United States Department of Energy
Office of Environmental Management

**Graphite Oxidation
Thermodynamics/Reactions**

September 1998

**U.S. Department of Energy
Environmental Management
Spent Fuel Management Office**

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Graphite Oxidation Thermodynamics/Reactions

W. A. Propp

Published September 1998

**Idaho National Engineering and Environmental Laboratory
National Spent Nuclear Fuel Program
Lockheed Martin Idaho Technologies Company
Idaho Falls, Idaho 83415**

**Prepared for the
U.S. Department of Energy
Assistant Secretary for Environmental Management
Office of Spent Fuel Management and Special Projects
Under DOE Idaho Operations Office
Contract DE-AC07-94ID13223**

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September, 1998

Prepared By: William Alan Propp
W. A. Propp

Date: 9/23/98

Approved By:

C. L. Bendixsen for C. L. BENDIXSEN
C. L. Bendixsen, Program Manager/Technical Lead

Date: 9/23/98

D. L. Batt
D. L. Batt, Manager, National SNF Program

Date: 23 September 1998

J. H. Boyd
J. H. Boyd, NSNF Program Manager

Date: 9/23/98

A. D. Anderson for R. D. Davis
R. D. Davis, Quality Assurance Program Manager

Date: 9/23/98

ABSTRACT

The vulnerability of graphite-matrix spent nuclear fuel to oxidation by the ambient atmosphere if the fuel canister is breached was evaluated. Thermochemical and kinetic data over the anticipated range of storage temperatures (200 to 400°C) were used to calculate the times required for a total carbon mass loss of 1 mg·cm⁻² from a fuel specimen. At 200°C, the time required to produce even this small loss is large, 190,000 yr. However, at 400°C the time required is only 1.9 yr. The rate of oxidation at 200°C is negligible, and the rate even at 400°C is so small as to be of no practical consequence. Therefore, oxidation of the spent nuclear fuel upon a loss of canister integrity is not anticipated to be a concern based upon the results of this study.

SUMMARY

This study assessed the vulnerability of graphite-matrix spent nuclear fuel to oxidation by the ambient atmosphere in a geologic repository if the fuel canister is breached. Decay heat generated by the fuel is expected to produce storage temperatures of 200 to 400°C. The pertinent thermochemical and kinetic data were reviewed for potential reactions of the graphite (carbon)/water/oxygen system in this temperature range.

The thermodynamic evaluation led to the following predictions and conclusions:

- Carbon dioxide is thermodynamically favored as the principal product of combustion
- There is a significant potential for the production of carbon monoxide; however, this carbon monoxide will subsequently be consumed to produce carbon dioxide
- The potential for direct reaction of water with graphite is small
- The most likely reaction in the presence of water is the water-gas shift reaction
- Neglecting radiolysis, the decomposition of water into elemental hydrogen and oxygen is negligible; in fact, the reverse reaction, the formation of water from the elements, is favored
- Methane formation is not significant
- The main effect of water radiolysis is to slightly increase the level of oxygen in the storage atmosphere.

The kinetic analysis, based upon these findings of the thermodynamic evaluation and assuming an Arrhenius-type rate expression for kinetics, concluded that the values of k , the reaction rate constant, are very small but exhibit a marked temperature dependence. At 400°C, k is over 2×10^5 times larger than at 200°C. To evaluate the significance of these results, the time required for a total carbon mass loss of $1 \text{ mg} \cdot \text{cm}^{-2}$ from a graphite sample exposed under these conditions was calculated. Even at 400°C the rate is so small to be of no practical consequence--approximately 2 yr are required to produce the insignificant mass loss of $1 \text{ mg} \cdot \text{cm}^{-2}$, which corresponds to a material thickness loss of approximately 0.4 mm in 190 yr. Therefore, oxidation of the spent nuclear fuel upon a loss of canister integrity is not anticipated to be a concern.

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Graphite Oxidation Thermodynamics/Reactions

INTRODUCTION

The Department of Energy's (DOE) spent nuclear fuel (SNF) inventory includes a variety of fuels with a graphite (carbon) matrix. The objective of this study was to identify and evaluate potential reactions between the SNF's carbon matrix and water and or oxygen in geologic a repository in the event of a breach of the fuel canister.

Carbon has been studied intensively because of its importance as a major energy source (through combustion) and its numerous industrial uses. Its applications in the nuclear industry include moderators, reflectors, heat shields and thermal columns, control rods, and matrix material in fuel rods. Because these varied applications are based on numerous studies of the behavior of carbon under exposure to air and water over a wide range of temperatures and pressures, the thermodynamics of the carbon/oxygen/water system are well established. However, there are still discrepancies between studies and uncertainties with regard to the kinetics and reaction mechanisms of this system.

For this study, a literature review of the thermodynamics of the carbon/oxygen/water system identified potential reactions; these were evaluated for possible adverse consequences. The kinetics of any thermodynamically favorable reaction were then evaluated to determine if the rates are sufficiently rapid under the stated conditions to create potential problems during storage of the SNFs. The potential carbon mass that might be lost from an SNF matrix was calculated and found to be insignificant.

The following sections present background on the carbon matrix of these fuels, a detailed evaluation of the thermodynamics of the carbon/water/oxygen system, and a detailed analysis of the kinetics of the reactions that were deemed to be most favorable thermodynamically. In this report the term "graphite" is used generically to refer to carbon-matrix SNFs composed of various forms of carbon, including both graphite and pyrolytic carbons. These materials are discussed in detail in the section on carbon allotropes.

BACKGROUND

Repository Disposal of Carbon-Matrix SNF

Carbon-matrix fuels typically are comprised of encapsulated fuel particles contained in some type of a carbonaceous matrix. The fuel itself is usually uranium dioxide, UO_2 , sometimes mixed with uranium carbide (either the monocarbide, UC, or the dicarbide, UC_2). The fuel particles often are coated with multiple layers of various forms of pyrolytic carbon and, in some cases, silicon carbide. The carbonaceous matrices are generally formed from graphite with the addition of a viscous organic liquid, such as pitch, to serve as a binder. After mixing the fuel components, green fuel compacts are formed by extrusion. The green compacts are fired to pyrolyze the binder to convert it into elemental carbon and to sinter and consolidate the fuel.

Fuels of this type include Peach Bottom, Fort St. Vrain, and others manufactured for high-temperature gas-cooled reactors. The majority of the spent fuels of this type are stored at the Idaho National Engineering and Environmental Laboratory (INEEL); the INEEL has approximately 236 m^3 of these fuel wastes.¹ Nearly all of this SNF is stored in a dry condition, although some moisture has been noted in dry well storage at CPP-749 at the INEEL.

In repository disposal, the SNF would be dry until failure of the engineered barrier systems allowed water ingress. Temperatures in the repository are expected to reach a maximum of approximately 200°C within 50 yr waste disposal. To provide a safety factor, current requirements for waste acceptance specify that the waste package, including the SNF and the canister or other barrier systems, be capable of withstanding repository temperatures up to 400°C .

Carbon Allotropes

Carbon is available in many natural and manufactured allotropic forms, including graphite (natural and synthetic) and various types of pyrolytic carbon (synthetic). Whether natural or synthetic, graphite is crystalline with plate-like structures. Most industrial graphite is produced by firing mixtures of carbonaceous particulates and binders of coal tar or pitch. Pyrolytic carbon, also referred to as chemical vapor deposited (CVD) carbon or pyrocarbon, is produced by CVD of gaseous hydrocarbons, such as methane, onto heated graphite substrates.²

The morphology of pyrolytic carbon depends upon the specific conditions of its production, with the temperature being the primary factor. At lower temperatures, on the order of 1800°C , the product will be amorphous. Whereas at higher temperatures, on the order of 2400°C , or if the production cycle includes a high temperature annealing step, the product will be crystalline with a lattice spacing comparable to that of graphite.² The different morphologies of carbon result in minor differences in the physical properties of the various allotropes, such as the degree of anisotropy and the lattice spacings. However, the carbon allotropes are essentially identical chemically, exhibiting negligible differences in chemical reactivity. Therefore, this study has not differentiated between crystalline material and the various forms of pyrolytic carbon, and the term graphite is used generically to refer to any of the various forms encountered in SNFs.

Radiation Effects

The majority of the studies reviewed and referred to in this study used unirradiated samples of graphite. The use of irradiated samples would have made the experiments more difficult without

affecting the reactions or the thermodynamics of the graphite/gaseous environment system. The effects of irradiation on the reaction kinetics can also be assumed to be negligible.

There are two main effects that irradiation can have on graphite. The magnitudes of these impacts depend upon the strength of the radiation field and the length of exposure. The first effect is swelling and an increase in total surface area caused by the introduction of defects such as vacancies and increased porosity in the graphite matrix. The increased surface area might increase the effective oxidation rate since this rate is implicitly dependent upon exposed surface area. However, such changes in surface area will not affect the fundamental thermodynamic reaction rate.

The second effect is the impact of the stored energy associated with the lattice strains and deformations produced by swelling. The impact of this stored energy has not been considered here. If large enough, it has the potential to lower the activation energy required for oxidation reactions, increasing the probability that they will occur.

Radiolytic decomposition of water to hydrogen and oxygen may also occur, increasing the concentration of oxygen in the atmosphere surrounding the SNF.

GRAPHITE OXIDATION THERMODYNAMICS/REACTIONS

The first consideration when determining the potential for the reaction of materials, such as spent nuclear fuel, with the environment is to identify the possible reactions that are thermodynamically favorable under anticipated conditions. There have been many studies of the reactions of various types of carbon exposed to gaseous environments containing elemental oxygen or oxygen compounds such as water and carbon dioxide. Most of these studies assumed that the atmosphere would be steam or dry oxygen, perhaps with inert gas diluents. Thus, the gaseous environment had a simple composition, with only one reacting species. This limits the number of reactions that are important and makes the reaction scheme was fairly straightforward.

In complex mixtures containing more than one reactant gas, the number of possible reactions is much larger, increasing the complexity of the reaction scheme significantly. Under these conditions, the reaction scheme must consider the possibility of competing reactions that occur either in parallel or consecutively. Studies under such conditions have established an accepted scheme summarizing all of the possible reactions of importance in the oxidation of graphite under a wide variety of conditions. This reaction scheme, which includes all of the potential reactions that could be of importance under exposure to complex reaction mixtures, has been summarized by a number of authors.^{3,4,5,6,7,8} Of particular interest is the paper by Walker, Rusinko, and Austin,⁸ which provides an extensive review of all of the pertinent work in the field. These authors present detailed discussions of all aspects of the reactions of graphite with oxygen-containing gases.

Reactions

The suite of reactions presented here encompasses all of those that might be important in the oxidation of graphite over the temperature range of interest, i.e., 200 to 400°C. It includes those that could proceed if water vapor is present, as well as those that could occur in the presence of oxygen. These overall reactions summarize the conversion of reactants to products but do not include all of the stepwise, detailed reactions that comprise the complete reaction mechanism. The relative importance of each of the reactions listed depends upon the environment, i.e., the temperature, pressure, composition of the atmosphere, and physical and chemical characteristics of the graphite.

Reactions for Oxidation of Graphite

At least four of these reactions have achieved some commercial importance. Rxn 1 is one of the basic reactions of the combustion process that supplies a major fraction of the world's energy requirements. Rxn 2 is combustion under conditions of insufficient oxygen. Rxn 3 is the water gas or synthesis gas reaction widely used to prepare carbon monoxide and hydrogen for industrial use. Finally, Rxn 5 is the water-gas shift reaction.

Most of the studies described in the literature exposed graphite to an atmosphere consisting either of steam or dry oxygen, perhaps with inert gas diluents. In a steam atmosphere, the pertinent reactions would be Rxns 3, 5, 7, and 8, with the primary oxidation reaction being Rxn 3 and carbon monoxide subsequently being converted to carbon dioxide by the water-gas shift reaction (Rxn 5). For a dry oxygen atmosphere, the pertinent reactions would be those not involving water, i.e., Rxns 1, 2, 4, and 6. In this case, Rxn 1 would be the primary oxidation reaction.

For repository disposal of SNF, the composition of the atmosphere is more complex. It is expected that loss of container integrity would expose the fuel to moist air (the water available depends on the relative humidity). Thus, for this scenario, the whole set of reactions listed above is potentially important. To determine the thermodynamic conditions favoring each of the reactions, the heats of reaction, equilibrium constants, and other thermodynamic parameters were compared.

Heats of Reaction and Changes in Mole Numbers

Table 1 presents the heat of reaction at 25°C (298°K) and 1 atm pressure, ΔH_{298} , for Rxns 1 through 8. These data were compiled from the *CRC Handbook*.⁹ For reactions involving only elements as reactants, ΔH_{298} corresponds to ΔH_f , the heat of formation of the products at 25°C. A positive value of ΔH_{298} indicates that the reaction, as written, is endothermic at 25°C and will not occur spontaneously; a negative value indicates that the reaction is exothermic and will occur spontaneously.

Also shown in Table 1 is the change in total moles of gas, Δn , that occurs during the course of each reaction. Here Δn is defined as the total moles of product gases minus the total moles of reactant gases. The change in mole numbers indicates of the effect of total applied pressure upon each of the reactions. Thus, if Δn is positive, the extent to which the reaction proceeds will decrease as the pressure increases. Conversely, if the change in moles is negative, the reaction will proceed to a greater extent at higher pressures. Finally, if Δn is zero, then the reaction should be unaffected by the total applied pressure. The pressure effect is in addition to the concentration effect produced by increasing the partial pressure of a gaseous reactant. For instance, the pressure effect can be due to introduction of an inert diluent gas.

Equilibrium Constants

The equilibrium constant, K_p , for Rxns 1 through 8 is formulated using the concentration of each of the gaseous species involved expressed as its partial pressure in atmospheres. The log of the equilibrium constant indicates the thermodynamic favorability of a reaction; if $\log(K_p)$ is positive the reaction will occur spontaneously. Furthermore, the greater the magnitude of $\log(K_p)$, the higher the tendency of the reaction to occur and the more complete the reaction will be. Conversely, if $\log(K_p)$ is negative, then the reverse of the reaction is more favored.

Gulbransen and Andrew⁷ and Walker, Rusinko, and Austin⁸ independently calculated the value of $\log(K_p)$ for Rxns 1 through 8 as a function of temperature from data¹⁰ compiled by the National Institute of Standards and Technology (formerly the National Bureau of Standards [NBS]). The NBS data was subsequently released as an official NBS publication.¹¹ The values of K_p in Table 2, taken from Gulbransen and Andrew⁷ and Walker, Rusinko, and Austin⁸, indicate the relative thermodynamic potential for the reaction to proceed spontaneously at the temperature for which K_p was calculated. Comparative K_p values indicate which reaction will be favored thermodynamically under those conditions. However, K_p does not include activation energy or the overall kinetics of the reaction.

TABLE 1. Heats of Reaction and Changes in Mole Numbers for Graphite Oxidation⁹

Reaction	Δn	ΔH_{298} (kcal/mole)
1. $C(s) + O_2(g) \rightleftharpoons CO_2(g)$	0	- 94.052
2. $C(s) + \frac{1}{2} O_2(g) \rightleftharpoons CO(g)$	+ $\frac{1}{2}$	- 26.416
3. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$	+ 1	+ 31.384
4. $CO(g) + \frac{1}{2} O_2(g) \rightleftharpoons CO_2(g)$	- $\frac{1}{2}$	- 67.636
5. $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$	0	- 9.836
6. $2 CO(g) \rightleftharpoons C(s) + CO_2(g)$	- 1	- 41.220
7. $C(s) + 2 H_2(g) \rightleftharpoons CH_4(g)$	- 1	- 17.889
8. $H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2} O_2(g)$	+ $\frac{1}{2}$	+ 57.80

TABLE 2. Log K_p as a Function of Temperature for Graphite Oxidation Reactions^{7,8}

Reaction	Temperature				
	25°C / 298.16°K	126.8°C / 400°K	226.8°C / 500°K	326.8°C / 600°K	426.8°C / 700°K
1	69.09	51.54	41.26	34.40	29.50
2	24.05	19.13	16.26	14.34	12.96
3	-16.00	-10.11	-6.63	-4.29	-2.62
4	45.04	32.41	25.00	20.06	16.54
5	4.99	3.17	2.11	1.43	0.96
6	20.99	13.28	8.74	5.72	3.58
7	8.90	5.49	3.43	2.00	0.95
8	-40.05	-29.24	-22.89	-18.63	-15.58

Discussion

Evaluation of the data presented in Tables 1 and 2 leads to some general observations about each of the reactions. These observations, summarized in Table 3, permit comparison of the relative pressure dependence and thermodynamic favorability of each of the reactions. Again, it must be noted that these observations are limited to the thermodynamics of the reactions and do not take into account the reaction kinetics.

From the thermodynamics information in Tables 1 through 3, the following predictions and conclusions about the proposed reactions can be made.

- Rxn 1, producing carbon dioxide by combustion of graphite, is the most thermodynamically favored reaction over the temperature range of interest
- Because it is energetically feasible, there is a significant potential for the production of carbon monoxide as a transitory combustion intermediate by means of Rxn 2; however, this carbon monoxide will be consumed to produce carbon dioxide by means of Rxns 4, 5, or 6, with Rxn 4 being most favorable energetically
- The potential for direct reaction of water with graphite (Rxn 3) is small because this reaction is highly unfavorable energetically. It becomes even more unfavorable when the low partial pressure of water vapor anticipated is taken into account
- Under the anticipated conditions, the most likely reaction in the presence of water is Rxn 5, the water-gas shift reaction
- Rxn 8, decomposition of water into elemental hydrogen and oxygen, will be of negligible importance over this temperature range. In fact, the reverse reaction, the formation of water from the elements, is favored energetically as a mechanism to consume the hydrogen produced by Rxns 3 and 5
- Methane formation by means of Rxn 7 is not expected to be a significant, particularly when the low levels of hydrogen anticipated to be present are taken into account.

Finally, as noted in the discussion of radiation effects, the radiolysis of water will serve primarily to increase the concentration of oxygen in the atmosphere.

TABLE 3. General Observations about Graphite Oxidation Reactions

Reaction	Observation/Comment		
	Exothermic/ Endothermic	Pressure dependence	Equilibrium
1. $C+O_2 \rightarrow CO_2$	highly exothermic	none	highly favorable at all temperatures
2. $C+O_2 \rightarrow CO$	exothermic	favored by low pressure	favorable at all temperatures
3. $C+H_2O \rightarrow CO+H_2$	endothermic	strongly favored by low pressures	not favored at any temperature
4. $CO+O_2 \rightarrow CO_2$	highly exothermic	favored by high pressures	very favorable at all temperatures
5. $CO+H_2O \rightarrow CO_2+H_2$	slightly exothermic	no pressure dependence	slightly favored at all temperatures
6. $CO \rightarrow C+CO_2$	moderately exothermic	strongly favored by high pressures	favorable at all temperatures
7. $C+H_2 \rightarrow CH_4$	slightly exothermic	strongly favored by high pressures	slightly favored at all temperatures
8. $H_2O \rightarrow H_2+O_2$	highly endothermic	favored by low pressures	highly unfavorable at all temperatures

KINETICS OF GRAPHITE OXIDATION REACTIONS

Background

The other major consideration when evaluating the potential for oxidation of graphite is the kinetics or rate of each of the proposed oxidation processes. Kinetics is significant because a reaction that is highly favored energetically may occur at such a slow rate that it is of no practical consequence. The term *process* is used for graphite oxidation because the reactions are heterogeneous, i.e., they involve reactions between the gaseous and solid phase. Heterogeneous processes are more complex and involve more steps than typical homogeneous reactions in the liquid or gas phase. For homogeneous reactions, rates are determined by the temperature and by the frequency of molecular collisions, which is proportional to the concentration of each of the reacting species. In the gas phase, concentration is directly proportional to the partial pressure for each species. For heterogeneous processes, physical processes may also affect the overall reaction or process. A process can typically be broken down into the following seven steps.

1. Diffusional transport of the reactant species across the boundary layer between the gas and solid phases
2. In-pore diffusion of the reactant to a suitable active site in the solid substrate
3. Adsorption of the reactant onto the active site
4. Chemical reaction between the reactant and the substrate
5. Desorption of the product species
6. In-pore diffusion of the product species away from the active site
7. Diffusional transport of the product species across the boundary layer.

Any of these steps may be rate determining under the right conditions. These steps each have some degree of temperature dependence. The rate of diffusion is typically proportional to $T^{0.5}$, where T is the absolute temperature. The rate of chemical reactions is proportional to $\exp(-A/T)$, where A is a constant. Because their temperature dependence is exponential, chemical reactions usually limit the process rate at low to moderate temperatures. At higher temperatures, where chemical reactions are very rapid, diffusion becomes rate determining.

The larger number of steps in heterogeneous processes increases the number of variables. Only temperature and pressure affect the rate of homogeneous reactions, but heterogeneous processes are affected by mass transfer, both within the gas phase and across the boundary regions between the gas and solid phases, and by the effective size of the solid phase participating in the various reactions. These two factors introduce the following additional parameters that may affect the overall rate of heterogeneous processes

- Physical properties of the gaseous phase, including
 - Diffusion constants
 - Flow rate
 - Viscosity coefficients.
- Physical and chemical properties of the solid phase, including:
 - Geometric surface area
 - Surface roughness
 - Surface area to volume ratio
 - Porosity or void volume
 - Pore diameter

- Pore length
- Pore tortuosity
- Particle size
- Morphology
- Bulk density
- Fraction of active sites
- Impurity content.

Many of the parameters describing the properties of the solid phase are not independent. For example, bulk density is dependent upon porosity, pore properties, particle size, and morphology.

Because of the plethora of variables, it is difficult to ensure that experiments isolate the effects of the experimental variables and obtain results that apply to fundamental processes involved in the overall heterogeneous process. Furthermore, it is difficult to compare results obtained by various researchers under different experimental conditions because, in most instances, the fundamental processes have not been identified, so the results are dependent upon the experimental conditions employed and are not applicable to other situations. Thus, in most cases the analytical rate expressions presented are only effective rate expressions applicable to the specific experimental conditions employed and are not fundamental rate equations suitable for extrapolation to other conditions.

With this general introduction, the specific case of the oxidation of graphite will now be considered in more detail. Graphite has some rather unique chemical properties as a result of its structure. Graphite consists of networks of condensed, six-member carbon rings occurring in a planar structure. These rings contain resonating double bonds that give the structure aromatic characteristics. The presence of the π -bonds that make up these resonating double bonds in the carbon rings affords the opportunity for stronger interactions between the terminal carbon atoms and the reactant molecules because of the potential for greater orbital overlap between the two species.

This structure of graphite leads directly to the prediction that the active sites are the terminal carbon atoms of each planar sheet;^{8,12,13} these atoms are bound to only two other carbon atoms rather than to three as are carbons in the interior of the sheet. This situation is shown schematically in Figure 1. The number of active sites represents only a small fraction of the total number of carbon atoms in the graphite matrix--estimates range from about 0.5% up to less than 6% of the total surface area.⁸ These estimates depend upon such variables as the type of carbon, the temperature, and the type of gas being adsorbed. The total number of sites available to participate in a reaction is adversely impacted by inert diluent gases, such as nitrogen, that compete with reactants, such as oxygen, for adsorption onto the active sites.

The adsorption process on graphite substrates is considered to be chemisorption rather than the much weaker physisorption typical of many other adsorption processes because of the stronger interactions afforded by the structure. Physisorption involves Van der Waal's forces, which are on the order of those between the molecules in a liquid. Thus, the heats of adsorption are on the same order as the heats of evaporation. Chemisorption involves much larger heats of adsorption. In fact, the term chemisorption implies formation of quasi-chemical bonds between the adsorbed species and the surface of the solid substrate. Chemisorption may also have a measurable activation energy. Three significant implications for reactions occurring on graphite substrates are:

- There may be finite and measurable reaction rates for both adsorption and desorption
- Either adsorption or desorption may be rate limiting in the overall process

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Figure 1. Energy vs. reaction coordinate curves for processes involved in oxidation of graphite to form carbon monoxide. The top part of the figure represents the three steps of the process: chemisorption of oxygen as the reactant, reaction to produce chemisorbed carbon monoxide, and desorption of the product carbon monoxide. Unsaturated bonding in the ring is indicated by the circle within each ring. The lower part of the figure shows the energy of the reacting system vs. the reaction coordinate. The activation energy, ΔH_i , associated with each of the steps is illustrated schematically in the energy plot.

- Chemisorption has an exponential temperature dependence similar to that of typical chemical reactions; however, the activation energy for chemisorption is much smaller, on the order of ten kcal-mole⁻¹ compared to tens of kcal-mole⁻¹ for chemical reactions.

Reaction Mechanisms

As noted in the thermodynamics section, the reactions that describe the potential oxidation processes for graphite (Rxns 1 through 8) are overall reactions and do not present the detailed mechanisms in going from reactants to products. The discussion of heterogeneous reactions showed that numerous steps may occur in an overall reaction. The importance of each step depends upon whether its rate is slow enough to impact the overall reaction rate. For the low temperatures of interest in the current study, the rates of diffusion and mass transport will be much larger than the rates of chemical processes. Therefore, it is anticipated that the kinetics of the chemical processes will determine the rates of the overall oxidation processes. Furthermore, because of the strength of the chemisorption forces involved, these steps have the potential for being the rate determining steps of the overall reaction.

As a specific example of the type of detailed mechanism that must be developed to explain the overall reaction, consider the case of the reaction of oxygen with graphite to form either carbon dioxide (Rxn 1) or carbon monoxide (Rxn 2). The detailed mechanisms consist of the following steps.

For Rxn 1

For Rxn 2

In these reactions, C_v represents a vacant active site in the graphite matrix while $C:O$ and $C:O_2$ represent the oxygen chemisorbed at the active site prior to reaction; correspondingly, $C:CO(s)$ and $C:CO_2(s)$ represent the chemisorbed products prior to desorption. The formation of carbon monoxide via Rxns 2a-2c is represented schematically in Figure 1, which has been adapted from Gulbrandsen.¹²

Similar detailed reaction mechanisms, including steps to account for the chemisorption of the primary reactant onto the solid substrate, can also be postulated for the cases where the primary reactant

is either water vapor, as in Rxn 3, or hydrogen, as in Rxn 7. These reactions all result in a net loss of carbon from the solid substrate. On the other hand, Rxn 6, the disproportionation of carbon monoxide into carbon and carbon dioxide, is unique because it results in the net addition of carbon to the solid substrate as a product of the reaction, i.e., the substrate grows. However, the detailed mechanism postulated for Rxn 6 still must include steps to account for chemisorption of the reactant carbon monoxide and the product carbon dioxide as discrete processes in the overall reaction.

Temperature Dependence and Activation Energies

Three distinct temperature regions are found for the oxidation of graphite,^{3,4,5,6,7} with a different rate controlling mechanism in each temperature range, as illustrated in Figure 2, adapted from O'Brien.⁴ In this figure, the different temperature regions are not sharply defined. However, the temperature region of immediate interest is the low temperature region, Regime 1. The upper temperature limit or crossover temperature for this regime has been variously reported as occurring somewhere between 700 and 825°C.⁵ The high temperature region, Regime 3, is generally thought to be above 1371°C.⁴ The specific temperatures marking the boundary between the various regimes depend upon factors such as sample geometry and flow velocities of the gaseous environment.

In the low temperature region, Regime 1, reaction rates are controlled by the rates of the fundamental chemical processes. As a result, the reaction rates have a marked temperature dependence, increasing significantly at higher temperatures. In addition, the reactions occur throughout the bulk of the graphite, depending upon the porosity of the sample. Furthermore, the concentrations of gaseous reactants within the graphite are constant and are the same as those in the environment.

In the high temperature region, Regime 3, the chemical reaction rates are so fast that the reactions are controlled by diffusion of the primary gaseous reactants to the surface of the sample. In this case, the boundary layer characteristics become important in determining the magnitude of the reaction rate, and the reactions occur at the surface of the graphite. The oxygen concentration within the sample becomes essentially zero. The temperature dependence of the reaction rate in this regime is small.

In the intermediate temperature region, Regime 2, a crossover between the two rate determining mechanisms occurs, as is indicated in Figure 2.

As shown by the large variations in slope of $\ln(k)$ versus $1/T$ in Figure 2, extrapolation of rate data to significantly different temperatures could introduce large errors. Thus, extrapolation of results must be limited to relatively short temperature ranges.

The temperature region of immediate interest is the low temperature region, Regime 1. The upper temperature limit or crossover temperature for this regime has been reported to be as low 700°C,⁵ which is well above the temperature range of concern, i.e., 200 to 400°C. Therefore, it is assumed that chemical kinetics will control the overall reaction rates and that reactions will occur throughout the bulk of the graphite, so sample porosity is a factor in the overall process.

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Figure 2. The three kinetic regimes and the relative activation energies (slopes). To illustrate the magnitude of temperature dependence of the reaction rate in each temperature region, the natural log of the reaction rate, k , is plotted schematically against the inverse of the absolute temperature, T , in the upper portion of the figure. The bottom portion of the figure is a schematic representation of the variation of the oxygen concentration in the environment and throughout the graphite sample for each of the three temperature regimes.

LITERATURE REVIEW

Numerous studies^{3,4,5,6,7,12,11,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37} of the oxidation of graphite have been reported in the literature. Generally, either steam or oxygen was the oxidizing reactant, although inert diluent gases were added in some cases. Various types of graphite were used as the solid substrate. The experimental conditions employed varied widely and in many cases were not completely defined. The results of these studies are subject to the limitations noted earlier in the discussion of the importance of experimental conditions (page 4). Furthermore, most of the studies supported reactor development, so their exposure temperatures were typically above 700°C. The temperature range of current interest is 200 to 400°C, where the rates of the chemical reactions are the controlling factor. Since 700°C is the upper boundary of this region, results for 700°C and above cannot be extrapolated to the present study.

Several authors^{3,11,25,26,27,28,29} studied graphite exposed to steam at temperatures from 649 to 1700°C and pressures ranging from 0.008 to 1556 cm Hg. These results are not directly applicable to SNF disposal because water vapor will not be a major component of the repository environment. However, exposure to such an environment could occur in one of the Design Basis Event (DBE) scenarios currently being considered.^a DBEs are accident or unexpected occurrence situations that are postulated to evaluate maximum environmental releases from the SNF repository in the event of their very unlikely occurrence. Because of they are extremely unlikely, DBE conditions have not been included in the scope of this study.

a. Thomas A. Thornton of CRWMS, personal communication on June 2, 1989.

ANALYSIS

This analysis is similar to that of Gulbransen and Andrew,⁷ who performed an extensive study of the oxidation of artificial graphite in dry oxygen atmospheres over oxygen pressures of 0.15 to 9.8 cm Hg and temperatures of 425 to 575°C. They related their results to the geometric surface area of their samples and did not account for surface roughness or total surface area. They found that at constant pressure the temperature dependence of the initial oxidation rate, k_i , can be expressed by an Arrhenius-type equation of the form:

$$k_i = Z \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where Z is a frequency factor with units of $\text{g} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$

E is the activation energy for the overall oxidation process

R is the universal gas constant, and

T is the absolute temperature.

From their data, Gulbransen and Andrew calculated a value of 36.7 kcal·mole⁻¹ for the activation energy of the process. They expressed k_i in units of $\text{g} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$. Subsequent work by Gulbransen, Andrew, and Brassart⁵ confirmed this form for k_i but revised the value for the activation energy, E , to 39.0 kcal mole⁻¹.

Gulbransen and Andrew⁷ also investigated the pressure dependence of the initial oxidation rate constant, k_i , at constant temperature. They found a linear pressure relationship that can be expressed as:

$$k_i = (a' + b'P) \quad (2)$$

where a' and b' are both functions temperature but are independent of pressure and P is the pressure in cm Hg.

The complete expression for k_i can be found by combining Eqs. 1 and 2 (evaluated at the same temperature, T_o) and solving for Z . In the following analysis it is assumed that the frequency factor, Z , is a function of pressure only and is independent of temperature, while as noted above, a' and b' are functions temperature but independent of pressure:

$$\begin{aligned} k_i &= Z \exp\left(-\frac{E}{RT_o}\right) = (a' + b'P) \\ \therefore Z &= (a' + b'P) \exp\left(\frac{E}{RT_o}\right) \end{aligned} \quad (3)$$

This result can be used to derive the most general form for the initial rate constant, k_i :

$$k_i = Z \exp\left(-\frac{E}{RT}\right) = (a + bP) \exp\left(-\frac{E}{RT}\right) \quad (4)$$

where:

$$\begin{aligned} a &= a' \exp\left(\frac{E}{RT_o}\right) \\ b &= b' \exp\left(\frac{E}{RT_o}\right) \end{aligned} \quad (5)$$

In this final form, a and b are constants that are independent of both temperature and pressure, while Z is independent of temperature and is a function of pressure only.

The values of a and b have been calculated from the results of Gulbransen and Andrew⁷ using their data at 450°C and their value of $E = 36.7 \text{ kcal-mole}^{-1}$. Thus, 450°C is T_o in the following calculations. Their values for a' and b' are as follows:

$$\begin{aligned} \exp\left(\frac{E}{RT_o}\right) &= 1.24 \times 10^{11} \\ a' &= 1.38 \times 10^{-8} \\ b' &= 4.98 \times 10^{-9} \end{aligned} \quad (6)$$

Using the results of Eq. 6 in Eq. 5 yields:

$$\begin{aligned} a &= a' \exp\left(\frac{E}{RT_o}\right) = 1.71 \times 10^3 \\ b &= b' \exp\left(\frac{E}{RT_o}\right) = 0.618 \times 10^3 \end{aligned} \quad (7)$$

The units of a are $\text{g} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ and of b are $\text{g} \cdot \text{min}^{-1} \cdot \text{cm}^{-2} \cdot (\text{cm Hg})^{-1}$.

Inserting the numerical values of a and b from Eq. 7 and the value of $39.0 \text{ kcal-mole}^{-1}$ for the activation energy (Gulbransen, Andrew, and Brassart⁵) into Eq. 5 and simplifying gives the final numerical result for k_i :

$$k_i = (1.71 + 0.618P) 10^3 \exp\left(-\frac{19628}{T}\right) \quad (8)$$

In this expression, k_i is only a function of the oxygen pressure in the atmosphere to which the graphite is exposed and the absolute temperature.

Gulbransen and Andrew⁷ also observed that, over the temperature range studied, graphite oxidation rate is not independent of time. Instead, they found that the rate showed a linear dependence upon time,

the magnitude of which was a function of temperature. They found that the experimental data could be fitted to an empirical rate expression of the form:

$$\frac{dM}{dt} = k_i + kt \quad (9)$$

where k_i is the initial rate constant discussed and evaluated above
 k is the first order rate constant, which is a function of time
 M is the carbon mass loss in units of $\text{g}\cdot\text{cm}^{-2}$
 t is time in min.

The total carbon mass loss over time can be found by integrating Eq. 9 with respect to time giving:

$$M = k_i t + \frac{k}{2} t^2 \quad (10)$$

While Gulbransen and Andrew observed that k is temperature dependent, they did not attempt to develop an analytical expression quantifying this dependence, nor did they investigate its pressure dependence in any detail. Table 4, presenting data on k as a function of temperature, was derived from the information presented in Table 3 of Gulbransen and Andrew.⁷ These data were taken at an applied oxygen pressure of 7.6 cm mercury. The information from Table 3 is also shown graphically in Figure 3.

TABLE 4. k as a Function of Temperature

Temperature ($^{\circ}\text{C}$)	k ($\times 10^8$)
425	- 0.0122
450	- 0.0282
475	0.0
500	- 0.032
500	0.0406
500	0.0
525	0.320
550	0.406
575	2.10

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Figure 3. Rate constant, k , as a function of temperature.

From inspection of Figure 3, above 500°C k is positive and increasing so that the rate of oxidation not only increases with time but does so at an ever faster rate as the temperature increases. In Table 2 the results between 475 and 500°C are mixed but the value of k is small, exerting little influence upon the rate of oxidation over this range of temperatures. Finally, in Figure 3 k is small but negative below 475°C, which means that the rate of graphite oxidation decreases with time. Thus, in this temperature regime it is anticipated that oxidation will be self limiting and that further loss of material will cease after some finite time. From the shape of the curve of k as a function of temperature, Figure 3, it is apparent that k cannot be described by an Arrhenius-type expression such as would be expected for a typical reaction rate constant.

Gulbransen¹² interpreted k as resulting from the increase in sample surface roughness, and thus total surface area, as oxidation progressed. (As stated earlier, Gulbransen and Andrew⁷ expressed their results in terms of the geometric area of the sample and not the total surface area, which may be significantly larger than the geometric area because of surface roughness and sample porosity.) This explanation also accounts for the apparent temperature dependence of k ; the rate of reaction would be anticipated to accelerate as the temperature increased.

In this framework, k is not a real rate constant, but a correction factor to account for the change in the number of active sites as the oxidation reaction proceeds. Thus, Eq. 10 is not the fundamental rate expression, but is the effective rate expression based upon the experimental conditions. However, this expression is suitable for the present study since the contribution of k will be small over the temperatures of interest.

For the purposes of the present study, it is sufficient to assume that the value of k is negligible at 400°C or less. Thus, Eq. 10 is simplified, and the total mass loss of carbon per square centimeter, M , becomes directly proportional to the total elapsed exposure time in minutes, t , as follows:

$$M = k_i t \quad (11)$$

where k_i has the numerical value given in Eq. 8.

The exposure conditions of interest in this study are contact with a standard atmosphere at 1 atm (76.0 cm Hg) total pressure over the temperature range of 200 to 400°C (473 - 673 K). The standard atmosphere consists of 20.9% by volume of oxygen.³⁸ Therefore, the oxygen partial pressure in the environment is 15.88 cm Hg. By inserting this value for the oxygen pressure in Eq. 8 and evaluating,

$$k_i = 1.152 \times 10^4 \exp\left(-\frac{19628}{T}\right) \quad (12)$$

Thus at 200°C k_i is $1.095 \times 10^4 \text{ g} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ and at 400°C is $2.485 \times 10^9 \text{ g} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$.

RESULTS AND DISCUSSION

As can be seen from the Analysis, the values of k_i over the temperature range of interest are very small, but they do exhibit a marked temperature dependence--at 400°C k_i is over 2×10^5 times larger than at 200°C. To evaluate the significance of this result, the time in years required for a total carbon mass loss of $1 \text{ mg} \cdot \text{cm}^{-2}$ from a graphite sample exposed under these conditions was calculated using Eq.11. At 200°C it is 190,000 yr, at 400°C it is 1.9 yr.

Although the times required to achieve a total carbon mass loss of $1 \text{ mg} \cdot \text{cm}^{-2}$ vary widely depending upon the temperature, even at 400°C the rate of loss is so small to be of no practical consequence. Using a nominal graphite bulk density³⁹ of $2.25 \text{ g} \cdot \text{cm}^{-3}$, the total mass loss at 400°C equates to a material thickness loss of approximately 0.4 mm in 190 yr. Therefore, oxidation of spent nuclear fuel upon loss of canister integrity is not anticipated to be a concern.

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