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ICP-MS measurement of iodine diffusion in IG-110 graphite for HTGR/VHTR

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HIGHLIGHTS

- ICP-MS was used to study diffusion of iodine in nuclear-grade graphite IG-110.
- The design simulates normal HTGR operation conditions.
- Diffusion coefficients for iodine in IG-110 were obtained.

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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 Fickain diffusion kinetics. Two sources of iodine were loaded into the graphite spheres; molecular iodine (I_2) 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:$D_{I,\ CsI\ infused} = \left(6 \times 10^{-12}\ \frac{\mathrm{m}^2}{\mathrm{s}}\right) \exp\left(\frac{30{,}000\ \frac{\mathrm{J}}{\mathrm{mol}}}{RT}\right)$And,$D_{I,\ I_2\ infused} = \left(4 \times 10^{-10}\ \frac{\mathrm{m}^2}{\mathrm{s}}\right) \exp\left(\frac{-11{,}000\ \frac{\mathrm{J}}{\mathrm{mol}}}{RT}\right)$

The results indicate that iodine diffusion in IG-110 graphite is not well-described by Fickan 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

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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.

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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 FRESCO [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 873–1293 K 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 Fickan 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:

$$\frac{\partial C}{\partial t} = D\nabla^2 C \tag{1}$$

where t is the time (s), C is the concentration (kg/m^3) of FP as function of position and time, and D is the diffusion coefficient (m^2/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 concentrationC_0, we have for the mass release rate:

$$\dot{m}(t) = 8\pi RDC_0 \sum_{n=1}^{\infty} e^{-\left(\frac{n\pi}{R}\right)^2 Dt} \tag{2}$$

And,

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

The diffusion coefficient may be obtained by fitting Eq. (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 Refs. [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 (I_2).

3.2.1.1. Cesium iodide source. Spheres with radius $R = 0.16$ 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 CsI 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 $R = 0.15$ cm using SiC sandpaper. Machining dust was removed with compressed air.

3.2.1.2. 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 10 s at a thermal neutron flux of 5.0×10^{13} n/cm^2/s. The irradiation induced ^{134m}Cs, ^{128}I, and, ^{88}Rb via the reactions following reactions:^{133}Cs(n,γ)^{134m}Cs, ^{127}I(n,γ)^{128}I, and ^{87}Rb(n,γ)^{88}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 (≈1 μg/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–1293 K. Data points (release rates for cesium, iodine, and rubidium) were acquired every 10 s. Release was measured for a period of approximately 5 h at all temperatures. The