity 10 or more times higher on the inside as compared to the outside. At FSV the coolant gas is almost always reducing to the catalysts of interest. Therefore this phenomenon will not occur in the reactor.

DETAILS

Scientists at GA, ORNL and BNWL agree that the most likely mechanism for inside/out oxidation is an increase in catalysis inside solid graphite samples. Catalysis would increase on the inside if the oxygen potential was lower on the inside as compared to the outside. This could occur if the oxidants CO_2 or H_2O reacted as they diffused in the sample forming the products CO and/or H_2 .

In the experiments at BNWL the concentrations of CO and CO_2 were 20 and 80% respectively. The sample temperature was 825°C . The CO/CO_2 ratio was 0.25 on the outside but could easily have been >10 on the inside due to conversion of CO_2 to CO . Furthermore, the thermodynamic equilibrium for the ratios CO/CO_2 over Fe/FeO is about 2 at the temperature of the BNWL experiment. Therefore, the iron impurities would have been in the oxide form, (FeO), which is known to be relatively non catalytic, on the outside of the sample and in the reduced form (Fe), on the inside. Reduced iron, Fe , is known to be highly catalytic in the steam graphite reaction.

In the ORNL experiments the oxidant was water vapor. In their loop system the products H_2 , CO , and CO_2 were allowed to build up. At least during a part of their test the outside of the samples were exposed to ratios of $\text{H}_2/\text{H}_2\text{O} \ll 2$ in which case the iron catalysts would be oxidized. (The thermodynamic equilibrium $\text{H}_2/\text{H}_2\text{O}$ ratio for the system Fe/FeO is also about 2 at the temperature of the ORNL tests, 900°C .) On the inside of the samples the $\text{H}_2/\text{H}_2\text{O}$ could be $\gg 2$ causing a greatly accelerated catalyzed reaction.

Of course, catalysts other than iron are prevalent in graphite, including Ni , Ti , V , Ca . These species may occur in clusters and/or in association with anion impurities such as oxides, carbides, sulfides, silicates, silicides. Therefore the true thermodynamic equilibria are complex and variable depending on the graphite samples and the specific impurity mix present.

All tests at GA use impurity ratios simulating those in the reactor, i.e., high ratios of H_2/H_2O and CO/CO_2 . In particular in our oxidation experiments we always work with $H_2/H_2O \geq 10$ which simulates the reactor conditions and which ensures that all the iron catalysts are in the reduced state. Over the last 3 or 4 years, we have determined a number of oxidation profiles on ATJ, SC2020, HLM, PGX, H-451 and ASR-1RG graphite using $H_2/H_2O \geq 10$. All of the profiles show normal behavior, that is, higher oxidation on the outside. In no case was inside/out oxidation observed. Furthermore, the profiles generated in the laboratory match quite closely with theoretical profiles calculated using our Standard GOP or OXIDE-3 formulae.

Our work on oxidation profile is continuing in our High Pressure Test Loop, HPTL. With this experiment we will determine rates of oxidation and oxidation profiles under the influence of real reactor pressure, 750 psia, and turbulent flow conditions. The loop is operating, presently, with annular shaped samples of PGX graphite (3 cm OD, 1 cm ID) similar to the surveillance samples in FSV. With some minor modifications larger solid samples up to approx. 6 cm could be used, but I don't see the need for it as long as we use high ratios of H_2/H_2O .

The staff at ORNL will document the conditions and results of their tests where they found inside/out oxidation in some samples. They believe they have enough data to describe an "envelope of conditions" which leads to this phenomenon. Their experimentally determined envelope of conditions will be compared to the theoretical thermodynamic equilibria for several of the important catalysts present.

cc: Jess Lopez
G. Engle
R. Vollman
A. Barsell
Bob Wichner - ORNL
Garth Tingey - BNWL