ICP-MS Measurement of Iodine Diffusion in IG-110 Graphite for HTGR/VHTR

L.M. Carter^a, J.D. Brockman^{b*}, J.D. Robertson^{a,b}, S.K. Loyalka^c

^aDepartment of Chemistry, University of Missouri, 125 Chemistry Building, Columbia, MO 65211, United States

^bUniversity of Missouri Research Reactor Center, University of Missouri, 1513 Research Park Dr., Columbia, MO 65211, United States

^cNuclear Science and Engineering Institute, University of Missouri, E2433 Lafferre Hall, Columbia, MO 65211, United States

*Corresponding author. Tel.: +1 573 884 8095

Email address: brockmanjd@missouri.edu

Abbreviations

HTGR: High Temperature Gas-Cooled Reactor

ICP-MS: Inductively Coupled Plasma-Mass Spectrometry

INAA: Instrumental Neutron Activation Analysis

FP: Fission Product

VHTR: very high temperature reactor

MURR: University of Missouri Research Reactor

Abstract

Graphite functions as a structural material and as a barrier to fission product release in HTGR/VHTR designs, and elucidation of transport parameters for fission products in reactor-grade graphite is thus required for reactor source terms calculations. We measured iodine diffusion in spheres of IG-110 graphite using a release method based on Fickian diffusion kinetics. Two sources of iodine were loaded into the graphite spheres; molecular iodine (I₂) and cesium iodide (CsI). Measurements of the diffusion coefficient were made over a temperature range of 873-1293 K. We have obtained the following Arrhenius expressions for iodine diffusion:

$$D_{I, CsI \text{ infused}} = \left(6 \times 10^{-12} \frac{\text{m}^2}{\text{s}} \right) \exp \left(\frac{30,000 \frac{\text{J}}{\text{mol}}}{RT} \right)$$

And,

$$D_{I, I_2 \text{ infused}} = \left(4 \times 10^{-10} \frac{\text{m}^2}{\text{s}} \right) \exp \left(\frac{-11,000 \frac{\text{J}}{\text{mol}}}{RT} \right)$$

The results indicate that iodine diffusion in IG-110 graphite is not well-described by Fickian diffusion kinetics. To our knowledge, these are the first measurements of iodine diffusion in IG-110 graphite.

1. Introduction

Release of iodine radioisotopes, particularly I-131, is of concern during both normal operation and accident scenarios involving HTGRs. In predicting iodine release from such reactors, complex mechanisms of interaction (e.g. diffusion, sorption, chemistry) of iodine with the fuel, core materials, and materials comprising the reactor cooling circuit must be considered. Nuclear graphite grade IG-110 comprises multiple permanent and replaceable core structures in the High-Temperature Engineering Test Reactor (HTTR) in Japan, and is currently a candidate graphite for use in other contemporary HTGR designs. The present work focuses on analysis of iodine transport in IG-110 by diffusion.

The transport of iodine in graphite has not been well characterized. In Matrix A3 graphite iodine transport under normal HTGR operational conditions has been described by Müller and summarized in IAEA TEC DOC 978[1,2]. The results demonstrate that iodine diffusion is described by either a pore diffusion mechanism or diffusion through graphite grains depending on the initial iodine loading conditions and the temperature [2]. Rapid release of iodine from graphite is attributed to fast transport through pores while a slow transport mechanism is connected to diffusion through the graphite grain. There is a recognized trapping effect of iodine in graphite that Verfondern, Cao, et al. describe as being attributed to heavy metal contamination in the graphite grains [3]. Though release mechanisms may be unknown or complex, it is normal to treat iodine diffusion using a simple Fickian model with an effective diffusion coefficient. This approach is used by the fuel performance modeling codes PARFUME, COPAR, ATLAS and the historic code FRESKO[3]. The effective diffusion coefficient is meant to encompass all of the complex transport mechanisms (pore diffusion, grain diffusion, trapping, etc).

The iodine diffusion data reported by Müller and summarized in IAEA Tecdoc 978 use A3 matrix graphite. However, iodine transport is reported to be sensitive to the type of graphite and therefore the structural and chemical characteristics of the graphite could alter transport of iodine out of graphite [4]. In this work we measured the diffusion coefficients of iodine in IG-110 graphite over the temperature range of 873-1293K using a release method based on a classical Fickian diffusion model. This approach is useful and consistent with the fission product release models model cause fission product release models and computer codes that use Fickian diffusion and effective diffusion coefficients to describe iodine transport.

2. Theory

The diffusion coefficient characterizes classical diffusive transport of a particular substance (fission product, or fission product surrogate) in a particular medium (graphite). The concentration of FP in the sample is described by the Fick's second law of diffusion:

$$\frac{\partial C}{\partial t} = D \nabla^2 C \quad (1)$$

where t is the time (s), C is the concentration (kg/m³) of FP as function of position and time, and D is the diffusion coefficient (m²/s).

Diffusion coefficients for FP's in graphite are commonly determined experimentally using the release method, wherein spheres of graphite material are uniformly infused with a fission product surrogate(s), and release of the FP in time is monitored isothermally in a separate experiment. In practice, the release rate or fractional release is typically measured. Fractional release is defined as the total cumulative mass release of FP divided by the total initial mass of FP present within the sample. For a sphere of radius R with an initial uniform concentration C_0 , we have for the mass release rate:

$$\dot{m}(t) = 8\pi R D C_0 \sum_{n=1}^{\infty} e^{-\left(\frac{n\pi}{R}\right)^2 D t} \quad (2)$$

And,

$$F(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\left(\frac{n\pi}{R}\right)^2 D t} \quad (3)$$

The diffusion coefficient may be obtained by fitting Eqs. (2) or (3) to the experimental data.

3. Experimental

3.1. Instrumentation

A specialized SiC diffusion cell coupled to a NexION™ 300X ICP-MS calibrated via INAA was used for quantification of the fractional release. Transport of FP from the sample to the ICP-MS was facilitated using an aerosol laden He jet system. A complete description of the instrumentation and INAA calibration procedures used in this analysis is found in Ref. [5,6].

3.2. Materials and Methods

3.2.1. Sample preparation

Spheres of reactor grade IG-110 graphite were infused with iodine using two different source materials. One set of spheres was infused with iodine using cesium iodide (CsI). A second set was infused with iodine using molecular iodine (I₂).

Cesium iodide Source

Spheres with radius $R=0.16\text{cm}$ were milled from as-received IG-110 stock material by the MURR Science Instrument shop. The spheres were added to a cylindrical quartz vial along with approximately 200 μg each of solid Cs and RbNO_3 (as-received from Fisher Scientific). The vial was sealed under 13 Pa vacuum with a flame sealing torch. The vial and samples were annealed at 1373 K and maintained at this temperature for four days in an effort to infuse iodine, cesium, and rubidium within the spheres. The CsI melts at 894 K and boils at 1550 K. The RbNO_3 decomposes at 863 K to the nitrite salt which is also unstable and decomposes to rubidium oxide. Previous groups have demonstrated that Cs metal is formed when Cs nitrate undergoes thermal decomposition in the presence of graphite [7]. We anticipated this would also be the case with Rb. The spheres were further machined to $R=0.15\text{ cm}$ using SiC sandpaper. Machining dust was removed with compressed air.

Molecular iodine Source

Spheres of IG-110 graphite were machined identically to those used in the CsI infusion. These were infused using approximately 200 μg of molecular iodine (crystalline I_2 as received from Fisher Scientific). In this case, the spheres were heated to 723 K for 4 days to infuse iodine as physisorbed molecular iodine [8]. The spheres were machined to a final radius of 0.15 cm after the infusion procedure, and machining dust and contamination removed with compressed air.

3.2.2. Initial elemental content analysis

Instrumental neutron activation analysis was conducted to determine the masses of cesium, iodine, and rubidium present within the spheres following the annealing procedure. The cesium and rubidium standards were prepared by drying aliquots of CsNO_3 and RbNO_3 (2% HNO_3 ICP-MS standards as received from High Purity Standards) onto stacked filter paper in polyethylene vials. Iodine standards were prepared by drying aliquots of iodide present in 0.01% KOH (as received from High Purity Standards) onto stacked filter paper in polyethylene vials. The samples and standards were irradiated simultaneously in the row 2 pneumatic tube position at the MURR facility for ten seconds at a thermal neutron flux of $5.0 \times 10^{13} \text{ n/cm}^2/\text{s}$. The irradiation induced $^{134\text{m}}\text{Cs}$, ^{128}I , and ^{88}Rb via the reactions following reactions: $^{133}\text{Cs}(n,\gamma)^{134\text{m}}\text{Cs}$, $^{127}\text{I}(n,\gamma)^{128}\text{I}$, and $^{87}\text{Rb}(n,\gamma)^{88}\text{Rb}$, respectively. The samples and standards were counted 1 cm away from the face of a 20% relative efficiency HPGe detector. Detector dead time was managed using the loss free counting technique.

Cesium, iodine, and rubidium were initially present in the sealed vial used in the multi-element infusion procedure. However, only iodine was found to have diffused into the spheres in appreciable amounts ($\approx 1 \mu\text{g/sphere}$) under the experimental conditions. The 95% confidence level minimum detectable activity (MDA) for Cs and Rb was 50 ng and 200 ng, respectively.

3.2.3. Diffusion measurements

The ICP-MS was used to measure release of cesium, iodine, and rubidium in time under isothermal temperature conditions in the range of 873 K to 1293 K. Data points (release rates for cesium, iodine,

and rubidium) were acquired every ten seconds. Release was measured for a period of approximately five hours at all temperatures. The cesium, iodine, and rubidium signals were monitored for approximately one hour before a sphere is introduced into the instrument diffusion cell to allow for correction due to detector background. Cesium and rubidium release was not observed in the ICP-MS spectrum which was expected based on the results of the INAA measurement (3.2.2). Fractional release was computed from a summation of the product of the ten second measurement interval and the ten second time-averaged fractional release rate.

3.2.4. Final elemental content analysis

Following ICP-MS release measurements, the iodine content of each sphere was determined again using standard comparator INAA as described in sections 3.2.2. The iodine mass difference before and after release measurements was used to determine the ICP-MS calibration factor, which scales the ICP-MS count rate to units of grams iodine/s, or cumulative release rate to grams iodine, respectively. The calibration method and related calculations are described in detail in Ref. [5,6].

4. Results

The masses of iodine present in each sphere before and after release measurements are given in Table 1, and fractional release data given in Figures 1 and 2.

Table 1. IG-110 sphere iodine content and effective diffusion coefficients calculated *via* Eqn. (3).

Temperature (K)	Iodine Source	$m_{I,initial}$ (μg)	$m_{I,final}$ (μg)	D_{eff} (m^2/s)
873	CsI	1.71	0.104	3.1×10^{-10}
983	CsI	0.790	0.0265	3.0×10^{-10}
1108	CsI	1.17	0.0730	2.5×10^{-10}
1193	CsI	1.41	0.0644	1.3×10^{-10}
1293	CsI	0.819	0.0837	7.6×10^{-11}
875	I ₂	30.4	4.19	7.0×10^{-11}
978	I ₂	31.0	1.98	1.6×10^{-10}
1080	I ₂	49.9	3.90	1.2×10^{-10}
1188	I ₂	30.0	2.36	1.2×10^{-10}
1270	I ₂	26.7	2.23	1.4×10^{-10}

Figure 1: Fractional release of iodine from $R=0.15$ cm spheres of IG-110 infused using Csl at 1373 K.

Figure 2: Fractional release of iodine from $R=0.15$ cm spheres of IG-110 infused with I_2 at 723 K.

The temperature dependence of the measured diffusion coefficients is plotted in Figure 3. The temperature dependence of Fickian diffusion kinetics is described using the classical Arrhenius form of the diffusion coefficient, via:

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where E_a is the activation energy (J/mol), D_0 is the diffusivity at infinite temperature (m^2/s), T is the temperature (K), and R is the universal gas constant (J/mol·K). The activation energies E_a and pre-exponential factors D_0 are given with respective uncertainties in Table 2, below:

Table 2. Arrhenius parameters for iodine diffusion in IG-110 spheres infused using CsI and I_2 as the iodine source.

Material	Diffusant	D_0 (m^2/s)	$\pm\Delta\ln D_0$	E_a (J/mol)	$\pm\Delta E_a$ (J/mol)
CsI-infused IG-110	Iodine	6×10^{-12}	1.1	-3.0×10^4	1×10^4
I_2 -infused IG-110	Iodine	4×10^{-10}	0.96	1.1×10^4	8×10^3

The negative value of the activation energy obtained from the CsI infused samples indicates a departure from Fickian diffusion kinetics (discussed further in Section 5). The P-values of the slope from the linear regression of $\ln D$ and reciprocal temperature for the I_2 -infused and CsI-infused samples were 0.27 and 0.054, respectively. A P-value of less than 0.05 indicates a slope that is significantly different than zero. The P-values for the slope in this analysis suggest that iodine diffusion is not temperature dependent or very weakly temperature dependent over the range of temperatures tested in this experiment. This is demonstrated by the overlapping 95% confidence interval of the linear regression fit shown in Fig 3.

Figure 3: Variation in diffusion coefficients of iodine with temperature; Müller's results are for Matrix Graphite A3 as obtained from the Studsvik fission (R/B) experiments from Ref [4]. The error bars for each data point are 5%. The data was fit using a linear regression analysis and the 95% confidence interval is shown in the figure.

5. Discussion

Eqn.'s 2 and 3 assume perfectly spherical samples that are not in contact with other materials and with an initially uniform distribution of diffusant. Due to the rapid release of iodine from the samples and comparatively long equilibration times for the infusions, we also assume the initial distribution of iodine was uniform throughout the spheres [6].

The calculated effective diffusion coefficients for iodine are larger than those reported by Müller in the 873-1293 K temperature range. This can be partially explained considering multichannel transport pathways for iodine transport in graphite; more specifically, a slow diffusion process occurring within the graphite grains and a fast diffusion process that occurs in the pores. The iodine in Müller's experiments was implanted in the graphite via irradiation of HTGR fuel, which may cause fission recoil of iodine into the graphite grains. In our experiments, the iodine is expected to be present more predominantly in the pores, which is reflected in the higher effective diffusion coefficients. Further, in

our experiments the diffusion coefficients were very similar for spheres infused using either Csl or molecular iodine. This suggests that either the iodine effective diffusion coefficient is very weakly dependent on the chemical form of the iodine (I^- , $I^\cdot$, I_2 , etc.), or that upon heating in the presence of graphite, the iodine is all converted to the same chemical form.

Though the temperature dependence of the diffusion coefficient was found to be weak in both the Csl-infused and I_2 -infused spheres, the effective diffusion coefficients extracted using the Csl-infused IG-110 spheres was observed to decrease with increasing temperature, the opposite of what would be expected based purely on classical diffusion theory. These results suggest that at higher temperatures, iodine is chemically converted to a more strongly bound form. Exploration of the chemical form of iodine is beyond the scope of the present experimental design. However, we have considered briefly the role iodine dissociation may play (see Ref [9] for a discussion of the role of dissociation in diffusion of a mixture of N_2O_4 - NO_2 in a condensed medium). The diffusion equations for the iodine radical (the monomer, C_1) and the iodine molecule (the dimer, C_2) may be written as (we are ignoring a cross-diffusion term used by Frisch; the nature of which is not clear to us):

$$\frac{\partial C_1}{\partial t} = D_1 \nabla^2 C_1 - R(C_1, C_2) \quad (5)$$

$$\frac{\partial C_2}{\partial t} = D_2 \nabla^2 C_2 + \frac{1}{2} R(C_1, C_2) \quad (6)$$

Where $R(C_1, C_2)$ is the net, local rate of conversion of monomer to dimer species, and D_1 and D_2 are the diffusion coefficients of the monomer and the dimer, respectively. Frisch assumes a local equilibrium between the two species so that the two concentrations are not independent, and we thus assume also that:

$$C_2 \approx \kappa C_1$$

Where κ is some temperature dependent function (it may depend on C_1 and C_2) relating to the equilibrium constant (the situation is complicated as the species are in a condensed material, and the equilibrium would be affected by it). Then combining eqs. (5) and (6), for the total concentration and the combined diffusion coefficients, defined respectively, as:

$$C = C_1 + 2C_2 \quad (7)$$

$$D = (D_1 + 2\kappa D_2) / (1 + 2\kappa) \quad (8)$$

We obtain the equation:

$$\frac{\partial C}{\partial t} = D \nabla^2 C \quad (9)$$

Thus our Eq. (1) remains valid, provided the diffusion coefficient is interpreted as the combined (or the effective) diffusion coefficient. This in itself does not necessarily explain the observed constancy or the decrease in the diffusion coefficient with temperature. It seems to us that one may need to account for the different bindings (absorption cross-sections) of two iodine species to graphite in the phenomenology (the equations) to clarify the observed lack of temperature dependence of the diffusion coefficient in the temperature range studied, and indeed over the entire temperature range of interest. It is possible that the effective diffusion coefficient first increases with temperature, then is almost constant or slightly decreases with temperature, and then increases again with temperature depending on the dissociation and different binding of the radical and molecular species with graphite. We note that in our measurements, at all temperatures, small residual amounts (~5%) of iodine remained in the graphite even at long times. We suspect this represents iodine that is very strongly bound to impurity sites in the graphite. Some idealized calculations have indicated that the most thermodynamically stable form of diffusing iodine in an HTGR is cesium iodide, while previous laboratory experiments and HTGR cooling circuit analyses have indicated the iodine behavior is more closely characterized by that of molecular or atomic iodine [10]. Therefore, it would be useful to infuse IG-110 with both cesium and iodine to investigate the effect of each component on the release rates.

In future work we will seek to compare reactor iodine diffusion in reactor irradiated graphite compared to non-irradiated graphite. It has been demonstrated that iodine is trapped in UO_2 fuel matrix when radiation induced dislocation damage occurs at concentrations above 10^{16} atoms/cm³ [11]. It is therefore likely that lattice damage in graphite and the ingrowth of fission products from burnup of fuel and diffusion will alter the transport of iodine and other fission products in graphite.

6. Conclusion

We have measured diffusion coefficients of iodine in IG-110 graphite using ICP-MS coupled to a carbon aerosol helium gas-jet system. In the 873-1273K temperature range, we have obtained:

$$D_{I, \text{CsI infused}} = \left(6 \times 10^{-12} \frac{\text{m}^2}{\text{s}}\right) \exp\left(\frac{30,000 \frac{\text{J}}{\text{mol}}}{RT}\right) \quad (10)$$

And,

$$D_{I, I_2 \text{ infused}} = \left(4 \times 10^{-10} \frac{\text{m}^2}{\text{s}}\right) \exp\left(\frac{-11,000 \frac{\text{J}}{\text{mol}}}{RT}\right) \quad (11)$$

As is typically done in fuel performance modeling, we have used the classical Fickian diffusion model for obtaining effective diffusion coefficients. The temperature dependence of the calculated effective diffusion coefficients was not well described by Fickian diffusion kinetics. As far as we know these are the only data for diffusion of iodine in IG-110 that are presently available.

Acknowledgements

This research has been supported by the U.S. Department of Energy Nuclear Energy University Program (NEUP-2982). The authors express gratitude to Drs. Tushar Ghosh, Matthew Simones, and Rajesh Gutti for helpful discussion and assistance with instrumentation, and to Saint Gobain-Hexaloy and the MURR Science Instrument Shop for mechanical support.

References

- [1] "Fuel performance and fission product behavior in gas cooled reactors," IAEA-TECDOC-978, International Atomic Energy Agency, Vienna, pp. 448-453 (1997).
- [2] A. Müller, Freisetzungsgasförmiger Spaltprodukte (Kr, Xe, J) aus Brennelementen für Gasgekühlte Hochtemperaturreaktoren, PhD thesis (Aachen), Jül 1295, Kernforschungsanlage, Jülich (1976).
- [3] K. Verfondern, J. Cao, T. Liu, H.-J. Allelein. Conclusions from V&V studies on the German codes PANAMA and FRESCO for HTGR performance and fission product release. Nucl. Eng. Des. 271 (2014) 84-91.
- [4] S. Yajima, S. Ichiba, Y. Kaemeto, K. Shiba. The Behavior of Fission Products Captured in Graphite Powder by Nuclear Recoil. III. Diffusion of Iodine-133 and Tellurium-123 in Graphite at High Temperatures. Bull Chem. Soc. Japan 34 (1961) 493-497
- [5] L.M. Carter, J.D. Brockman, S.K. Loyalka, J.D. Robertson. Measurement of Cs diffusion coefficients in IG-110 graphite. J. Nucl. Mater. 460 (2015) 30-36.
- [6] L.M. Carter, J.D. Brockman, J.D. Robertson, S. K. Loyalka. ICP-MS Measurement of Cs diffusion coefficients in NBG-18 graphite. J. Nucl. Mater. 460 (2015) 30-36.
- [7] R. B. Evans, W. Davis, A.L. Sutton. "Cesium diffusion in graphite". ORNL-5648, Oak Ridge National Laboratory, Tennessee, US. (1980)
- [8] K. Iwamoto, J. Oishi. The Behavior of Iodine in Adsorption and Desorption by Graphite, J. Nucl. Sci. Technol. 5 (1968) 437-446.
- [9] H. L. Frisch. Diffusion of an Equilibrium Mixture of a Dissociating Gas. Macromolecules 6 (1973) 758-760.
- [10] O. K. Tallent, R. P. Wichner, R. L. Towns, T. T. Godsey. "Analysis of Iodine and Cesium Chemical Forms Evolved from Graphite Surfaces at Temperatures from 452 to 1400°C" HTGR-85-069 ORNL/TM-9218, Oak Ridge National Laboratory, Tennessee, US. (1985).
- [11] W. H. Hocking, R. A. Verrall, I. J. Muir. J. Nuc. Materials 294 (2001) 45-52.