

AN EVALUATION OF THE SIGNIFICANCE OF
INVERSE OXIDATION FOR HTGR GRAPHITES

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1. Introduction

Walker and his co-workers¹ have observed the inverse oxidation phenomenon following gasification of graphite cylinders to relatively high burnoffs. The inverse oxidation refers to a higher mass loss inside the graphite than the outside. In 1980, Wichner et al² reported this phenomenon (referred to as inside/out corrosion) observed in some H451 graphites, and offered an explanation that a catalyst (almost certainly Fe) is activated by the progressively increasing reducing conditions found in the graphite interior. Recently, Morgan and Thomas³ (1982) investigated this phenomenon in PGX graphites, and agreed on the existing mechanism to explain this phenomenon. They also called for attention to the possibility that this phenomenon may occur under HTGR (High Temperature Gas-Cooled Reactor) operating conditions.

The purpose of this paper is to confirm the above mentioned explanation for this phenomenon and to evaluate the significance of this effect for HTGR graphites under realistic reactor conditions.

2. Discussion

Morgan and Thomas³ oxidized PGX graphite blocks (115 x 165 x 190 mm) in 80% CO₂/20% CO at 875°C and observed an inverse oxidation. Two other grades of graphites (P3W and ATJ) also showed similar behaviors. Auger electron spectroscopy (AES) showed that the impurities at the bottom of the voids formed by oxidation are mainly iron, sulfur and calcium. They proposed the same explanation that was given by Walker et al¹ and Wichner et al² for the observed inverse oxidation; the limited access of CO₂ to the interior of the graphite against the countercurrent of CO causes a higher ratio of CO/CO₂ inside the graphite than outside and, as a result, FeO is reduced at a certain distance from the surface to Fe that accelerates the oxidation reaction through catalysis.

For the oxidation of Fe in a CO/CO₂ gas mixture,



At $T = 875^\circ\text{C}$,

$$R^* (\text{CO}/\text{CO}_2) = \left(\frac{P_{\text{CO}}}{P_{\text{CO}_2}} \right)^* = \exp \left(\frac{-\Delta G^\circ}{RT} \right) = 1.64$$

where ΔG° is a standard free energy change for the reaction, R is a gas constant and R^* (CO/CO₂) is the equilibrium CO/CO₂ ratio.

For the oxidation of FeO to Fe₃O₄ in a CO/CO₂ gas mixture,



At $T = 875^\circ\text{C}$,

$$R^* (\text{CO}/\text{CO}_2) = \left(\frac{P_{\text{CO}}}{P_{\text{CO}_2}} \right)^* = \exp \left(\frac{-\Delta G^\circ}{RT} \right) = 0.267$$

Morgan and Thomas used a gas ratio,

$$\frac{P_{\text{CO}}}{P_{\text{CO}_2}} = 0.25$$

which is close to the equilibrium gas ratio for FeO/Fe₃O₄. Thus, the outer part of the sample probably contained FeO, and as the

oxidation proceeded the ratio $\left(\frac{P_{\text{CO}}}{P_{\text{CO}_2}} \right)$ in-

creased and reached the R^* value of ~1.67 that converted FeO to Fe. As a result, oxidation accelerated at a distance that was determined by the diffusion rates of CO₂ and CO, and showed the inverse oxidation phenomenon.

At the Brookhaven National Laboratory,⁴

the effect of the gas ratio, $\frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$, on the

reaction rate of PGX graphite containing about 100 ppm Fe at four different temperatures was studied and the results are shown in Figures 1 and 2. The gas ratio was changed by adding H₂ gas to an atmosphere of 0.63% H₂O in He.

For the reduction of FeO in a H₂/H₂O gas mixture, the free energy change is



the calculated equilibrium gas ratios are ~1.64, ~1.5 and ~1.37 for 760°C, 875°C and 956°C, respectively.

⁴ Thermodynamic values are from Ref. 4.

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Figure 1 shows that the reaction rates for 857°C and 956°C decreased until the gas ratio reached ~1.2, and then increased. The decrease at the beginning is reasonable, because H₂ is a product gas for the reaction:

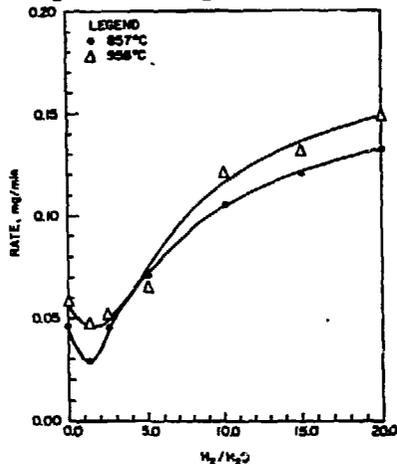


Figure 1 Dependence of the PGX Graphite Oxidation Rate on H₂/H₂O Ratio at 857 and 956°C.

At 760°C, Figure 2, the decrease of the reaction rate was not observed because of the low reaction rate when H₂ was not added. The reaction rate increased at the gas ratio of 1-1.6. At 660°C, the increase of the rate was not observed because of the very low rate of overall reaction.

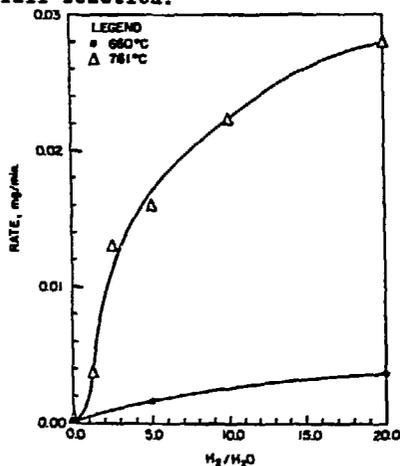


Figure 2 Dependence of the PGX Graphite Oxidation Rate on H₂/H₂O Ratio at 761 and 660°C.

All these critical gas ratios for the accelerated oxidation are in very good agreement with the R* values calculated from the thermodynamic data for the reduction of FeO to Fe. Based on the above discussion, it can be said that when the H₂/H₂O ratio in the He coolant is higher than the equilibrium H₂/H₂O ratio for FeO/Fe, there will be no inverse oxidation. On the other hand, if the ratio is below the critical ratio, inverse

oxidation is expected, and the degree of this phenomenon will be decided by the actual oxidant activity.

Wichner et al² reported that when the average H₂/H₂O ratio during the run at the exterior of the sample was less than 0.8, inverse oxidation was observed in some degree for all cases, and never observed for average ratios about 1.2. These agree very well with our calculations.

At Fort St. Vrain Power Station, the H₂/H₂O ratio under the normal operating conditions remains between 10 and 20.⁶ However, when there was a water ingress, this ratio decreased to about 1-2.⁶ In case there is a large ingress of water, this ratio should become even lower.

3. Conclusion

We have confirmed the existing explanation for the inverse oxidation phenomenon. If the H₂/H₂O ratio in the He coolant at 850°C becomes lower than ~1.5, the inverse oxidation will occur. It was reported that the H₂/H₂O ratio can go below this value when there is a water ingress. Thus, it is possible for the HTGR graphite to suffer the inverse oxidation. The degree of this phenomenon and the depth where it occurs will depend on the position of the graphite block, the amount of the water ingress and the impurity levels and pore structure of the graphite. More investigations are warranted.

Acknowledgments

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References

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6. Unpublished information from General Atomic Company.

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