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### Abstract

Concentration profiles have been obtained for the migration of  $\text{Mo}_2\text{C}$  in H451 graphite at temperatures above the melting point of the carbide (2690°C). The diffusion is consistent with the Fickian model and the diffusion coefficients which have been obtained are several orders of magnitude greater than those predicted from lower temperature thermodynamic data.

High Temperature Gas Cooled Reactor, molybdenum, diffusion, graphite.

### Introduction

In a hypothetical worst case scenario the complete loss of cooling of the core of a High Temperature Gas Cooled Reactor (HTGR) could ultimately result in core temperatures as high as 3600°C. The prediction of migration of radioactive materials through the graphite is necessary for the analysis of such hypothetical accidents.

Since extrapolation from models formulated for lower temperatures is uncertain, experimental determinations of diffusion coefficients were initiated.

In our initial work on this problem, molybdenum, in the form of  $\text{Mo}_2\text{C}$ , has been chosen as the migrating species. This is because molybdenum is a fission product, is chemically stable as a carbide and has non-decaying isotopes that can be used to simulate the active isotopes.

### Experiment

The experiments are performed by loading a thin layer of  $\text{Mo}_2\text{C}$  into a flat bottomed cavity in a H451 graphite (Great Lakes Carbon Corp.) cylinder used as the susceptor of a 30 kw induction furnace.

After heating the sample to temperatures spanning the melting point of  $\text{Mo}_2\text{C}$  (2690°C), the graphite is machined to separate the cylindrical portion lying directly below the plane of the  $\text{Mo}_2\text{C}$  melt. This cylinder is then sliced along planes parallel to the plane of the melt and these slices are ashed and assayed for molybdenum. This results in values of concentration averaged over the volume of the slice for various distances from the  $\text{Mo}_2\text{C}$  source.

To check the possibility that molybdenum was diffusing into the sample susceptors from the surrounding environment (e.g. the insulating medium), a blank graphite susceptor containing no molybdenum was heated to a temperature of 3000°C for 4 hours and then assayed. No molybdenum other than an approximate 0.5 ppm background was found.

### Results

It is noteworthy that the family of curves (Figure 2) generated by this series of experiments seem to extrapolate back to a virtual source of about 30 ppm concentration. This would seem to indicate that there is more than one phenomenon involved in the diffusion process, since the real source has a molybdenum concentration orders of magnitude greater. Interestingly, 30 ppm molybdenum corresponds to less than monolayer coverage of the graphite. Accordingly, the "apparent" diffusion coefficients,  $D$ , have been calculated using the assumption that the molybdenum is drawn from a non-depletable source of 30 ppm concentration. Under these circumstances, the diffusion very closely resembles Fickian diffusion in the geometry of the experiment.

The geometry of the sample had been selected originally to approach a constant infinite plane source to simplify the analysis. However, the region in which the molybdenum concentration is non-negligible was found to have dimensions comparable with the lateral dimensions of the source and of the diffusion volume. Therefore, the fitting of the data for the inference of an effective diffusion coefficient required a two dimensional time dependent analysis. The heat conduction computer code, TAC-2D(-) was used to solve the time dependent two dimensional analog. The geometrical dimensions were retained in the calculation and the diffusivity was set to  $1 \text{ cm}^2/\text{sec}$ . Adiabatic boundary conditions were assumed for the outer surfaces of the volume. Since the time scales inversely proportional to the diffusion coefficients, is the distribution observed after  $T$  seconds

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matches the distribution computed for t seconds;

$$D = \frac{t}{\pi} \text{ cm}^2/\text{sec} .$$

The computed diffusion equation solutions were averaged over the cross section of the cylinder sliced for samples for analysis. The average concentration as a function of distance from the source was plotted as a function of distance from the source with time as a parameter. This set of curves was used to match the results and determine the time t, and thereby infer D.

The experimentally obtained diffusion coefficients are;

$$D = 5.6 \times 10^{-4} \text{ cm}^2/\text{sec} \quad @ 3200^\circ\text{C for 1 hour}$$

$$D = 4.0 \times 10^{-4} \text{ cm}^2/\text{sec} \quad @ 3100^\circ\text{C for 33 minutes}$$

$$D = 2.4 \times 10^{-4} \text{ cm}^2/\text{sec} \quad @ 3000^\circ\text{C for 8 hours}$$

$$D = 2.8 \times 10^{-4} \text{ cm}^2/\text{sec} \quad @ 3000^\circ\text{C for 4 hours}$$

$$D = 8.3 \times 10^{-5} \text{ cm}^2/\text{sec} \quad @ 2900^\circ\text{C for 1 hour.}$$

The results appear to be internally self-consistent, with two independently obtained coefficients at 3000°C agreeing within 16%. Noteworthy is the fact that the experimentally observed results give a diffusion coefficient which is several orders of magnitude greater than that calculated using the correlation used in the SORS code (2):

$$-\log_{10} D = A + \frac{B \times 10^3}{T}$$

where, for MO: A = 1.0, B = 19.2 and T is in °K. The data incorporated into the SORS code have been obtained from the review by Norman, (3) whose model for the estimation of diffusion coefficients is based upon the premise that the activation energy for diffusion is nominally 55% of the heat of vaporization of the element of interest in graphite. The log of the pre-exponential factor,  $D_0$  is taken as 2.36% of the heat of vaporization.

$$\begin{aligned} -\log_{10} D &= -\log_{10} D_0 + \frac{\Delta H_d}{RT} \\ &= .0286 \beta_{\text{vap}} - \frac{.55}{T} \beta_{\text{vap}} \\ &= A + \frac{B \times 10^3}{T} . \end{aligned}$$

This expression was developed using the scant experimental data for the diffusion of Th, Sr, Ba, U and Ce in graphite. Since diffusion data were not available for the other fission product elements of interest in the HTGR, the above expression was extrapolated to those systems using the heuristic relationship between the heat of vaporization and the activation energy for diffusion in graphite. The experimentally obtained diffusion coefficients for molybdenum point out the inherent dangers in making this sort of an extrapolation.

Although several experiments were performed at temperatures below the melting point of  $\text{Mo}_2\text{C}$  (2690°C), diffusion coefficients for these have not been obtained. At these lower temperatures the diffusion is so slow that the molybdenum present as background in the graphite (0.1-0.5 ppm) masks any due to diffusion. In any case, the sub-ppm region is at the lower limits of detectability for the wet chemical method used for analysis.

#### Conclusion

The experimental results, which are of a preliminary nature, indicate that the migration of molybdenum in H481 graphite is much faster than expected.

#### Acknowledgments

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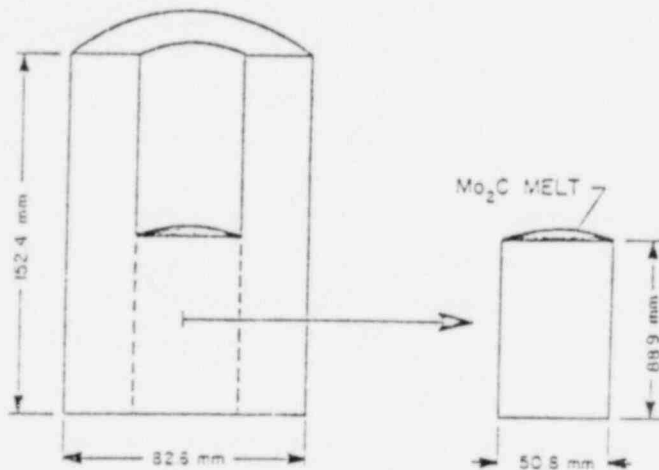


FIGURE 1 ONE HALF OF A SUSCEPTOR SHOWING THAT REGION DIRECTLY UNDER THE PLANE OF THE MELT WHICH IS SUBJECTED TO WET CHEMICAL ANALYSIS SLICES OF THICKNESS  $125'' - 500''$  ARE TAKEN IN THE PLANE PARALLEL TO THE MELT.

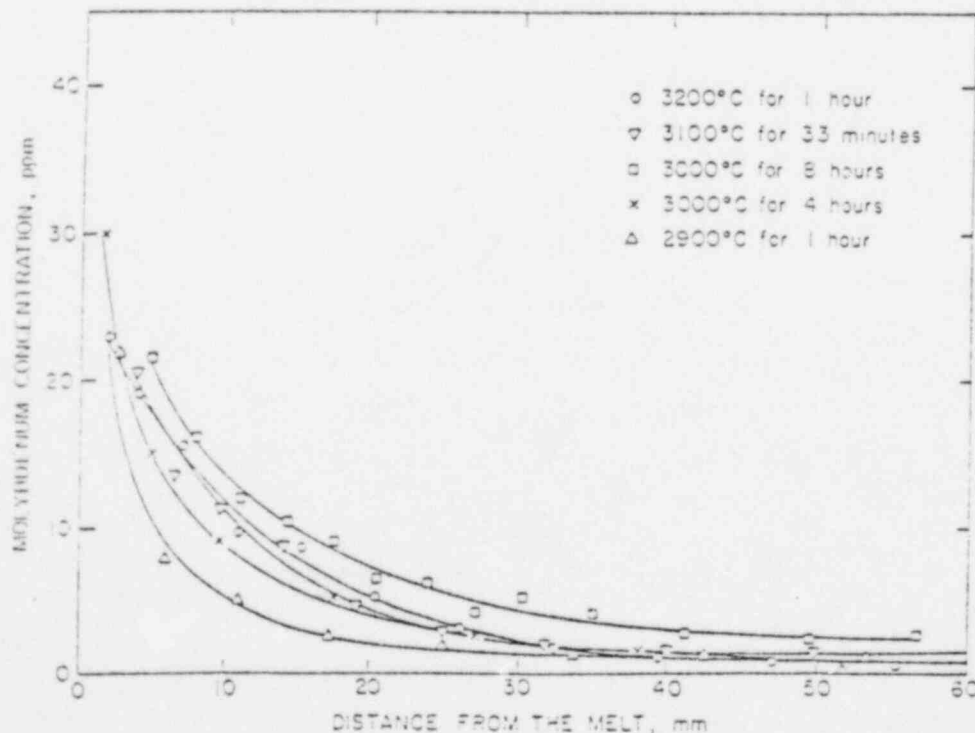


Figure 2. Experimentally obtained diffusion profiles for the migration of molybdenum in H451 graphite.

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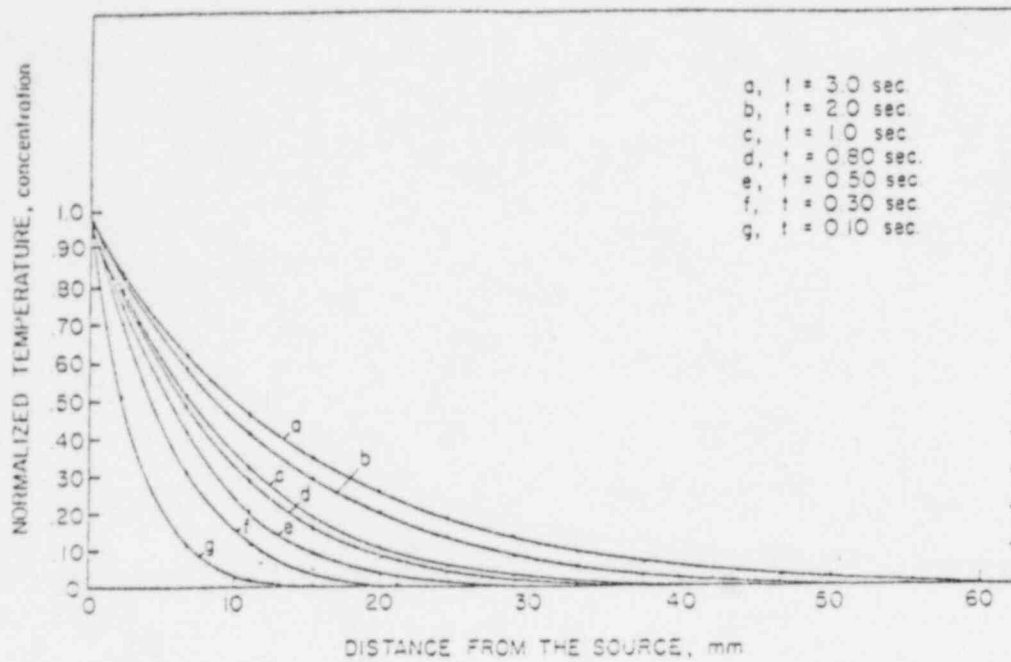


Figure 3. Solutions, in the experimental geometry, generated by the computer code TAC2D.