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EVALUATION OF CARBON TRANSPORT PHENOMENA IN HTGR SYSTEMS

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1.0 SUMMARY

This report describes the results of a technical evaluation of the carbon transport cycle which under certain conditions could occur in a high-temperature, gas-cooled, graphite-moderated reactor (HTGR). The basis of the carbon transport cycle is that the impurity species water and carbon dioxide react with the hot graphite in the core, producing carbon monoxide and hydrogen, which in turn react at heat exchanger surfaces to form carbon deposits. Results of the evaluation are summarized here.

Gaseous impurities arise in the coolant of an HTGR as a result of (1) outgassing of the graphite core, (2) residual air in the primary system prior to charging with helium, and (3) in-leakage of water.

The most important graphite oxidation process is the water-graphite reaction. The rate of the reaction is controlled by several variables: (1) temperature, (2) steam concentration, (3) hydrogen concentration, (4) catalysts present, and (5) degree of burnoff (or graphite weight loss). Numerous investigations have led to considerable knowledge of the effects of these variables.

Carbon deposition will occur on steel and low-chrome-alloy surfaces at metal temperatures of 350° to 650°C , provided the metal surfaces are in a catalytic (reduced, oxide-free) state.

The $\text{H}_2/\text{H}_2\text{O}$ ratio in the coolant is important. It controls the formation of iron oxide on metal surfaces in the coolant circuit, and iron-oxide formation limits carbon deposition. At the typical heat exchanger surface temperature of around 400°C , iron oxide is stable at $\text{H}_2/\text{H}_2\text{O}$ ratios less than about 10 and carbon deposition will not occur. Under steady-state reactor conditions, the $\text{H}_2/\text{H}_2\text{O}$ ratio in the coolant is proportional to R_c/r , where R_c is the graphite oxidative reactivity and r is the purification rate.

A computer program (GOP) developed at Battelle Northwest Laboratory (BNWL) has been particularly useful in predicting H_2/H_2O and the degree of core corrosion for HTGR systems for steady-state cases where the partial pressure of hydrogen and water are constant and low. Application of the code to a typical case (a 330-MW(e) plant where impurity $P_{H_2} + P_{H_2O}$ is equivalent to 10 ppm in helium) yielded a H_2/H_2O ratio of 4, indicating that under the given conditions carbon deposition should not occur. Also, the calculation showed that localized corrosion will not be a problem.

A water-injection experiment was performed in the Dragon High Temperature Reactor. The measured H_2/H_2O ratio was around 1.2. In an analysis of the experiment, the GOP computer code calculated $H_2/H_2O = 1.1$, which is in excellent agreement with the measured value.

If massive carbon deposits develop, dust formation may be a problem.

Carburization in depth with subsequent embrittlement of steam generator tubes will not be a problem unless carbon deposition proceeds unchecked for years.

Work needed in the continuing effort to study carbon transport phenomena consists of (1) continued development and utilization of computer codes, (2) continued studies to improve the reliability of input data for the computer code (3) further reactor steam injection experiments, and (4) continued studies of carbon deposition processes.

Investigators at three laboratories in the United States Gulf General Atomic (GGA), Oak Ridge National Laboratory (ORNL), and BNWL are conducting experimental work related to carbon transport phenomena.

2.0 INTRODUCTION

In a high-temperature, helium-cooled, graphite-moderated reactor (HTGR), sufficiently high levels of gaseous impurities could lead to the occurrence of the carbon transport cycle, where the impurity species water or carbon dioxide react with graphite in the core, producing carbon monoxide and hydrogen, which in turn react at heat exchanger surfaces to form carbon deposits.

This report describes briefly (1) what is known about carbon transport phenomena, (2) what experimental work is needed, and (3) what experimental work is under way at various laboratories.

This evaluation was performed in fulfillment of an item of work included in Task IV of the HTGR Base Program.

Reactor accident situations were not included in this study because the carbon transport cycle is not expected to be operative under such conditions. High in-leakage of water, as might occur in an accident situation involving a steam tube rupture, could cause core corrosion problems. It is expected, however, that carbon deposition would not occur to an appreciable extent in this situation because temperatures would drop rapidly in the heat exchangers and oxidizing conditions in the coolant would prevail. (As will be pointed out in the following sections, carbon deposition does not occur at low temperature and under oxidizing conditions.)

3.0 IMPURITY LEVELS IN THE HELIUM COOLANT OF AN HTGR

Gaseous impurities normally arise in the coolant as a result of initial outgassing of the graphite core or as the result of residual air in the primary system prior to charging with helium. Both of these sources are transient in nature, because after several days of operation at temperature, outgassing of the core will be essentially complete and the coolant purification system will reduce most of the initial impurity species to negligible levels.

One notable exception, however, is hydrogen. Recent full-power operation of both the Dragon reactor and Peach Bottom HTGR systems have indicated that H_2 is a persistent coolant impurity. In the Dragon reactor, H_2 levels of around 1 ppm have persisted after several months of reactor operation. The concentrations of the other species -- N_2 , CH_4 , and CO -- are found to be in the one-tenth ppm range. Similarly, for the Peach Bottom HTGR, the level of H_2 in the helium coolant after 180 days of full power operation has been measured to be 9 and 10 ppm, whereas the other constituents remain at 0.5 ppm each.

The source of the excessive H_2 contamination is unknown. Part of the H_2 may arise from long-term graphite outgassing or from minor steam leaks. A speculative source of H_2 is the result of thermal decomposition of oil vapor which may have leaked in from various sources. Another possible source is diffusion of protons through heat exchanger tube walls.

Ultimately, the extent of core corrosion in an HTGR depends on the amount of water in-leakage, which is, of course, dependent on the integrity of the steam generator. Small pinhole leaks, perhaps at welded joints, may develop and result in a steady-state steam leak, where the combined pressure of hydrogen and water remain essentially constant. In the case

of the two HTGR systems, Peach Bottom and Fort St. Vrain, water in-leakage rates of 0.01 lb/hr and 0.04 lb/hr, respectively, result in $P_{H_2} + P_{H_2O}$ equivalent to 10 ppm.

Considerably higher concentration levels of water could be reached in a steam-leak accident, such as a steam tube rupture. In this case the reactor is automatically scrammed and water in the affected heat exchanger is dumped.

4.0 REACTIONS OF IMPORTANCE IN THE CARBON TRANSPORT CYCLE

There are four important reactions involved in the carbon transport cycle:

Reactions (1) and (2) are thermally-induced and proceed at significant rates at graphite temperatures above about 700°C. Reactions (3) and (4) are known to be much slower thermally than the first two reactions, but may become more important due to radiation-induced processes. The change of thermodynamic equilibrium of Reactions (1) and (2) with temperature favors the components to the left at lower temperatures. Furthermore, these reactions are catalyzed by metal surfaces in the temperature range of 300°C to 700°C. Thus, the species H₂O and CO₂ oxidize the hot core by Reactions (1) and (2) and produce CO and H₂, which could in turn react to deposit carbon on heat exchanger surfaces by the reverse of Reactions (1) and (2).

Reaction (3) is not directly involved in the carbon transport cycle but is important because it may alter the steady-state concentration of gaseous impurities in the HTGR core.

Reaction (4) may transport carbon in a direction opposite to Reactions (1) and (2). That is, from the colder graphite (i. e. 300°C-500°C) to the hottest graphite (up to 1000°C).

5.0 GRAPHITE OXIDATION

This section summarizes what is known about the oxidation of graphite and how the information is used in understanding and predicting the extent of carbon transport in HTGR systems. It describes two recent developments that have contributed a great deal to the continuing effort to assess the degree of graphite oxidation of an HTGR core. They are (1) the application of computer codes and (2) the Dragon reactor steam injection experiments.

Reviews of graphite oxidation reactions have been written by Walker, et al., ⁽¹⁾ and Clark, et al. ⁽²⁾ The thermal reactions of gaseous impurities and graphite leading to carbon transport were investigated by Antill and Peakall. ⁽³⁾

5.1 THERMAL REACTIONS

The graphite oxidation process of most concern in the HTGR program is the thermally induced steam-graphite (H_2O-C) reaction. The H_2O-C reaction rate is at least three times faster than that of the CO_2-C reaction. ⁽¹⁾ Reaction (3), the shift reaction, and Reaction (4) are not important thermally but may be enhanced by radiolytic processes, which are discussed in more detail in a later section.

The reaction rate of the H_2O-C reaction is controlled by several variables:

1. Temperature,
2. Steam concentration,
3. Hydrogen concentration,
4. Length of exposure (percent burnoff),
5. Catalysts present (fission products or graphite impurities).

The effects of these variables are discussed separately below.

5. 1. 1 Effect of Temperature

The relationship of temperature to the reaction rate for heterogeneous reactions involving a porous solid was first described by Wicke⁽⁴⁾ and later amplified by Walker et al.⁽¹⁾ Wicke's analysis indicates three temperature zones in which the overall reaction rate is controlled differently: (1) a low temperature ($\sim 500^{\circ}$ to 800°C) zone (Zone I) in which the chemical reactivity of the substrate controls and in which the reaction rate is so low that diffusion of oxidant throughout the solid occurs with the concentration virtually undepleted; (2) an intermediate temperature (800° to 1000°C) zone (Zone II) in which chemical reactivity, together with in-pore diffusion, controls; and (3) a high temperature (above 1000°C) zone (Zone III) in which mass transport of reactants and products to and from the exterior surface of the solid controls. For a typical HTGR core, the effects corresponding to Zone II (and possibly to the II-III transition zone) are of primary concern.

5. 1. 2 Effect of Steam and Hydrogen Concentrations

There has been general agreement among investigators that the $\text{H}_2\text{O-C}$ reaction rate fits the Langmuir-Hinshelwood equation

$$-\frac{dP_{\text{H}_2\text{O}}}{dt} = \frac{K_1 P_{\text{H}_2\text{O}}}{1 + K_2 P_{\text{H}_2} + K_3 P_{\text{H}_2\text{O}}} \quad (5)$$

where K_1 is a constant describing the rate of the reaction of water with the carbon surface, and K_2 and K_3 are equilibrium adsorption constants for hydrogen and water on carbon, respectively.

This relationship indicates that the reaction is first order with respect to water at low steam pressures, but approaches zero order at higher pressures. Hydrogen is seen to have an inhibiting effect (depending on the magnitude of K_2) because of competition with water for the active sites on the substrate.

Experimentally, one observes reaction orders of from zero to one depending on temperature, gas flow rates, sample geometry, and water and hydrogen pressures. In general, however, in the range of water pressures of interest for a steam tube rupture (0.1 to 1.0 atm) and at high temperatures (1000°C or more) orders approaching one have been observed. This is because K_2 and K_3 are low at high temperatures. At temperatures of 900°C and lower, K_2 and K_3 become more important, and the reaction order is usually observed to be less than one. At water concentrations of 0.01 atm or lower, the H_2O -C reaction order is observed to approach one.

The effect of hydrogen as a separate variable has been studied by Johnstone, Chen, and Scott,⁽⁵⁾ Riedinger et al.,⁽⁶⁾ and more recently by Giberson and Walker.⁽⁷⁾ Giberson and Walker show experimental data for low pressures (≤ 1 mm Hg) of hydrogen and water which fit the following equation

$$-\frac{dP_{H_2O}}{dt} = \frac{K_1 P_{H_2O}}{1 + K_2 (P_{H_2})^{1/2} + K_3 P_{H_2O}} \quad (6)$$

They suggest that hydrogen inhibition is by reversible dissociative adsorption of hydrogen on active sites, which explains the 1/2 power in the hydrogen adsorption term.

5.1.3 Effect of Burnoff

Graphite oxidation rates show three phases with respect to extent of weight fraction oxidized. Up to about 1% burnoff, the rate is seen to increase by a factor of about 10. This effect is believed to be due to an increase in internal surface area or active sites. The second phase exists up to 50 to 60% burnoff, during which the reaction rate is relatively constant. During this phase, one active site is generated for each one destroyed. During the third phase, which occurs at high burnoff, the oxidation rate decreases because the active surface is being depleted. Experimental work

on the effect of carbon burnoff has been performed by Johnstone, Chen, and Scott,⁽⁵⁾ Blakely and Overholser,⁽⁸⁾ and investigators at Gulf General Atomic.⁽⁶⁾

5.1.4 Effect of Catalysts

Catalysis of the H_2O-C reaction by various metals is well known.^(9, 10, 11, 12) Normally, graphite can be made reasonably free of metal impurities. In a reactor core, however, fuel element graphite may be substantially contaminated with metal fission products such as barium, strontium, cesium, europium, cerium, and others. The possibility of iron contamination due to machining dust, welding slag, and other construction debris cannot be discounted.

The catalytic effect of barium, strontium, and cesium was studied extensively at General Atomic.⁽⁹⁾ Barium was found to be more catalytic than strontium, and cesium was not catalytic at all. For relatively high concentrations of barium (0.5 mg Ba/g C), an increase in reaction rate of around a factor of 10 was observed. For a more reasonable end-of-life barium concentration of 0.1 mg/g, the reaction rate is increased by a factor of 2 to 3.

The effects of several catalysts were studied by Dragon project workers.⁽¹⁰⁾ They found that oxides of barium and strontium are active catalysts, whereas the transition metals iron, cobalt, nickel, vanadium, and molybdenum are active only in the reduced state. Alumina, silica, and zirconia were found to inhibit the reaction rates markedly.

5.2 RADIOLYTIC PROCESSES

The corrosion of an HTGR core during irradiation may be enhanced by metastable species. These metastable species may include H , H_2 , O , O_2 , CO_2 , OH , and H_2O_2 in ionized or excited forms. They are expected to arise as a result of direct gamma and fast neutron irradiation or transfer of energy from excited helium atoms. The energy transfer mechanism

is suggested by Tingey⁽¹³⁾ to be due to both charge exchange and excitation transfer from the electronically excited inert gas atoms.

Although experimental data on the radiation-induced H_2O -C reaction are quite meager, evidence to date indicates an almost negligible effect due to radiation. Work is presently under way at Battelle Northwest Laboratory by R. Woodley,⁽¹⁴⁾ using a cobalt-60 gamma source. Employing a once-through flow system, he reported no measurable reaction rate for 200 ppm water vapor at $675^\circ C$ exposed to 2.86×10^6 r/hr.

In more recent tests, Woodley used a technique employing sealed Pyrex ampoules. Steam-graphite reaction rates were observed for long exposure to dose rates of 2.1×10^7 r/hr. A G value (molecules carbon reacted/100 eV gamma energy absorbed) of 0.75 was calculated from an estimated graphite oxidation rate of 10^{-8} hr⁻¹.

In-pile experiments at $1000^\circ C$ performed recently at Oak Ridge National Laboratory by Overholser et al.⁽¹⁵⁾ indicated no measurable increase in graphite corrosion over the thermal rate.

Much experimental work and reactor operating experience on the radiation-induced CO_2 -C reaction has been performed by the British in support of their carbon dioxide-cooled reactors. The results of this experience show quite enhanced corrosion rates for pure systems at low temperatures (300° to $500^\circ C$).

Work on irradiation effects has been performed for the Dragon project.⁽¹⁶⁾ These tests were performed at Mol, Belgium, using carbon dioxide or water in their In-Pile Carbon Transport Loop (IPCTL) system. The results show a slight increase in the CO_2 -C reaction rate due to irradiation. The observed rates, however, are still lower than the thermal H_2O -C reaction. Because of this, and also because carbon dioxide impurity levels in an HTGR will be much lower than water impurity levels, the radiation-induced CO_2 -C reaction is not expected to increase significantly the degree of core corrosion in an HTGR.

Work by Tingey^(17, 18) and Giberson et al.⁽¹⁹⁾ have shown that the shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) and methane formation reaction ($\text{C} + 2\text{H}_2 = \text{CH}_4$) are appreciably affected by radiation.

Tingey's results indicate, however, that corrosion of an HTGR core due to steam oxidation would not be significantly affected by radiation-induced reactions. It appears that at the high graphite temperatures involved in HTGR systems (800° to 1000°C) the thermal oxidation reactions predominate over the radiolytic processes. At lower graphite temperatures (below 800°C), the radiolytic reactions could become significant. This could prove to be beneficial, however, because graphite oxidation in an HTGR core would be spread over a larger surface area, thereby minimizing localized core corrosion.

Enhancement of the rate of the shift reaction by radiation is expected to increase carbon dioxide levels over what is normally expected. In this case radiation could have an additional beneficial effect because the shift reaction replaces the reactive water species with the less active carbon dioxide molecule. Graphite oxidation would therefore be slightly decreased, and the ratio $\text{H}_2/\text{H}_2\text{O}$ would be increased.

5.3 MASS TRANSFER AND DIFFUSION PARAMETERS AFFECTING HTGR CORE CORROSION

In order to assess the overall effect of steam attack on a reactor core, it is necessary to extrapolate from laboratory-scale experimental reaction rate data, taking into account the expected conditions of steam and hydrogen concentrations, temperature distribution (both radially and axially), and catalyst concentration.

Other parameters of importance, considering the high helium pressures and turbulent gas flow conditions of an HTGR core, are mass transfer and in-pore diffusion effects.

In order to assess the reactant mass transfer limitation, it is necessary to factor in total helium pressure, flow rate, and coolant hole

geometry. These effects have been calculated by Pointud and Romberg⁽²⁰⁾ from the expression

$$K_{MT} = D d / 0.023 H_{Re}^{0.78} N_{Sc}^{0.33}, \quad (7)$$

where

D = diffusion coefficient of H_2O in the boundary layer,

d = hydraulic diameter of a coolant channel,

N_{Re} = Reynold's number,

N_{Sc} = Schmidt number, and

K_{MT} = mass transfer coefficient.

In general, their calculations show that the steam-graphite reaction for turbulent flow conditions becomes mass-transfer-limited above $800^\circ C$.

Another important consideration concerning the reaction of gases with porous solids is the effect of in-pore diffusion. This may be especially important in reactors where the temperature gradient across the graphite septum will tend to increase corrosion in depth. These effects have been considered by Wicke, et al.⁽²¹⁾ for the Dragon project. They found that application to HTGR conditions indicates that in-pore diffusion is severely restricted at high helium pressures; therefore, graphite corrosion should occur almost entirely at the coolant surface.

5.4 ANALYTICAL APPROACH DEVELOPED UNDER THE DRAGON REACTOR PROJECT

Everett, Kinsey, and Romberg⁽¹⁶⁾ of the Dragon project in England have developed an integrated theory of carbon transport for HTGRs. They show that the reactivity of the core and the coolant purification rate determine the level and relative concentrations of the impurities hydrogen and water. Furthermore, they suggest that the most important parameter in

this regard is the H_2/H_2O ratio $\left(P_{H_2}/P_{H_2O} \right)$. In their analytical approach, they derived the relationship

$$\frac{P_{H_2}}{P_{H_2O}} = \frac{R_c}{r}, \quad (8)$$

where

$$R_c = \text{core reactivity} \left(\frac{\mu \text{atm } H_2O \text{ reacting}}{\mu \text{atm } H_2O \text{ present}}, \text{ hr}^{-1} \right), \text{ and}$$

$$r = \text{purification rate constant} \left(\frac{\text{purification flow}}{\text{coolant inventory}}, \text{ hr}^{-1} \right).$$

The importance of the H_2/H_2O ratio is seen by considering the following reactions

or

and

Reactions (9a) and (9b) are important in considering carbon deposition phenomena because iron oxide formation limits carbon deposition. (Carbon deposition occurs only on reduced metal surfaces; see Section 6.1.5.)

The equilibrium constants for the above reactions are

$$K_{9a} = \frac{P_{H_2}}{P_{H_2O}},$$

$$K_{9b} = \frac{P_{H_2}}{P_{H_2O}},$$

and

$$K_{10} = \frac{P_{CO} P_{H_2}}{P_{H_2O}}.$$

In a similar fashion carbon and iron can be oxidized by carbon dioxide, by these reactions:

which give rise to the equilibrium constants

$$K_{11a} = \frac{P_{CO}}{P_{CO_2}}$$

$$K_{11b} = \frac{P_{CO}}{P_{CO_2}}$$

$$K_{12} = \frac{(P_{CO})^2}{P_{CO_2}}$$

Thus, low values for H_2/H_2O and CO/CO_2 favor oxidation of both iron and carbon. High H_2/H_2O and CO/CO_2 ratios favor reduction of iron oxide and deposition of carbon.

Everett et al.⁽¹⁶⁾ have calculated values of the equilibrium constants for Reactions (9a), (9b), (10), (11a), (11b), and (12). Their results clearly show how carbon deposition is limited at low temperatures by iron oxide formation and at high temperatures by shifting Reaction (10) to the right, i. e., by shifting from the carbon deposition side of equilibrium to the graphite oxidation side. For example, at $P_{CO} = 10^{-3}$ atm and $P_{H_2}/P_{H_2O} = 20$, carbon deposition can occur only between approximately 300° and 500°C. (At low temperatures, kinetic effects also restrict carbon deposition.)

At 400°C (a typical temperature for steam generator metal surfaces), K_{9b} has a value of 8 and K_{11b} has a value of around 0.7. Therefore, at this temperature carbon deposition cannot proceed if the H_2/H_2O ratio is equal to or less than 8 and/or if the CO/CO_2 ratio is equal to or less than 0.7. It is apparent from Eq. 8, therefore, that for a particular integrated core reactivity, R_c , the size of the reactor purification system could be chosen so that $H_2/H_2O \leq 8$; consequently, carbon deposition would not occur in this case.

It is possible to calculate the expected H_2/H_2O and CO/CO_2 ratios (neglecting the extra impurities due to graphite outgassing and other sources) for a particular reactor from the fixed purification rate constant, r , and from estimates of the integrated graphite reactivity, R_c . These calculations have recently been made using computer analytic techniques (see Section 5.5).

5.5 COMPUTER ANALYSES FOR STEAM GRAPHITE SYSTEMS

Computer codes have been developed at Gulf General Atomic, Oak Ridge National Laboratory, and Battelle Northwest Laboratory for analyzing core corrosion in HTGRs. The Gulf General Atomic code⁽²²⁾ was developed primarily for reactor accident analysis, as in the case of a steam tube rupture. The ORNL computer program (Steamcar)⁽²³⁾ was also developed for the analysis of the accidental, large-steam-leak case. The ORNL code will be used in conjunction with a high pressure, high flow steam-graphite loop experiment presently being developed at ORNL.

The computer program (GOP) developed at Battelle Northwest Laboratory⁽²⁴⁾ has been applied by BNWL personnel for calculating gaseous impurity concentrations and core corrosion profiles for the Fort St. Vrain reactor for the steady-state case where $P_{H_2} + P_{H_2O}$ is constant and low. The GOP program accomplishes the following:

1. Utilizes reaction rate constants for the thermal and radiolytic Reactions (1) and (2) and for the radiation-induced shift Reaction (3).
2. Adjusts reaction rates for axial temperature profiles.
3. Factors in mass transfer and in-pore diffusion parameters.
4. Calculates axial graphite corrosion profiles.
5. Calculates changes in gaseous impurity concentrations as well as equilibrium or steady-state levels, taking into account the water in-leakage rate and helium purification rate.

The steady-state gas impurity concentrations for the Fort St. Vrain reactor have been calculated by the GOP code where $P_{H_2} + P_{H_2O} = 10$ vpm (in He at 48 atm). Table 1 lists the results of the analysis for the case where thermal processes only are considered. Table 2 shows data for both thermal and radiation induced reactions.

It is of interest that for the purely thermal case quite low H_2/H_2O ratios persist even at relatively high assumed graphite oxidative reaction rates. Since the equilibrium H_2/H_2O ratio for the iron-iron oxide system is 4.2 at 500°C, the maximum surface temperature for the steam generators, the metal surfaces should be in the oxidized state and consequently carbon deposition is not expected to occur.

In Table 2, where both thermal and radiolytic processes are considered, the H_2/H_2O ratios are from 4.0 to 11.6, (for the two graphite reactivities of interest) which somewhat exceeds the equilibrium H_2/H_2O

Table 1

STEADY-STATE GAS COMPOSITION IN FORT ST. VRAIN
HTGR; THERMAL REACTIONS ONLY*

Relative Graphite Reactivity ⁺	mm Hg					
	H ₂ O	CO	CO ₂	H ₂	H ₂ /H ₂ O	CO/CO ₂
0.1K	1.69×10^{-1}	1.82×10^{-1}	1.9×10^{-3}	1.91×10^{-1}	1.1	96
1.0K	7.72×10^{-2}	2.82×10^{-1}	6.10×10^{-4}	2.83×10^{-1}	3.7	460
10.0K	3.18×10^{-2}	3.27×10^{-1}	1.5×10^{-4}	3.29×10^{-1}	10.3	2180

Table 2

STEADY-STATE GAS COMPOSITION IN FORT ST. VRAIN
HTGR; THERMAL AND RADIATION REACTIONS*

Relative Graphite Reactivity ⁺	mm Hg					
	H ₂ O	CO	CO ₂	H ₂	H ₂ /H ₂ O	CO/CO ₂
0.1K	8.0×10^{-2}	5.0×10^{-2}	1.5×10^{-1}	3.2×10^{-1}	4.0	0.33
1.0K	2.80×10^{-2}	1.05×10^{-1}	1.15×10^{-1}	3.25×10^{-1}	11.6	0.91
10.0K	9.0×10^{-3}	2.3×10^{-1}	6.0×10^{-2}	3.6×10^{-1}	40.0	3.8

* Taken from BNWL report by Giberson and Tingey, Ref. 19.

⁺ Since the true reactivity of the Fort St. Vrain reactor graphite is unknown, results of calculations are given for three different graphite reaction rates. The reactivity designated by 1.0K is in fact the reactivity of TSX graphite following oxidation to 5% burnout, which is known to increase the reactivity by approximately a factor of 10. Thus, it is estimated that the three reactivities considered cover the full range of reactor core oxidative susceptibility. That is, 0.1K is considered to be the reactivity of new, noncatalyzed graphite. 1.0K might well approximate HTGR graphite whose reactivity has been increased by fission product catalysis and or substantial oxidative burnout. 10K is regarded as extreme and is listed here only for comparative purposes. A reactivity of 10K would arise only if the HTGR graphite is quite heavily contaminated with catalysts, such as impurity metals or fission products.

ratio for the iron-iron oxide system at 500°C . The CO/CO_2 ratio, however, is seen to range between 0.33 and 0.91. Since the equilibrium CO/CO_2 ratio for the iron-iron oxide system is 0.8 at 500°C , one speculates that carbon deposition will not occur at these conditions.

The GOP computer analysis for the Fort St. Vrain reactor also showed that maximum localized corrosion through one core lifetime for a constant water ingress of 0.04 lb/hr will be less than 2%. Therefore, no significant effect on the physical properties of the graphite is expected.

The GOP program was used also to calculate a value of the $\text{H}_2/\text{H}_2\text{O}$ ratio for the Dragon Reactor steam injection experiment.

5.6 THE DRAGON REACTOR STEAM INJECTION EXPERIMENT⁽²⁵⁾

In a simple and important experiment, Dragon project personnel obtained data that aid prediction of the integrated reactivity of an HTGR core. The experiment involved injecting water into the primary helium coolant system of the Dragon reactor during full power operation, where the peak graphite temperature was about 1000°C .

Injection of water was accomplished at a rate of approximately 3 g/hr for 18 hours following an initial injection of 10 g during the first hour. All chemical species in the coolant were carefully monitored during the test.

The measured $\text{H}_2/\text{H}_2\text{O}$ ratio throughout the first test was 1.2 to 1.3. This value is somewhat lower than the Dragon workers' calculated prediction based on thermal reaction rate data. They concluded that the steam injection tests results showed that thermal oxidation reactions controlled the core reactivity, and that radiolytic processes were relatively unimportant.

The GOP computer code at BNWL (described above) was programmed with the conditions of the Dragon steam injection tests. The code calculated that $\text{H}_2/\text{H}_2\text{O} = 1.1$, which is in excellent agreement with the measured values.

5.7 CONCLUSIONS ON GRAPHITE OXIDATION WORK

Graphite oxidation work has led to the following conclusions which pertain to normal reactor operation:

1. The graphite oxidation process of most concern in the HTGR program is the thermally induced steam-graphite reaction.
2. The reaction rate of the steam-graphite reaction is controlled by (1) temperature, (2) steam concentration, (3) hydrogen concentration (4) catalysts present, and (5) burnoff. Considerable experimental data are available on the effects of these variables.
3. At the graphite temperatures involved in reactor operation (800° to 1000°C), the thermal oxidation reactions predominate over the radiolytic processes.
4. In-pore diffusion is severely restricted at the high helium pressures in an HTGR; therefore, graphite corrosion should occur almost entirely at the coolant surfaces.
5. The ratios of hydrogen to water and carbon monoxide to carbon dioxide in the helium coolant are important because the relative concentration of these species controls the formation of iron oxide on the metal surfaces in the coolant circuit. (Carbon deposition does not occur on oxide-coated surfaces.) Thermodynamic considerations indicate that at the typical metal surface temperature of 400°C , iron oxide is stable at $\text{H}_2/\text{H}_2\text{O}$ ratios less than about 8, and CO/CO_2 ratios less than 0.7.
6. These ratios are also important because at a given CO concentration they fix the direction of the carbon deposition reactions $\text{CO} + \text{H}_2 = \text{H}_2\text{O} + \text{C}$ and $2\text{CO} = \text{CO}_2 + \text{C}$.
7. Under steady-state conditions, the $\text{H}_2/\text{H}_2\text{O}$ ratio is related to R_c/r , where R_c is the core reactivity ($\mu\text{ atm H}_2\text{O reacting} / \mu\text{ atm H}_2\text{O present}$) and r is the purification rate (purification flow/coolant inventory) per unit time.
8. A computer program (GOP) developed at Battelle Northwest Laboratory has found application in predicting gas impurity concentrations and core corrosion profiles for HTGR reactors.
9. Application of the GOP computer code to the case of the Fort St. Vrain reactor where $P_{\text{H}_2} + P_{\text{H}_2\text{O}} = 10\text{ ppm}$ yielded low

values for the H_2/H_2O and CO/CO_2 ratios at steady state, indicating that, on the basis of existing data and neglecting other sources of impurities, carbon deposition should not be a problem. The calculation indicated that localized graphite oxidation will not be a problem.

10. In a Dragon steam injection experiment, the measured H_2/H_2O ratio was around 1.2. The GOP computer code at BNWL calculated $H_2/H_2O = 1.1$, which is in excellent agreement with measured values.

6.0 CARBON DEPOSITION REACTIONS

The carbon deposition reactions

and

occur on certain metal surfaces. They do not occur to a measurable extent in the gas phase or on graphite. They are, however, somewhat enhanced by radiolytic processes.

Carbon deposition is observed to proceed under reducing conditions after a suitable incubation period during which the metal surface is rendered catalytic by reduction or by carbide formation. The carbon deposit grows from the metal surface as long graphite tendrils.

Possible effects of carbon deposition in an HTGR reactor are:

1. Carburization of heat exchanger tubes in depth, resulting in metal embrittlement.
2. Production of sooty carbon dust which may foul exchanger surfaces, resulting in poorer heat transfer properties. This effect is deemed unimportant.
3. Production of carbon dust which could become entrained in the He coolant. This dust could act as a carrier for fission products.
4. Production of carbon dioxide and water which enhance core corrosion.

Carbon deposition is of concern in the HTGR program because, as discussed below, the necessary parameters that tend to maximize the process may occur in a portion of the heat exchangers of an HTGR reactor.

6.1 FACTORS AFFECTING CARBON DEPOSITION

The metal-catalyzed carbon deposition reactions have been shown to be influenced by the following parameters:

1. Temperature
2. Reactant concentration (CO and H₂)
3. Kind of metal catalyst
4. Surface pretreatment
5. Water or carbon dioxide content
6. Other factors

Each of these parameters is discussed below in terms of experimental results obtained at Gulf General Atomic and under the Dragon reactor project in England

6.1.1 Temperature

Carbon deposition reactions are observed to occur in the temperature range 300° to 600°C. The reaction rate maximizes at 450° to 500°C, depending on the gas composition. The reason for this temperature dependence is that the reactions are inhibited at higher temperatures by thermodynamic considerations (that is, at high temperatures the reactions tend to proceed in the reverse direction) and at lower temperatures by reaction kinetics. Thus, it appears that the reaction rates maximize at typical heat exchanger temperatures (in the range 400° to 500°C).

6.1.2 Reactant Concentration

Experiments at Gulf General Atomic⁽²⁶⁾ have shown that at 500°C each of the two carbon deposition reactions obeys approximately second-order kinetics. Studies on mild steel and 2-1/4% Cr-1% Mo alloy yielded the rate expressions

$$R (\mu\text{g C/cm}^2 \text{ hr}) = 5 \times 10^4 (P_{\text{CO}})^{1.6}$$

for Reaction (13) and

$$R (\mu\text{g C/cm}^2 \text{ hr}) = 5 \times 10^4 (P_{\text{CO}} P_{\text{H}_2})^{0.8}$$

for Reaction (14), where the pressures are in atmospheres. These rate equations were obtained from experiments on highly catalytic surfaces (i. e., the samples had experienced massive carbon deposition) and therefore must be regarded as approximate maxima.

The slight departure from regular second-order kinetics may be explained by invoking the Langmuir adsorption kinetic approach to heterogeneous reactions. This approach says that the rate of a reaction occurring on a catalyst surface is proportional to θ , the fraction of the surface covered with reactant molecules; but θ is limited by co-adsorption of reaction products, as indicated by the expression

$$-\frac{d(\text{CO})}{dt} = K'\theta = \frac{K_1 P_{\text{CO}} P_{\text{H}_2}}{(1 + K_2 P_{\text{CO}} + K_3 P_{\text{H}_2} + K_4 P_{\text{CO}_2} + K_5 P_{\text{H}_2\text{O}})^2}$$

where K_2 , K_3 , K_4 , and K_5 are equilibrium adsorption constants for the respective gases. Depending on the magnitude of the denominator, the apparent order of the reaction must be less than 1, and, as mentioned above, the reaction order has been found experimentally to be 0.8.

6.1.3 Type of Metal Surface

It has been shown that iron, cobalt, and nickel are effective catalysts for the carbon deposition reactions. The metals must be in the reduced state as the oxides are noncatalytic. Chromium, for instance, is noncatalytic because chromium oxide (Cr_2O_3) is relatively stable. Thus, it has been shown that alloys with high chromium content are quite noncatalytic under reactor conditions because of a coherent chromium-oxide film that covers the surface. Carbon deposition experiments using high-chromium alloys invariably show declining reaction rates with time because of the development of chromium oxide surface protection.

The time dependence of the carbon deposition rates on mild steel or low-chromium alloys is quite different. No carbon deposition is seen for the first several hours, owing to the so-called incubation period during which time the iron surfaces are being reduced. The reaction then increases rapidly, and after a few hours a heavy carbon deposit forms.

6.1.4 Surface Pretreatment

Because of the inhibition due to surface oxides, carbon deposition is enhanced by removing the oxide layer either by acid etching or by hydrogen reduction, prior to starting the test. Roughened cold-worked surfaces appear to be more catalytic than bright, smooth, annealed surfaces. Selective preoxidation of chromium alloys has also been shown to reduce substantially the ultimate rate of deposition.

6.1.5 Effect of Oxidizing Gaseous Impurities

Oxidizing impurities in the reactor coolant, such as water, carbon dioxide, and oxygen, can inhibit carbon deposition by oxidation of the catalytic metal surface. During reactor operation, carbon dioxide and water will be the oxidants of consequence. During periods of shutdown, oxygen may be a contaminant and would be expected to contribute to passivation of the metal surfaces, even at quite low temperatures. Reactor shutdown, however, is expected to occur infrequently; thus the major mechanism for metal oxidation must be by carbon dioxide and water.

The thermodynamic equilibria for the Fe-FeO-Fe₂O₃-H₂-H₂O-CO-CO₂ system have been treated by Everett, Kinsey, and Romberg⁽¹⁶⁾ (see Section 5.4 for details). The important point of their analysis is that carbon deposition cannot occur under oxidizing conditions where iron oxide is stable. Their thermodynamic treatment indicates that at the typical metal surface temperature of 400°C carbon deposition cannot occur if $P_{H_2}/P_{H_2O} \leq 8$ or $CO/CO_2 \leq 0.7$.

It is apparent that the integrated chemical reactivity of the graphite core to gaseous impurities (and the presence of other H_2 impurities) will establish the ratios H_2/H_2O and CO/CO_2 and will therefore dictate whether or not carbon deposition will occur.

6.1.6 Other Factors Affecting Carbon Deposition

The above treatment lists the conditions under which carbon deposition will or will not occur. There are apparently other more subtle factors that partially control the process.

In experiments at Gulf General Atomic, ^(26, 27, 28) it has been shown that for laminar flow conditions carbon deposition always occurs to a large extent on the leading edge of steel foil samples. Moreover, if samples are placed in tandem, invariably only the first specimen develops a massive carbon deposit, the downstream samples remaining free from surface carbon.

One speculates that the reaction on the downstream samples may be inhibited by the reaction products CO_2 and H_2O arising from the first sample. This may be true even though the CO_2 and H_2O levels over these samples are too low to be on the oxidizing side of the thermodynamic equilibrium. It is suggested that small amounts of H_2O or CO_2 may interfere with the kinetics of carbon deposition by competitive adsorption on sites preferred by CO.

Everett et al. ⁽¹⁶⁾ reported the results of experiments in which for low concentrations of reactant and H_2 (i.e. below 1300 ppm) the carbon deposition rate reached a maximum (after an incubation period) and then declined to an immeasurable value. It was theorized that a protective layer of iron carbide forms. In a recent private communication, Everett related that they no longer believe these earlier results. They now believe that after a period of time or after a change in conditions, further carbon deposition will occur.

In more recent experiments at Gulf General Atomic, (29, 30, 31) two specimens of mild steel were exposed to 1000 ppm CO and 1000 ppm H₂ in He at 500°C. In both tests the inlet gas was scrubbed free of CO₂ and H₂O. In one test, however, 10 to 20 ppm H₂O was continuously added to the gas mixture (i. e., H₂/H₂O was 50 to 100). In both tests, carbon deposition proceeded unchecked after an incubation period of 120 days.

The results suggest that low concentrations of H₂O vapor are not inhibiting. Whether or not CO₂ is an inhibitor is an area for future study.

6.2 CARBURIZATION OF METALS

Experiments were performed by Weinberg and Scoffin⁽³²⁾ and others at Gulf General Atomic. In these tests several candidate metals, including both high-chrome and low-chrome alloys, were exposed to CO-H₂-He mixture at 1100° and 1375°F. Exposure times to 9000 hours were employed. Changes in weight, carbon content, strength, and ductility were measured for both thin and thick bar specimens. Results and conclusions of the tests are as follows:

1. Carburization of nickel-based and austenitic stainless steels by carbon deposition processes occurs to a slight extent at 1100° and 1375°F.
2. The depth of carbide penetration never exceeded 0.010 in., and the rate of diffusion became extremely slow after 6000 hours.
3. A dense layer of carbide and spinel appeared to effect a barrier to further diffusion and precipitation of carbon.
4. Embrittlement of thin foil specimens occurred. The mechanical properties of 0.095-in. -thick samples was unaltered.
5. Low Cr-Mo alloys were unaffected by the impure atmosphere at 1100°F.

These data indicate that embrittlement of steam-generator tubes due to carburization will be negligible for times up to 9000 hours. However, a 9,000-hour test is only a small fraction of the proposed 30-year steam generator life.

6.3 CARBON DUST PROBLEM

Entrainment of carbon dust in the helium coolant could arise if the fluffy carbon deposit extended above the stagnant gas film into the turbulent stream where the shear forces are great. This dust would tend to sorb fission products and thus become a potential source of gas-borne radioactivity. The dust would be filtered out of the coolant stream.

It is difficult to estimate the production rate of carbon dust in a reactor as brought about by carbon transport and deposition because of the discontinuous nature of the reactions. By direct extrapolation from laboratory data, however, one can arrive at a maximum carbon dust generation rate by this mechanism for the Fort St. Vrain reactor.

The metal surfaces in the reactor have $5.6 \times 10^7 \text{ cm}^2$ of catalytic surface area (considering only mild steel or low-chrome-alloy surfaces which operate in the temperature region 350° to 600°C) for which the normalized carbon deposition rate is $0.28 \mu\text{g C/cm}^2 \text{ hr}$ (corresponding to an impurity concentration of 5×10^{-4} atm each CO and H_2). The resulting maximum carbon dust generation rate is approximately 300 lb/year.

It should be stressed that this calculation, which is based on laboratory data, is probably conservative (too high) because of the inhibiting effects of surface oxides and gas-phase oxidant levels upon the carbon deposition process.

6.4 CONCLUSIONS ON CARBON DEPOSITION STUDIES

Carbon deposition studies have led to the following conclusions:

1. Carbon deposition will occur on steel and low-chrome-alloy surfaces of a reactor if the following conditions exist:
 - a. Metal temperatures of 350° to 650°C prevail.
 - b. The coolant gas mixture is reducing to iron.
 - c. Carbon monoxide and hydrogen partial pressures are maintained at sufficiently high levels and for a sufficiently long period of time to render the metal surfaces catalytic. With CO and H_2 each at $500\text{ }\mu\text{atm}$, the incubation period for mild steel is estimated to be 4 to 6 months.
2. Carburization in depth with subsequent embrittlement of steam generator tubes may occur if carbon deposition is allowed to proceed unchecked for several years.
3. If massive carbon deposits develop, then dust entrainment may prove to be a problem.

7.0 NEEDED WORK

Even though much is known about the carbon transport cycle, the incentive for further studies remains. Studies are needed (1) to verify that carbon transport is not a problem in the Fort St. Vrain reactor and (2) to furnish accurate information for use in the design of future HTGR reactors.

For reactors having large coolant purification systems, such as Peach Bottom or Dragon, results of both computer-code calculations and the Dragon steam injection experiment indicate that the H_2/H_2O ratio will be in the range in which oxide formation limits carbon deposition. This desirable condition should persist even after several years of operation when the core graphite is more reactive to steam due to fission product catalysis.

The situation is not as clear for the second generation HTGR such as the Fort St. Vrain reactor. For this case, assuming a noncatalyzed core, the calculated H_2/H_2O and CO/CO_2 ratios are below the thermodynamic limits for the iron-iron oxide systems.* It is possible, however, that the H_2/H_2O or CO/CO_2 ratio could increase in time due to increased graphite reactivity or to other sources of impurity contamination in the primary coolant.

The design of future HTGRs may result in higher graphite temperatures (increased core reactivity), and information on carbon transport phenomena will be important in designing purification systems that will maintain H_2/H_2O ratios within acceptable levels.

The work needed in the continuing effort to study the carbon transport cycle consists of (1) continued development and utilization of computer codes, (2) continued studies to improve the reliability of input data for the computer codes, (3) further reactor steam injection experiments, and (4)

* See Section 5.4.

continued investigation into carbon deposition processes. These are discussed in more detail in the following:

1. Computer Code Studies - Owing to the complexity of the oxidation of a graphite core, it is realized that only suitable computer codes can successfully analyze the problem. Engineering scale loop experiments are hampered by the difficulty of duplicating all pertinent reactor conditions. Therefore, future work needs to be directed toward perfecting existing computer codes and supplying additional needed fundamental reaction rate data.
2. Experimental Data - More fundamental experimental data are required in the following areas:
 - a. Effect of catalysts on reaction rates. Much work has been done in the past on iron, barium, strontium, and cesium. More work on the effect of these and other fission products, such as europium and cerium, on graphite oxidation rates is needed. The effect of catalyst concentration gradients should also be investigated.
 - b. Effect of temperature gradients. In the HTGR fuel elements, a sharp temperature gradient exists from the fuel hole centerline ($\sim 1200^{\circ}\text{C}$) to the surface of the coolant channel ($\sim 900^{\circ}\text{C}$). This effect, combined with the catalyst concentration gradient could lead to enhanced oxidation of graphite in depth.
 - c. Effect of in-pile radiation on the steam-graphite system.
 - d. More fundamental data on the effect of such variables as temperature, burnoff, and hydrogen and carbon monoxide concentrations, especially for various candidate nuclear graphites.
 - e. Effect of helium pressure. Data are needed on the effective diffusion coefficient of water through graphite as a function of helium pressure.
3. Future Reactor Steam Injection Tests - The Dragon reactor in England has been used for steam injection experiments. (The procedure is to slowly add water vapor to the main helium circuit at a specified rate. All gas phase constituents are then carefully monitored throughout the test. From the measured $\text{H}_2/\text{H}_2\text{O}$ the core reactivity is then calculated.) Similar tests

at the Peach Bottom HTGR or the Ultra-High-Temperature Reactor Experiment (UHTREX) in the United States should be instituted. The resulting data could be compared with expected results based on a computer analysis. A steam injection experiment, therefore, not only yields direct measurement of the core reactivity but also serves as an excellent check on computer analytic techniques.

8.0 EXPERIMENTAL WORK UNDER WAY

Investigators at three laboratories in the United States (GGA, ORNL, and BNWL) are conducting experimental work related to carbon transport phenomena. A brief outline of these experimental programs is given below.

1. Work at Gulf General Atomic - Apparatus is being set up for use in experimental work to study the effect of helium pressure on steam graphite reaction rates. A high-pressure furnace capable of temperatures to 1000°C and gas pressures to 750 psig is presently under construction. The technique will be to measure reaction rates by sample weight change and gas analysis as a function of helium pressure from one to 50 atm. The same equipment will be used to determine the effective diffusion coefficient of water through graphite at varying helium pressures.
2. Work at Battelle Northwest Laboratory - Experiments on the radiation-induced steam-graphite reaction using a cobalt-60 source are in progress. Analytical work using the GOP computer code is being pursued. Oxidation of boronated graphite by oxygen and water is also presently being studied.
3. Work at Oak Ridge National Laboratory - Fundamental studies on the steam graphite reaction are continuing. This includes work on the oxidation of fueled graphite compacts. Data on fission product release and transport during steam attack is being obtained for both in-pile and out-of-pile tests. Engineering scale tests on steam attack at high temperatures using a high pressure steam loop system will yield data on extreme accident conditions. Data from this work are to be analyzed by use of the Steamcar computer program.

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