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EVALUATION OF GRAPHITE/STEAM INTERACTIONS FOR ITER

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Abstract

In this report we present the results of an experimental/analytical study designed to determine the quantity of hydrogen generated during a coolant inleakage accident in ITER. This hydrogen could represent a potential explosive hazard, provided the proper conditions exist, causing machine damage and release of radioactive material. We have measured graphite/steam reaction rates for several graphites and carbon-based composites at temperatures between 1000 C and 1700 C. The effects of steam flow rate, and partial pressure were also examined. The measured reaction rates correlated well with two Arrhenius type relationships. We have used the relationships for GraphNOL N3M in a thermal model to determine that for ITER the quantity of hydrogen produced would range between 5 and 35 kg, depending upon how the graphite tiles are attached to the first wall. While 5 kg is not a significant concern, 35 kg presents an explosive hazard.

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Introduction

The International Thermonuclear Experimental Reactor (ITER) is an ignited, long pulse engineering fusion reactor. Unlike present tokamaks, this device will produce high levels of thermal power, and will require active cooling of the divertor, first wall, and blanket components. During operation, the graphite protective tiles of the vacuum chamber can reach temperatures as high as 1800 C. As a consequence, these tiles contain enough residual thermal energy to generate significant quantities of hydrogen, by dissociating water vapor, should a break occur in a cooling tube that releases water directly into the vacuum chamber. The safety concern associated with the production of hydrogen is the explosive potential of this gas in air given the correct conditions. Additional concerns produced by this accident are: the production of carbon monoxide, (a toxic gas), over-pressurization of the vacuum vessel or other pressure boundaries, and the possible release of radioactive tritium and activated material inventories.

To determine the amount of hydrogen generated by a coolant inleakage accident, one needs to know the rate at which the graphite-steam reaction proceeds as a function of graphite temperature. Prior to this study, these rates were not known for anticipated ITER conditions during inleakage accidents. We have therefore performed tests on the primary candidate graphite for ITER (GraphNOL N3M), as well as other graphites, at the Idaho National Engineering Laboratory (INEL). The literature regarding graphite-steam reactions is summarized in Section 2. The test apparatus and measurement methods used to perform these experiments are described in the experimental procedures section, Section 3, of this report. Measured reaction rates for GraphNOL N3M are given in Section 4. Since other graphite types are being considered for ITER, and since the type of graphite greatly influences the rate of reaction, measurements for several other graphites are presented in Section 5. We also discuss the potential these graphites have for lowering the amount of hydrogen generated.

We have correlated the GraphNOL N3M data with Arrhenius type relationships, and have incorporated these relationships in a thermal model of ITER. Given the range of possible break sizes, tube sizes, and operating

pressures and temperatures for ITER cooling systems, a variety of coolant flow rates could be produced by ruptures in either the first wall or divertor cooling systems. To cover the range of possible break scenarios, we have parametrically studied the effect of leak rate on the extent of graphite oxidation with our thermal model. Details of our modeling, and the results appear in Sections 6 and 7. Finally, in Section 8 we summarize our findings and comment on the implications these findings have regarding ITER safety.

2. Literature Review

Various mechanisms which have been associated with controlling reaction rates of graphites in oxidant gases at different temperature regions were reviewed in Reference 1. We show in Figure 1 a schematic from this reference illustrating three temperature regions along with suggested rate controlling mechanisms. The rate of reaction in the low temperature regime is controlled by the chemical reactivity of the graphite, and not by the rate at which the reactant gas permeates the graphite. In the intermediate temperature regime, the rate of reaction is being controlled by a mixed mode of mass transport of reactant or product gases, most likely by in-pore diffusion, and availability of reactive graphite sites within the bulk. The transition between these modes is reflected by a decrease in the slope of reaction rate versus reciprocal temperature plot. At still higher temperatures the graphite sites become so reactive that the rate of reaction is controlled by the transport of reactant and product gases across a gaseous boundary layer at the outer surface of the graphite. We expect reaction rates in this region are somewhat temperature independent.

Most investigations of graphites in steam have been performed at temperatures below 1200 C and vapor pressures of less than 5 kPa[2-7]. These investigations have also shown considerable variances. Transition temperatures reported for the low to intermediate regimes have ranged from 800 C to 1250 C. Other variances include reaction activation energies (40 to 70 kcal/mole), inhibition effects due to the presence of gaseous reaction products, and reaction rate dependence on reactant gas partial pressure, for example proportionality with pressure is expressed as P^n where n varied from 0.5 to 0.7. These differences may stem from catalytic effects of impurities,

the reactivity of the graphite type, and temperature range investigated.

In addition, no reports of the temperature dependence of reaction rates based upon experimental confirmation existed for temperatures greater than 1300 C. Reference 8 proposed an extrapolation into higher temperature regimes which would relate reaction rates to temperature by a proportionality of $T^{3/2}$. Verification of such extrapolations to temperatures of 1700 C, and the determinations of influences of steam partial pressure, steam flow rate, and graphite types, were needed before credible hydrogen calculations could be performed.

3. Experimental Procedures

Figure 2 schematically shows the test apparatus used for the reaction rate experiments. Reaction rates were obtained by inductively heating cylindrical graphite specimens 25.3 to 28.6 mm in diameter, by 12.7 to 25.4 mm in length. A 9 mm diameter cylindrical channel was drilled along the central axis of the specimen. This channel formed the test surface where the graphite-steam reaction predominantly occurred. A 9 mm diameter, 5 cm long quartz tube was situated below the specimen to minimize entrance effects within the reaction channel of the specimen. The test specimens were contained within two concentric quartz tubes. Good specimen to tubing fit-up allowed us to obtain an airtight system and to purge with argon prior to testing. In addition, we were able to capture the product gases for volumetric and chemical determinations.

Preheated steam (600 C) at a flow rate of approximately $4.2\text{E-}4 \text{ m}^3/\text{s}$ was introduced from the bottom of the test apparatus at the start of each test. We ran a few tests at $8.3\text{E-}5 \text{ m}^3/\text{s}$ to determine what affect flow velocity has on reaction rates. These two flow rates provided average velocities within the specimen test channel of 6.6 and 1.3 m/s, respectively, which are both well within the laminar flow regime. Test environments were varied to include 100% steam, 50% steam-50% argon, and 10% steam-90% argon. The system was operated at an ambient pressure of 86 kPa, providing steam partial pressures of 86, 43, and 8.6 kPa, respectively.

Temperatures were monitored by a thermocouple embedded in the graphite, and by an infrared pyrometer directed at the outer circumference of the

specimen which was isolated from the test environment. Samples were tested at temperatures between 1000 C and 1700 C at times long enough to achieve about a 15 percent mass loss. Reaction rates were then determined by both mass loss and volume of the product gas.

4. Experimental Results For GraphNOL N3M

We obtained good agreement between reaction rates from both weight loss and product gas measurements. Gas chromatography showed that the product gas was approximately 50% hydrogen, 45-50% CO, and the remainder essentially CO₂. This confirmed that the primary reaction was:

There was also visible evidence of some nonreacted soot-like material being carried away from the test specimen by the flow. The amount of material physically lost in this manner appears to be about 10 percent based upon the average difference between reaction rates as determined by the weight loss and volumetric methods for several tests. We estimate maximum uncertainties for an individual test by the volumetric and weight loss methods to be ± 7 percent and ± 15 percent, respectively.

Our measured reaction rates for GraphNOL N3M appear in Figure 3. Reaction rates expressed as kg/m²-s and plotted versus reciprocal temperature (1/K) show good linear fit for Arrhenius relationships over two different temperature ranges. The relationships are:

$$R_{ox} = 8.54 \times 10^7 e^{-70,800/RT} \quad T \leq 1460 \text{ K} \quad (2a)$$

$$R_{ox} = 5.18 e^{-22,500/RT} \quad 1460 \leq T \leq 2000 \text{ K} \quad (2b)$$

These relationships indicate activation energies for this graphite of 70.8 kcal/mole for the lower temperature regime and 22.5 kcal/mole for higher temperature regime. To determine if our data could be represented as proposed by Reference 8, that is proportional to T^n , we have plotted this data in log-log format in Figure 4. This plot shows that although there is a

decreasing dependence of reaction rate with temperature at higher temperatures, the rate increases as $T^{6.8}$. This behavior plus the observed differences between the various classes of graphites indicates that the reaction rate is not entirely controlled by diffusion within a gaseous boundary layer. Instead, at least two mechanisms appear to be rate controlling and one or more involve either diffusion processes or population of active sites within the graphite.

Effects of steam pressure and flow rate were also determined from tests on the GraphNOL N3M. Reaction rates in steam partial pressures of 8.6, 43, and 86 kPa at temperatures near 1300 C, 1500 C and 1700 C are shown on log-log plots in Figure 5. These plots show that the order by which the reaction rate increases with pressure changes from 0.81 to 0.97 with increasing temperature. This order approaches unity at the higher temperatures. We can therefore justify a linear scaling of reaction rate with steam partial pressure in our thermal model since the majority of the hydrogen will be generated at higher temperatures. Tests with the two flow rates of $4.2E-4 \text{ m}^3/\text{s}$ and $8.3E-5 \text{ m}^3/\text{s}$ were performed at five temperatures. While not included in this paper, data for the higher flow rate was 50% higher than that for the lower flow rate. While this shows that increased flow rate was somewhat instrumental in increasing the reaction rate, the increase did not scale according to the thickness of the gaseous boundary layer. We would expect the boundary layer to vary by the square root of flow velocity. This again implies that the reaction rate was not entirely controlled by diffusion through a gaseous boundary layer but that diffusion in the graphite and availability of graphite activation sites also played a significant role.

5. Experimental Results for Other Graphites

Other types of graphites such as carbon/carbon fiber composites are being considered for armor tile materials for ITER. The materials we tested to check for variations among reaction rates, listed in Table 1, represent three types of material. Type I is bulk extruded or pressed graphites which have been given a high temperature heat treatment. These include GraphNOL N3M, H451, and an experimental boronated series (GB) containing various contents of boron. Type II and Type III represent pyrolytic graphite, and

three different carbon fiber-carbon composites, respectively.

Table 1
Various Materials Tested in Steam Environments

Material	Source/Description	Type	Density g/cm ³
GraphNOL N3M	ORNL-Great Lakes Research/ Extruded: 3200 C graphitization	I	1.84
H451	Great Lakes Carbon Corporation/ Extruded: 2800 C graphitization	I	1.80
GB100	Toyo Tanso/ 0 % boron, 2000 C	I	1.76
GB103	Toyo Tanso/ 3 % boron, 2000 C	I	1.79
GB110	Toyo Tanso/ 10% boron, 2000 C	I	1.80
pyrolytic	Pfizer/Chemical vapor deposition	II	2.18
FMI 4-D	FMI/Four dimensional weave	III	1.93
FMI HDFG	FMI/High density compress	III	1.72
DUNLOP CFC	Dunlop/Two dimensional weave	III	1.73

The complete data set of reaction rates for the various graphites determined from product gas measurements is shown in Figure 6. Greater variations were found at lower temperatures near 1100 C. Reaction rates for the various materials, however, showed a tendency to group according to the three types listed above, particularly at temperatures ≥ 1300 C. This is significant since most of the hydrogen generated during an ITER accident[8] will be generated at temperatures above 1300 C. The graphite with 10 percent boron (GB110) had a reaction rate equivalent to GraphNOL N3M and H451 near 1300 C (Figure 6). We have therefore averaged reaction rates for the various graphites within each type and included GraphNOL N3M, H451 and GB110 within the bulk graphite type. Figure 7 shows this data along with high and low values versus reciprocal temperature. A relative ranking of the various types of graphites indicate: 1) Pyrolytic graphite has reaction rates 1/5th to 1/10th that of bulk graphites, and 2) Composite materials have reaction rates 50 percent higher than bulk graphites.

The reactivities of the various graphites were checked with respect to densities (see Figure 8). A correlation between reactivity and density should exist because bulk density is an indicator of porosity and the extent of crystalline phase. These parameters control the rate of gaseous permeation

and the number of available reactive sites within the bulk of a graphite. Both the porosity and the amount of crystalline material within conventional bulk graphites are influenced by the heat treatment during manufacturing (see Table 1). Graphitization is a high temperature heat treatment process which restructures a mixture of various products, for example petroleum coke and coal tar pitch, into less porous material containing more crystalline phase. This generally requires heating into the 2315 C to 3040 C range[9]. The data in Figure 8 show a general trend of decreasing reaction rates with increasing density for the bulk graphites at 1300 C. The more perfect crystalline structure of the higher density pyrolytic graphite has significantly lower reaction rates. Densities and reaction rates of GraphNOL N3M, H-451, and GB110 are very similar. We found that the composites, on the other hand, showed significant differences in densities but essentially the same reaction rates. We noted visually that the matrix of the composites was preferentially attacked. The matrix material apparently remains highly reactive to steam at 1300 C, and consequently results in similar reaction rates for the composites examined.

Changes occurring during the heat treatment of the graphites containing boron are not fully understood. The graphites we examined were produced from mixtures of carbon and B_4C powders heated at 2000 C in vacuum. The extent of graphitization is not known. An equilibrium phase diagram by Lowell[10] indicates the coexistence of B_4C and a solid solution of boron in carbon (B-C) for 2000 C and the possibility of a liquid B-C phase at 2300 C. Kinetics, however, may prevent the attainment of such equilibrium conditions. The B_4C phase will require a temperature of 2450 C to melt. Eatherly[11] expressed that little boron would be dissolved from the B_4C phase below 2200 to 2450 C and that little graphitization would occur below 2400 C. There are reports, however, that low concentrations of boron will act as a catalyst in promoting graphitization in pyrolytic graphite at temperatures as low as 2000 C, and in graphites made from coke doped with boron[12]. Woodley[13] has reported on boronated graphites containing 5 wt. % boron, and indicated mixed behavior with regard to microstructural development within the materials. His materials, developed for neutron-absorption in fission reactors, were prepared from B_4C and carbon powder mixtures but heat treated at 2450 C. Two grades of graphite were developed. One grade retained a "black" appearance, which is

typical of material that has undergone little graphitization. A second grade developed a "grey" metallic like appearance, which presumably results from a more complete melting of the B_4C particles. This later condition is representative of graphites which have experienced more extensive recrystallization. Eatherly[11] also expressed that since little reaction was expected between the B_4C and carbon powder the final densities should vary according to the amount of the B_4C phase. Although our density measurements (see Table 1) do not support this latter trend, our samples did have a blackish appearance. We therefore believe that these boronated graphites are similar to the "black" materials tested by Woodley[13] and have not experienced extensive reaction or restructuring during the 2000 C heat treatment.

Mechanisms involved in the reaction of the boronated graphites with steam have been revealed by Woodley[13]. He shows the following two reactions to be predominant in moist environments in the temperature range of 830 C to 930 C:

B_2O_3 formed during the initial stage of exposure, for example, 20 minutes at 930 C, produces a weight gain and an accompanying decrease in the rate of hydrogen generation. The B_2O_3 is molten and acts as a barrier to water penetration, probably by pore plugging. Water vapor also reacts with the B_2O_3 to form boric acid, which is quite volatile at these temperatures. The sample begins to lose weight due to this latter mechanism and eventually sustains a constant rate of hydrogen release. Woodley noted influences of water vapor concentration and type of boronated graphite upon reaction rates. The "grey" material with the more homogeneous distribution of boron was more reactive in steam. He also reported that at 928 C and in 3 vol. % water vapor the boronated graphite was twenty times less reactive than TSX nuclear grade graphite. This mechanistic description helps explain the reductions in reaction rates with increasing boron content within the experimental (GB) series of our investigation. The reductions evident in Figure 6 within this

experimental series, and previously reported[14], represent factors of five and two, respectively, at 1100 C and 1300 C. Our results coupled with Woodley's observations show a decrease in the retardation effects of the B_2O_3 formation in the boronated graphites as temperature increases. The formation and volatilization rates of the boric acid are apparently increased and thus the protective nature of the molten B_2O_3 phase decreases with increasing temperature. We believe that except for an initial transient stage, boronization would have little effect on the graphite/steam reaction at temperatures above 1300 C. Boronization, therefore, offers little potential of reducing hydrogen generation during an ITER accident since most of the hydrogen is generated above 1300 C.

One may question whether the hydrogen generated from a boronated graphite comes from the B_4C and H_2O reaction (Equation 3) or the graphite-steam reaction (Equation 1), and if this influences the accuracies of the reaction rates we measured. Woodley noted through gas chromatography that tests performed at 930 C had produced concentrations of CO plus CO_2 that were less than 15 percent that of hydrogen. This suggests that most of the hydrogen at these temperatures is coming from the reaction with the B_4C phase. However, the rate of the graphite-steam reaction rapidly increases with temperature in going from 930 C to 1300 C (see Figure 3), and our gas chromatography measurements show comparable amounts of H_2 and CO in the product gas. We are, therefore, confident that the majority of the hydrogen we measured resulted from the graphite-steam reaction.

6. Thermal Model Description

The thermal model we developed for analyzing a coolant inleakage accident in ITER accounts for graphite-steam reactions, graphite tile heat transfer, and steam/reaction product flow within the vacuum chamber. The ITER vacuum chamber was modeled as 21 equal toroidal segments, with the break occurring in the eleventh segment.

As the water from a break jets into the vacuum chamber, it vaporizes until it comes into equilibrium with the vapor pressure of the vacuum chamber. We model this flashing process as occurring in homogeneous thermodynamic equilibrium, with the flow quality calculated from the enthalpy of the fluid

and water saturation properties. Water that does not flash will come in contact with the graphite tiles near where the break occurs. Upon contact, this water will boil. We model this boiling process as described later. Water that does not flash or boil was assumed to be lost to the vacuum pumping ducts. The steam generated by flashing or boiling was used as a source of mass for the fluids equations of our model as described below.

We solve the compressible fluid flow conservation equations to determine the steam/reaction product mixture flow rate through the vacuum chamber.

These equations are as follows:

Conservation of mass,

$$\frac{\partial \rho}{\partial t} + \frac{1}{A} \frac{\partial}{\partial x} (\rho u A) = S_m \quad (5)$$

Conservation of energy,

$$\frac{\partial \rho E}{\partial t} + \frac{1}{A} \frac{\partial}{\partial x} (\rho u E A) = Q_c - \frac{p}{A} \frac{\partial}{\partial x} (u A) \quad (6)$$

Conservation of momentum,

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} = -\frac{1}{\rho} \frac{\partial p}{\partial x} + f_v + f_b - u \frac{S_m}{\rho} \quad (7)$$

where ρ - mixture density (kg/m^3)
 A - cross-section area (m^2)
 u - fluid velocity (m/s)
 S_m - source and sinks of mass, steam plus reaction products ($\text{kg/m}^3\text{-s}$)
 E - internal energy density (J/kg)
 Q_c - convective bulk heating (W/m^3)
 p - mixture pressure (Pa)
 $f_{v,b}$ - viscous losses, body force (Pa/m).

Conservation of mass equations are also solved for each fluid specie, that is for H_2O , CO , and H_2 . All of these equations are solved in each of the 21 toroidal segments of our model. The combined volume and first wall surface area of these 21 toroidal segments are 1000 m^3 and 800 m^2 , respectively. A pressure relief system was included that vents the vacuum chamber if the pressure exceeds $1.5 \times 10^5 \text{ Pa}$. This vent was located 180° away from the break.

The rate of graphite-steam reactions was determined from Equations 2. The sources of mass produced by this reaction process were related stoichiometrically to the rate of the graphite/steam reaction by Equation 1.

We solve the following one-dimensional conduction equation at each toroidal segment to determine graphite tile temperatures:

$$\rho c_p \frac{\partial T}{\partial t} + \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) = 0 \quad (8)$$

where c_p - specific heat (J/kg-K)

k - thermal conductivity (W/m-K))

The boundary conditions for this equation are radiative heat transfer at $x=0$ (the back surface of the tile), and convective plus endothermic heat transfer at $x=L$, (the front surface of the tile, $L=2.4 \times 10^{-2}$ m). Radiative heat transfer from the back of the tile to the first wall was modeled by the standard Stefan-Boltzmann equation for gray surfaces, with the first wall a thermal sink at 150 C, and an effective emissivity between wall and tile of 0.7. We modeled the convective heat transfer at the front surface of the tile with the Dittus-Boelter[15] correlation in all segments except at the break, and as film boiling at the break segment with the following modified Bromley correlation proposed by Breen and Westwater[16]:

$$h_{fb} = \left[0.59 + 0.069 \frac{\lambda_c}{D} \right] \left[\frac{(\rho_f - \rho_g) \rho_g k_g^3 i_{fg}}{\lambda_c \mu_g \Delta T} \right] \quad (9)$$

where λ_c - critical Taylor wavelength (m)

i_{fg} - an effective latent heat of vaporization (J/kg)

μ_g - vapor viscosity (kg/m-s)

ΔT - wall superheat (K).

The assumption that the break occurs within a single segment results in a water/graphite contact surface area of 38 m², which we believe to be a conservative upper limit.

The oxidation of graphite in steam is an endothermic chemical reaction. This reaction is driven by the latent energy of the graphite tiles. We modeled this energy consumption process as the product of the rate of graphite-steam reaction, Equations 2, and the difference in the heat of formation of carbon monoxide and water. The heats of formation were

determined from temperature dependent relationships of Reference 17, evaluated at the predicted graphite surface temperature.

There are presently two first wall tile attachment configurations being considered for ITER[18]. Each configuration produces a different tile operating temperature. The first arrangement is radiative cooled tiles covering 100% of the first wall surface area. The operating temperature for these tiles will be 1500 C. The second configuration has 10% of the tiles radiatively cooled and operating at a temperature of 1800 C, with the remaining tiles conductively cooled and operating at or below 1000 C. The second arrangement is being considered by the ITER design team as a means of reducing the amount of hydrogen gas produced by this accident. We will demonstrate in the section which follows that this is a very effective method for achieving this goal.

7. Modeling Results

We found that several factors affect the rate of hydrogen production, these include: 1) the rate of the graphite-steam reaction (Equations 2), 2) the quantity of steam generated by flashing or boiling, 3) the rate at which the stream propagates through the vacuum chamber, and 4) the rate at which the tiles cool by radiative heat transfer. The results of this section will address these affects.

Based on information found in Reference 19, a single tube break in either the first wall or divertor cooling systems will produce mass flow rates ranging from 3 to 18 kg/s. Figure 9 shows the hydrogen generated for the first wall tiles at 1500 C, and break flows ranging from 5 to 100 kg/s. Reference 18 states that if the amount of hydrogen gas generated during this accident remains below about 10 kg, then it is unlikely that an explosive admixture will exist for ITER. For this scenario the hydrogen production exceeds safe levels. We note only a slight dependence between the quantity of hydrogen gas generated and rate of leak flow. The predicted value for 5 kg/s is 28.2 kg of H_2 , while that for 100 kg/s is 34.1 kg of H_2 .

The difference between curves of Figure 9 illustrates the affect of increased steam production. In this case the steam is produced by flashing. Figure 10 gives more insight into the rate of steam production for the 50 kg/s

break flow rate case. Plotted are the fractions of leak flow that either flash, boil on contact with tile surfaces, or is lost by draining into vacuum ducts. These are time integrated quantities divided by the time integrated break flow rate. Initially about 25% of the water either flashes or boils. As the vacuum chamber pressurizes, the 100 C water entering the vacuum chamber stops flashing. And, as the tiles in the vicinity of the break cool, the rate at which the water boils declines. Most of the water flows into the vacuum ducts. This demonstrates that the latent energy of both the water and the graphite tiles turns only a small fraction of the break flow to steam.

The rate at which the steam propagates through the torus can be seen in the results of Figure 11. This figure contains toroidal steam partial pressure profiles at two minute intervals during the 50 kg/s break flow rate case. The ratio of this partial pressure to the total vacuum chamber pressure equals the mole fraction of the steam in the steam/reaction product mixture. The predicted total pressure of the vacuum chamber nearly uniformly reaches the relief pressure of 1.5×10^5 Pa within the first minute of the accident. Based on this information, the fraction of the gas mixture being vented at four minutes is only about 20% steam.

Figure 12 gives the toroidal tile temperature profile for the 50 kg/s break flow rate case. These temperatures represent poloidal average values. The temperature at the location of the break drops very rapidly due to film boiling heat transfer. The remaining toroidal locations all cool at equal rates, as the primary mechanism for cooling the tiles of these locations is radiative heat transfer. By four minutes the tiles have cooled to temperatures where the rate of oxidation is relatively slow. By comparing the results of Figures 11 and 12, it can be seen that the oxidation reaction in parts of the torus is being limited by steam availability.

Figure 13 contains the predicted mass of carbon monoxide gas generated, and graphite lost during this accident. The toroidal average tile recession caused by this mass lost is less than 1% of the tile thickness. For the quantity of carbon monoxide generated not to represent a toxic hazard, it would have to be either further reacted to form carbon dioxide, or mixed with 5×10^5 m³ of air[20].

If either the latent energy of the first wall cooling water, or the first wall armor tiles are raised above that analyzed above, an increase in

the quantity of hydrogen generated would be expected. This could happen if:

- 1) higher operating temperatures are chosen, 2) thicker tiles are required, or
- 3) a larger area of contact between the water and the tiles can be envisioned.

We have parametrically examined these possibilities for a leak flow rate of 50 kg/s. For an increase in water operating temperature from 100 C to 130 C and 170 C, the amount of hydrogen generated increases from 31 kg to 41 kg and 54 kg, respectively. If the tile operating temperature were to increase from 1500 C to 1650 C and 1800 C, the hydrogen generation would increase from 31 kg to 43 kg and 57 kg, respectively. And finally, if the tile thickness were increased by 25% and 50%, the hydrogen generation would increase to 41 kg and 49 kg, respectively.

Given the quantities of hydrogen and carbon monoxides gas generated by the 100%/1500 C tile configuration, ITER designers have been considering a 10%/1800 C and 90%/1000 C tile attachment configuration. Our predicted quantities of generated hydrogen for this configuration is given in Figure 14. During a break that introduces 100 kg/s into the vacuum chamber, the amount of hydrogen gas generated is only 5.7 kg, which is below the 10 kg level thought to be an explosive hazard. The quantity of carbon monoxide gas generated is 80 kg for this same case. This gas would have to be either reacted to form carbon dioxide, or diluted with $8 \times 10^4 \text{ m}^3$ of air to become nontoxic. In either case, this latter design proves to be the better option.

8. Implications for ITER Design

This investigation illustrates that hydrogen generation during coolant inleakage accidents in ITER can represent an explosive hazard. The quantity of hydrogen generated by GraphNOL N3M reaction with steam can be as high as 35 kg for radiatively cooled first wall tiles. We have also demonstrated that conductively cooling the first wall tiles, a design measure already under consideration, significantly reduces the quantity of hydrogen generated. This reduction occurs because the graphite-steam reaction is highly temperature dependent. Apart from alleviating any concerns regarding hydrogen generation, steps still have to be taken to deal with the carbon monoxide generated during these accidents. There are probably other design measures that could be investigated, such as inerting various compartments near the reactor to reduce

explosive potential of the hydrogen produced should bonding of the tiles to the first wall prove not to be feasible.

There are other mitigative measures which could be pursued to reduce the potential hydrogen generation in ITER, such as material choice or development. Reaction rates are material dependent at the high temperatures anticipated for accident conditions. Pyrolytic graphite displays the best resistance to high temperature steam, but has other disadvantages; high costs, poor resistance to thermal shock, and poor resistance to irradiation damage. Carbon fiber/carbon composites, on the other hand, have many attractive engineering properties, including good resistance to thermal cycling and the potential of fabrication methods to facilitate tile attachment. This type of material, however, displays the highest rates of reaction in steam. The matrix phase remains highly reactive and thus all composites tested exhibited similar rates at the higher temperatures. Perhaps alloy additions and infiltration methods could be developed which could help lower the reaction rates of the matrix phase in steam. This may be an important consideration for future development of carbon based composites. The ideal graphite armor material for ITER should incorporate and optimize the various engineering needs and safety requirements.

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Figure 1. Schematic of kinetic regimes and associated mechanisms for graphite-gas reactions. The relative activation energies are shown by the slopes (top curve). The lower diagrams show profiles of the oxidant gas in the graphite for the corresponding regimes. Reference 1.

Figure 2. Schematic of test system.

Figure 3. Weight loss of GraphNOL N3M in steam as represented on a reciprocal temperature plot.

Figure 4. Temperature dependence of GraphNOL N3M-steam reaction rate. Rates are proportional to $T \exp(n)$.

Figure 5. Pressure dependence of reaction rates of GraphNOL N3M in steam. The rates are proportional to $P \exp(n)$.

Figure 6. Rate of hydrogen generation by several graphites.

Figure 7. Reaction rates observed for various types of materials as a function of temperature.

Figure 8. Plot of densities versus reaction rates in steam for various graphites.

Figure 9. Kilograms of H₂ produced during a coolant inleakage accident in ITER for 100% of tiles initially at 1500 C.

Figure 10. Fraction of leak flow that flashes, boils, or drains into vacuum ducts during a coolant inleakage accident in ITER for 100% of tiles initially at 1500 C.

Figure 11. Torus pressures during a coolant inleakage accident in ITER for 100% of tiles initially at 1500 C.

Figure 12. First wall graphite tile surface toroidal temperatures during a coolant inleakage accident in ITER for 100% of tiles initially at 1500 C.

Figure 13. Kilograms of carbon monoxide produced and graphite consumed during a coolant inleakage accident in ITER for 100% of tiles initially at 1500 C.

Figure 14. Kilograms of H₂ produced during a coolant inleakage accident in ITER for 10% of tiles at 1800 °C.

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