

## **OXIDATION PERFORMANCE OF BOTTOM GRAPHITE REFLECTORS IN THE PEBBLE BED REACTOR**

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### **ABSTRACT**

The core of the High Temperature Gas-cooled Reactor (HTGR) is constructed from closely packed graphite blocks. The bottom reflectors of the pebble bed core HTGR are un-replaceable and under relative high service temperature through the reactor lifetime. In the decades-long period, the graphite material would be corroded by such oxidizing impurities as O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> in the coolant, resulting in the degradation of its thermal and mechanical properties. Consequently accurate predictions of the oxidation performance of the graphite components are of key importance.

In the present paper, a reasonable model considering the porosity changing as well as the burn-off effect of the oxidized graphite on the oxidation rate is established, and the physical basis and assumptions behind the model are reported. The model predictions are compared with experimental data for IG-110 graphite. Using the model, the oxidation performance of the bottom reflector blocks of the Chinese 10MW High Temperature Gas-cooled Reactor(HTR-10) through the 20-year reactor lifetime is analyzed. The distributions of the burn-off and the corrosion depth into the graphite surface with the temperature, service time and positions of the structure are quantified based on simplifying assumptions. Finally, the structural integrity of the bottom reflector is assessed.

### **INTRODUCTION**

High Temperature Gas-cooled Reactors (HTGR) utilize helium and graphite material as coolant and reflector respectively. Under normal operating condition, due to the leakage of steam generator tubes, the outgas of inner structures as well as the maintaining operation, etc., there would be unavoidable impurities such as CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, etc. in the helium coolant[1]. The oxidative gases among these impurities could react with graphite material under high temperature, leading to the corrosion of structures. The bottom reflector, designed as permanent structure, serves in a relative high temperature condition and supports the load of all the pebble fuel elements. Thus the integrity of the bottom reflector during its lifetime should be assessed to determine the safety of the reactor.

There are not many researches on the oxidation performance of the graphite materials in the pebble bed reactors under normal operating conditions. Additionally, the limited researches all focused on the oxidation behavior of the fuel matrix graphite [2-4]. In Luo's calculation on the HTR-10 graphite reflectors [5], only the effect of oxygen was considered. However during the normal operating conditions, water vapor is the dominated impurity in the coolant, caused by the leakage of steam generator tubes. Thus there will be more significance to study the graphite corrosion caused by the water vapor. In the present paper, a reasonable model considering the porosity changing as well as the burn-off effect of the oxidized graphite on the oxidation rate is established based on several simplifying assumptions. Utilizing this model, the oxidation behavior of the bottom reflector blocks of a pebble bed type reactor (similar to HTR-10) through the 20-year reactor lifetime is analyzed.

### **BOTTOM REFLECTOR STRUCTURE OF PEBBLE BED REACTOR**

The geometry model of HTR-10 bottom reflector is shown in Fig. 1 (axial symmetric). The equivalent diameter of the bottom reflector is 1.8m, with a 0.5m-diameter central hole as the fuel discharge tube in line with the core axis.

The structure above the hot gas chamber has three layers of graphite blocks, and each layer has 10 segmental bricks. The top surface of the bottom is designed as a 30-degree bevel to improve the fuel elements' flow. There are two rings in the radial direction of the first layer block with a equivalent diameter of 1.33m and 1.8m respectively. The inner ring bricks have a total amount of 640 machined holes, each with a diameter of 16 mm (Fig. 2). The total height of layer 2&3 graphite blocks is 0.63m, with vertical, straight gas passages between edges of the contacting segmental bricks. The heated helium flows from the reactor core through the holes and passages to the hot gas chamber. The mass flow rate of the helium coolant through the reactor core is 4.3kg/s, and the velocity in the machined holes is approximately 15m/s, while about 4m/s in the passages.

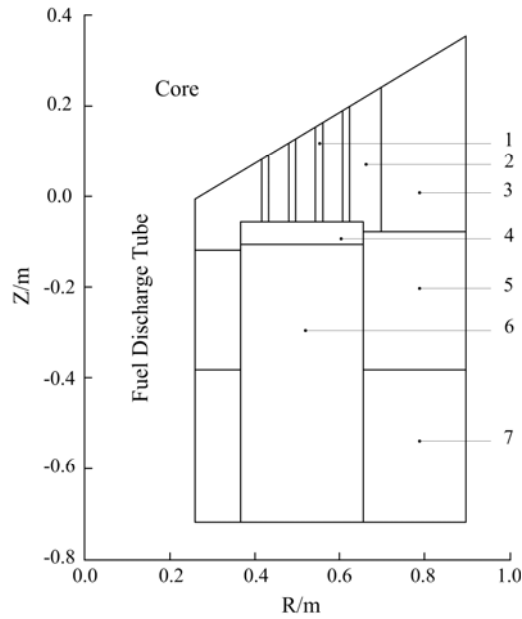


Fig.1 Schematic Diagram of HTR-10 Bottom Reflector

1-machined holes; 2-inner ring bricks of Layer 1; 3- outer ring bricks of Layer1 4-plenum; 5- block Layer2; 6-flow passage; 7- block Layer3

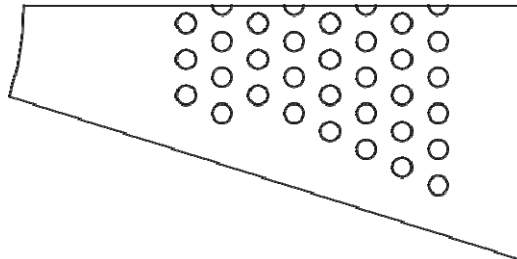


Fig.2 Sectional Schematic Diagram of the Inner Ring of Graphite Block Layer 1(1/20)

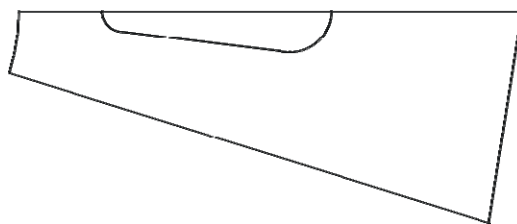


Fig.3 Sectional Schematic Diagram of Graphite Block Layer 2&3(1/20)

The fine-grained isotropic IG-11 graphite (Toyo Tanso Co.) is used in the HTR-10 reflector, its properties are listed in Tab.1 [6].

Table 1 Material properties of IG-11 graphite

Bulk density (g·cm <sup>-3</sup> )	Mean porosity (%)	Mean pore size (m)	Compressive strength (MPa)	Tensile strength (MPa)
1.76	20	1.6×10 <sup>-5</sup>	76.22	25.4

The temperature distribution in the bottom reflector under normal operating condition is cited from reference [4], and is described in Fig.4. The impurity contents in the coolant are listed in Tab. 2[5, 8].

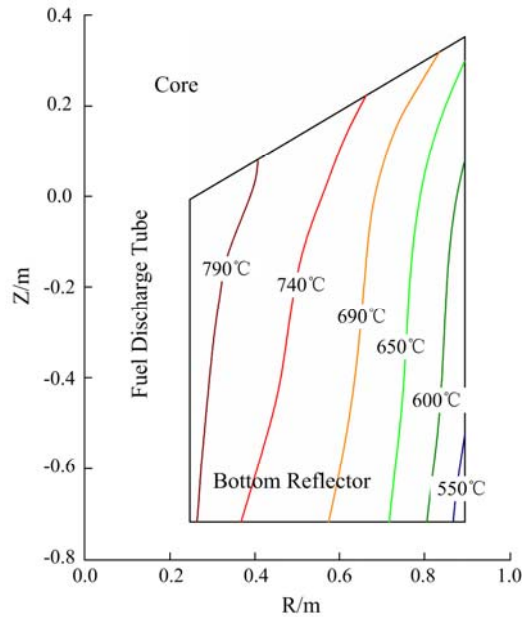


Fig.4 Isotherm for the HTR-10 Bottom Reflector

Table 2 Impurity Contents in HTR-10 Coolant

Impurity	H <sub>2</sub> O	H <sub>2</sub>	CO <sub>2</sub>	CO	N <sub>2</sub>	O <sub>2</sub>	CH <sub>4</sub>
Permit Value (cm <sup>3</sup> m <sup>-3</sup> )	2.0	30	6.0	30	2.0	0.2	5.0
Actual Value (cm <sup>3</sup> m <sup>-3</sup> )	0.33	20	~0.2	1.4	0.2	<0.1	0.25

### MATHEMATICAL MODEL

The diffusion of water vapor within the graphite is generally assumed to follow the Fick’s second law. The general diffusion equation can be written as follows.

$$\frac{\partial C}{\partial t} + \nabla(-D_{eff} \nabla C) = -R \tag{1}$$

where, C is the concentration of water vapor, mol·m<sup>-3</sup>; D<sub>eff</sub> is the effective diffusion coefficient, m<sup>2</sup>·s<sup>-1</sup>; R is the reaction rate between H<sub>2</sub>O and graphite, mol·m<sup>-3</sup>·s<sup>-1</sup>.

Since the mean free path of H<sub>2</sub>O molecules is equivalent with the size of the pores through which diffusion proceeds, the Knudsen diffusion should be taken into consideration. The effective diffusion coefficient is written as,

$$D_{eff} = \frac{\varepsilon}{\tau} \left( \frac{1}{D_{H_2O}} + \frac{1}{D_{Kn}} \right)^{-1} \tag{2}$$

where ε is the local porosity in the graphite; τ is the tortuosity of the graphite, usually the reciprocal of porosity. D<sub>H<sub>2</sub>O</sub> is the bulk diffusion coefficient of water vapor in the carrying gas He, m<sup>2</sup>·s<sup>-1</sup>, expressed as[9],

$$D_{H_2O} = \frac{1.858 \times 10^{-7} T^{3/2} \left[ \frac{1}{M_{H_2O}} + \frac{1}{M_{He}} \right]^{1/2}}{P \sigma_{H_2O-He}^2 \Omega_D} \quad (3)$$

where, T is temperature, K;  $M_{H_2O}$  and  $M_{He}$  are mole weight of H<sub>2</sub>O and He respectively, g·mol<sup>-1</sup>; P is the total pressure of the environment, atm;  $\sigma_{H_2O-He}$  is the average collision diameter;  $\Omega_D$  is a temperature-dependent collision integral; the Knudsen diffusion coefficient  $D_{Kn}$  is

$$D_{Kn} = 48.5 d_{pore} \sqrt{\frac{T}{M_A}} \quad (4)$$

m<sup>2</sup>·s<sup>-1</sup>; where  $d_{pore}$  is the mean pore size of graphite, m.

The reaction equation between H<sub>2</sub>O and graphite is



According to the experimental results obtained by Velasquez, et al. [10], the reaction rate could be described as,

$$R = \frac{\rho_c K_1 F_b P_{H_2O}}{M (1 + K_2 P_{H_2}^\beta + K_3 P_{H_2O})} \quad (6)$$

Where,  $\rho_c$  is the bulk density of graphite,  $K_1$ ,  $K_2$  and  $K_3$  are reaction rate constants,

$$K_1 (\%s^{-1} Pa^{-1}) = 2.0 \times 10^3 \exp(-32963/T) \quad (7)$$

$$K_2 (Pa^{-0.75}) = 1.10 \times 10^2 \exp(-8958/T) \quad (8)$$

$$K_3 (Pa^{-1}) = 2.01 \times 10^2 \exp(-11524/T) \quad (9)$$

$\beta=0.75$ ,  $P_{H_2O}$  and  $P_{H_2}$  are partial pressure of H<sub>2</sub>O and H<sub>2</sub> respectively, Pa;  $F_b$  is the burn-off factor, described as,

$$F_b = (1-b) [1 - \psi \ln(1-b)]^{1/2} \quad (10)$$

where  $\psi$  is a structural parameter of graphite; b is the local burn-off of graphite,

$$b = \frac{\rho_{c0} - \rho_c}{\rho_{c0}} = 1 - \frac{\rho_c}{\rho_{c0}} \quad (11)$$

where  $\rho_{c0}$  is the initial bulk density of graphite, while  $\rho_c$  is the transient bulk density. If the initial average porosity of graphite is  $\varepsilon_0$ , the transient porosity could be expressed as below, according to the mass conservation of graphite.

$$\varepsilon = \varepsilon_0 + (1 - \varepsilon_0) \cdot b \quad (12)$$

At any time, the burn-off rate of graphite material changes over time is the oxidation rate of graphite,

$$\frac{\partial b}{\partial t} = R_c \tag{13}$$

**RESULTS**

The calculation results based on the geometry model and the mathematics model show a significant relationship between the temperature and corrosion status of the HTR-10 bottom reflector. The graphite corrodes most seriously at the entrance of fuel discharge tube, where the temperature is the highest. As shown in Fig. 5, if the H<sub>2</sub>O value is in permit condition (2.0cm<sup>3</sup>m<sup>-3</sup>), the maximum local burn-off at this position could reach 21.8% at the end of the 20-year service time. Nevertheless, the corrosion depth, namely the distance where the burn-off is greater than 5%, is only 7.5mm. This is because when the temperature is high, the oxidation rate, or the H<sub>2</sub>O consuming rate is much faster than the gas transport rate. The water vapor runs out quickly before it reaches deeper from the surface of the graphite. The oxidation mechanism is in the in-pore diffusion regime. Similar results could be found from Fig. 6&7. In Fig.6, since the temperature decreases along the r-direction, the H<sub>2</sub>O concentration profiles around the holes edge become wider. Because the temperature is relatively low at places far away from the core axis, the gas could transport much deeper into the graphite. Figure 7 demonstrates the burn-off profiles around the straight passage of block layer 2&3 along the z-direction. It could be found that the burn-off gets larger as the temperature increases from the bottom to the top. The porosity profiles at actual H<sub>2</sub>O content(0.33 cm<sup>3</sup>m<sup>-3</sup>) between two adjacent holes of the inner ring of graphite block layer 1 are demonstrated in Fig. 8.

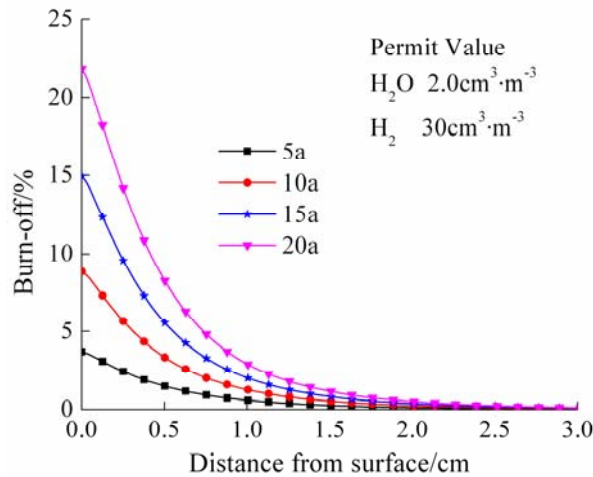


Fig.5 Burn-off Distribution at the Inlet of the Fuel Discharge Tube

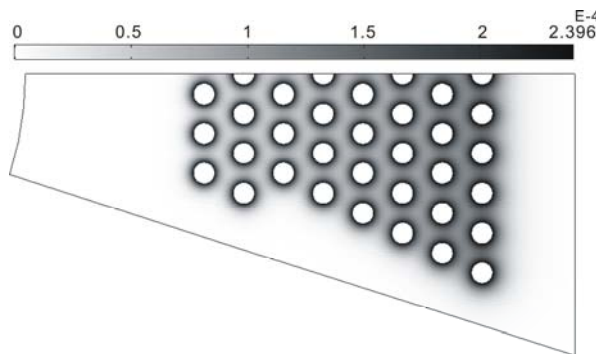


Fig.6 Water Vapor Concentration Distribution at the Inner Ring of Bottom Graphite Block Layer 1

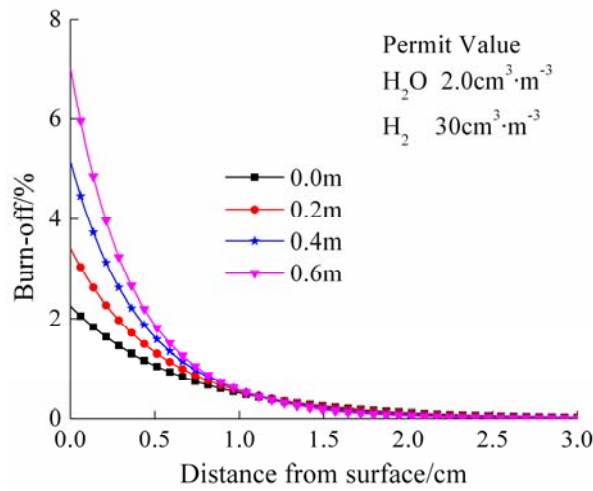


Fig.7 Burn-off Distribution along Heights of Bottom Graphite Block Layer 2&3

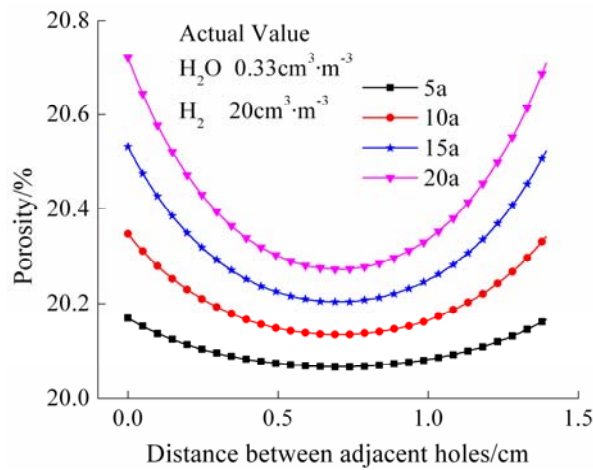


Fig.8 Porosity Distribution between Adjacent Holes of the Inner Ring of Bottom Graphite Block Layer 1

It has been showed in Reference [11] that the correlation between IG-110 graphite’s compressive strength and density is

$$S/S_0 = (\rho/\rho_0)^{6.5} \tag{14}$$

where,  $S$  is the compressive strength;  $\rho$  is the density; the subscript 0 means before oxidation. It could be seen that with the oxidation of the graphite, the density decreases, as a result the material’s compressive strength degrades significantly. The integral weight loss and the relevant compressive strength degradation of the bottom reflector during the whole service time under different conditions are shown in Fig.9.

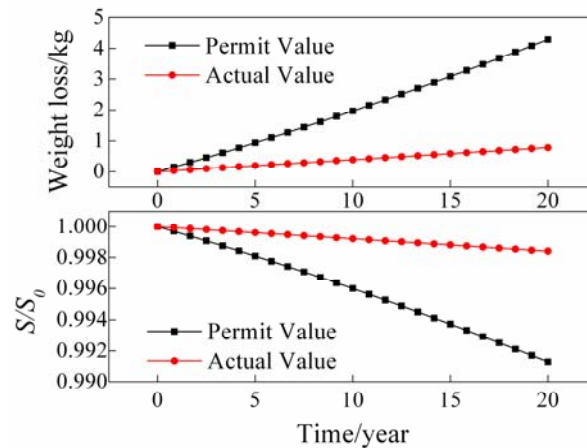


Fig.9 Variation of Weight Loss and Compressive Strength of Bottom Reflector with Service Time

## CONCLUSION

The graphite bottom reflector in pebble bed HTGRs is not replaceable during the 20 years service time, coupled with the relative high service temperature, thus the oxidation behavior of the structure should be assessed to determine the integration and safety. The present paper established a geometry model of the bottom reflector structure of HTR-10, as well as a mathematical model of gas transportation and graphite oxidation. Then the models are utilized to analyze the oxidation performance of the whole structure. The whole weight loss and the compressive strength degradation of the bottom reflector during the service time is also calculated. It shows that,

1. The burn off of the graphite is mainly affected by the temperature distribution. In the sections with higher temperature, the local burn-off of the graphite is larger. But the corrosion depth is small, with a burn-off higher than 5% within a thickness of about 7.5mm.

2. The total weight loss of the whole structure is not significant: the mass corroded at the end of 20-year service time is about 4.29kg, if the H<sub>2</sub>O content is of permit value; while the weight loss is only 0.78kg in actual H<sub>2</sub>O concentration.

3. There is little compressive performance degradation of the bottom reflector, thus the integrity of the component is maintained.

## REFERENCES

- [1] Kissane, M. P., 2009, "A Review of Radionuclide Behaviour in the Primary System of a Very-High-Temperature Reactor," *Nuclear Engineering and Design*, 239(12), pp. 3076-3091.
- [2] Yu, X., Luo X. and Yu, S., 2010, " Simulation of Oxidation in HTR-10 Core," *Nuclear Power Engineering*, 31(2), pp. 81-84. (in Chinese).
- [3] Yu, X., and Yu, S., 2010, "Analysis of Fuel Element Matrix Graphite Corrosion in Htr-Pm for Normal Operating Conditions," *Nuclear Engineering and Design*, 240(4), pp. 738-743.
- [4] Richards, M. B., 1990, "Reaction of Nuclear-Grade Graphite with Low Concentrations of Steam in the Helium Coolant of an Mhtgr," *Energy (Oxford)*, 15(9), pp. 729-739.
- [5] Luo, X. W., and Yu, S. Y., 2007, " Assessment of Graphite Oxidation in HTR-10," *Nuclear Power Engineering*, 28(5), pp.67-70 (in Chinese).
- [6] Luo, X. W., Robin, J. C., and Yu, S. Y., 2004, "Effect of Temperature on Graphite Oxidation Behavior," *Nuclear Engineering and Design*, 227(3), pp. 273-280.
- [7] Gao, Z. Y., and Shi, L., 2002, "Thermal Hydraulic Calculation of the Htr-10 for the Initial and Equilibrium Core," *Nuclear Engineering and Design*, 218(1-3), pp. 51-64.
- [8] Yao, M., Wu, X., and Weng, X., 1995, "Purification of Helium Gas for the Helium Test Loop," *Nuclear Power Engineering*, 16(5), pp. 470-475. (in Chinese).
- [9] J.R.Welty, C.E.Wicks, R.E.Wilson, and G.L.Rorrer, 2005, *Fundamentals of Momentum, Heat, and Mass Transfer*, 4ed, Wiley.

- [10] Velasquez, C., Hightower, G., and Burnette, R., 1978, "The Oxidation of H-451 Graphite by Steam, Part 1: Reaction Kinetics," Technical Report No. GA-A14951, General Atmotics, San Diego, USA.
- [11] Chang Oh, Eung Kim, Jong Lim, Richard Schultz, and David Petti, 2009, "Effect of Reacting Surface Density on the Overall Graphite Oxidation Rate," Tokyo, Japan, INL/CON-09-15461.