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# Transient analysis of nuclear graphite oxidation for high temperature gas cooled reactor

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ABSTRACT

Graphite is widely used as moderator, reflector and structural materials in the high temperature gas-cooled reactor pebble-bed modular (HTR-PM). In normal operating conditions or water/air ingress accident, the nuclear graphite in the reactor may be oxidized by air or steam. Oxidation behavior of nuclear graphite IG-110 which is used as the structural materials and reflector of HTR-PM is mainly researched in this paper. To investigate the penetration depth of oxygen in IG-110, this paper developed the one dimensional spherical oxidation model. In the oxidation model, the equations considered graphite porosity variation with the graphite weight loss. The effect of weight loss on the effective diffusion coefficient and the oxidation rate was also considered in this model. Based on this theoretical model, this paper obtained the relative concentration and local weight loss ratio profile in graphite. In addition, the local effective diffusion coefficient and oxidation rate in the graphite were also investigated.

## 1. Introduction

The high temperature gas-cooled reactor pebble-bed modular (HTR-PM) has advanced inherent safeties. The analyses of HTR-PM show that the highest fuel temperature in the reactor core will not exceed the design limit (about 1600 °C) in any accidental condition (Zheng et al., 2009).

In the preliminary design stage of HTR-PM, as discussed by Zheng et al. (2010), a double-ended guillotine break of a steam generator heating tube is considered to be the most serious design basis accident (DBA) for water ingress into the primary circuit. Besides, there are two severe cases as the typical beyond design basis accidents (BDBA) of postulated large amount of water ingress are analyzed: one is failure of the steam generator emergency draining system after the double-ended guillotine break of a steam generator heating tube, the other is break of the main collection plate of the live-steam at the outlet of all the heating tube bundles (Zheng et al., 2010). In the air ingress accident analyses of HTR-PM, there are also two kinds of air ingress accidents which are regard as BDBA: one is the double-ended guillotine break of the horizontal coaxial gas duct which could result in large amount of air ingress into the primary circuit, the other is the simultaneous rupture of both upper and lower fuel discharging pipes connected to the primary loop which could also cause large amount of air ingress due to the chimney effect (Zheng and Shi, 2010). In these water/air ingress accidents, nuclear graphite in HTR-PM would be oxidized by steam or air. The structural integrity of reactor may be damaged, the mechanical strength of nuclear graphite may be degraded and flammable water gas will be produced in water ingress accident. The oxidation behavior of nuclear graphite plays an important role in the accident analyses of HTR-PM.

In normal operating conditions, there are some impurities like steam and oxygen in the helium flowing in the primary circuit. Table 1 shows the upper limit value of impurity contents in primary circuit of HTR-10 and HTR-PM. Even though the amount of impurities and the reaction rate between impurities and graphite is very small under normal operating conditions, in the lifetime of a spherical fuel element (about 3 years in the core) and the lifetime of reflector and structural materials (same with the whole lifetime of the reactor), the matrix graphite, the reflector and the structural materials still may be oxidized. The analysis of nuclear graphite oxidation by oxygen or steam under normal operating conditions is important for the safety related analyses of HTR-PM.

The mechanism of graphite oxidation is very complex. According to the temperature, the reaction mechanism can be divided into three zones: the chemical regime at low temperature, the in-pore diffusion controlled regime at medium temperature and the mass transfer controlled regime at high temperature (Penner

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**Table 1**
The upper limit value of impurity contents in primary circuit of HTR-10 and HTR-PM (Yu and Yu, 2009).

| Impurity contents | HTR-10 ($cm^3 \cdot m^{-3}$) | HTR-PM ($cm^3 \cdot m^{-3}$) |
|---|---|---|
| $H_2O$ | 2 | 2 |
| $H_2$ | 30 | 30 |
| CO | 30 | 30 |
| $O_2$ | 0.2 | 2 |
| $N_2$ | 2 | 2 |
| $CO_2$ | 6 | 6 |
| $CH_4$ | 5 | 5 |

and Richards, 1988; Hinssen et al., 2008; Zheng and Stempniewicz, 2012). There are many factors which could affect the graphite oxidation rate, such as the temperature, the graphite porosity, the oxidant gas concentration and so on.

Some experiments (Fuller and Okoh, 1997; Kim et al., 2008; Wang, 2013) have shown that the oxidation rate varied with weight loss in the oxidation process. It is shown that the graphite oxidation rate firstly increases with burn off and then decreases with burn off. According to Su and Perlmutter (1985), this phenomenon is attributed to the reaction surface area firstly increasing with weight loss and then decreasing with weight loss. A factor named $F_b$ whose expression is shown in Eq. (16) was defined to describe the influence of weight loss on the oxidation rate. Bhatia and Perlmutter (1980) developed a random pore model to describe the relationship of $F_b$ and weight loss ratio b whose expression is shown in Eq. (4). Based on the linear oxidation theory, many researchers investigated the graphite oxidation in different conditions. Wichner et al. (2009) gave the analytic results under the assumptions of constant graphite density and zero weight loss ratio which means $F_b$ is always equal to 1 in the process of oxidation. The analytic results showed the oxidation depth and equilibration time under different temperatures. Hinssen et al. (2008) gave an overview of theoretical nuclear graphite oxidation also under the assumption of constant graphite porosity.

Based on the random pore model, it is known that during the process of graphite oxidation, the pore walls in the graphite firstly increase and then decrease due to the pore walls growing larger and joining each other. The graphite porosity increased with weight loss because of the total pore volume increasing with weight loss. In addition, the graphite density, pore diameter, effective diffusion coefficient as well as the oxidation rate also varied with the weight loss ratio. Taking nuclear graphite IG-110 for example, one dimensional spherical partial differential equations have been derived to indicate the graphite oxidation model, which considers the effect of porosity and density variation on the graphite oxidation. The effective diffusion coefficient in this paper considers the effect of molecular diffusion and Knudsen diffusion. The influence of weight loss on the effective diffusion coefficient is also taken into consideration. This paper mainly studies the oxidation behavior of nuclear graphite IG-110 in the in-pore diffusion controlled regime. Because the oxidation in this regime has a significant effect on the graphite mechanical strength. The effective diffusion coefficient and oxidation rate trending over time and space are also been discussed.

## 2. Graphite oxidation model

### 2.1. Chemical reaction expression

The chemical reaction expression of graphite oxidation by oxygen can be written as (Wang, 1994):

$$\begin{aligned} & C + zO_2 \rightarrow xCO + yCO_2 \\ & \Delta H(CO) = -110.52\ \text{kJ/mol} \\ & \Delta H(CO_2) = -393.51\ \text{kJ/mol} \end{aligned} \tag{1}$$

$x$, $y$ and $z$ is the stoichiometric number of the chemical expression.

The $CO/CO_2$ ratio is $f$, then from $x + y = 1$, $x$, $y$ and $z$ can be expressed as:

$$x = \frac{f}{f+1}, \quad y = \frac{1}{f+1}, \quad z = \frac{f+2}{2(f+1)} \tag{2}$$

From (Kim and No (2006), the $CO/CO_2$ ratio $f$ can be expressed as:

$$f = 7396 \exp\left(-\frac{69,604}{R_g T}\right) \tag{3}$$

$R_g$ is the gas constant, 8.314 $J \cdot mol^{-1} \cdot K^{-1}$; $T$ is the graphite temperature, K.

### 2.2. Weight loss and porosity

The weight loss ratio means the ratio of the reduced graphite density and the initial density.

$$b = \frac{\rho_{c0} - \rho_c}{\rho_{c0}} \tag{4}$$

The symbol $\rho_{c0}$ is the initial local density of graphite. $\rho_c$ is the instantaneous local density. The weight loss ratio $b$ is an important parameter in the oxidation model. Many other parameters are related to $b$.

The instantaneous local density $\rho_c$ can be expressed as:

$$\rho_c = \rho_{c0} - \rho_{c0} \cdot b \tag{5}$$

The instantaneous oxidation rate of graphite $R_c$ ($s^{-1}$) can be written as:

$$\frac{\partial b}{\partial t} = R_c \tag{6}$$

The local porosity $\varepsilon$ is defined as the pore volume per unit graphite volume. $\varepsilon_0$ means the initial porosity before the graphite is oxidized. The relationship between local porosity $\varepsilon$ and the weight loss ratio $b$ can be written as:

$$\varepsilon = \varepsilon_0 + (1 - \varepsilon_0)b \tag{7}$$

### 2.3. Effective diffusion

Graphite is usually regarded as a kind of porous medium. The gas diffusion in the graphite includes the binary molecular diffusion and the Knudsen diffusion. So the effective diffusion coefficient can be written as:

$$D_{eff,i} = \frac{\varepsilon}{\tau}\left(\frac{1}{D_{b,i}} + \frac{1}{D_{Kn,i}}\right)^{-1} \tag{8}$$

$\tau$ is the tortuous ratio which defined as the ratio of the length of real aperture within porous material and the length of superficial aperture. The tortuous ratio $\tau$ will change with the consumption of solid phase and it similarly is the reciprocal of $\varepsilon$ (Wakao and Smith, 1962)

$$\tau = 1/\varepsilon \tag{9}$$

$D_{b,i}$ is the binary molecular diffusion coefficient of component $i$ ($m^2 \cdot s^{-1}$), it can be expressed as (Wang, 2013):

$$D_{b,i} = \frac{1.834 \times 10^{-2} T^{\frac{3}{2}} \left(\frac{1}{M_i} + \frac{1}{M_j}\right)^{\frac{1}{2}}}{P \sigma_{i,j}^2 \Omega_D} \tag{10}$$

In the above expression, $M_i$ and $M_j$ respectively means the molecular weight of component $i$ and $j$ ($g \cdot mol^{-1}$). $P$ means the pressure of the gas mixture (Pa). $\sigma_{i,j}$ means the collision diameter of component $i$ and $j$ (m). $\Omega_D$ means the collision integral parameters for molecular diffusion.