ICP-MS Measurement of Diffusion Coefficients of Cs in NBG-18 Graphite

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Abbreviations

HTGR: High Temperature Gas-Cooled Reactor

ICP-MS: Inductively Coupled Plasma-Mass Spectrometry

LA-ICP-MS: Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry

INAA: Instrumental Neutron Activation Analysis

FP: Fission Product

Abstract

Graphite is used in the HTGR/VHTR as moderator and it also functions as a barrier to fission product release. Therefore, an elucidation of transport of fission products in reactor-grade graphite is required. We have measured diffusion coefficients of Cs in graphite NBG-18 using the release method, wherein we infused spheres of NBG-18 with Cs and measured the release rates in the temperature range of 1090-1395 K. We have obtained:

$$D_{Cs,NBG-18} = \left(1.0 \times 10^{-7} \text{ m}^2/\text{s}\right) \exp\left(\frac{-1.23 \times 10^5 \text{ J/mol}}{RT}\right)$$

These seem to be the first reported values of Cs diffusion coefficients in NBG-18. The values are lower than those reported for other graphites in the literature.

1. Introduction

Release of fission products from nuclear reactors is a fundamental safety concern. The High Temperature Gas-Cooled Reactor (HTGR/VHTR) uses graphite as a moderator and as a barrier to fission product release in the reactor core. The VHTR is expected to operate with a maximum core outlet temperature of 950°C, and in an accident scenario may reach temperatures in excess of 1600°C. At these temperatures, diffusion becomes an important mechanism of fission product transport and release from the core. Improvements in manufacturing techniques coupled with unavailability of historical graphite grades (e.g. H-451) have led to the development of contemporary grades of nuclear graphite including IG-110, NBG-18, and PCEA, and these and other candidate graphites need to be well qualified [1]. Currently, material properties and diffusion/oxidation behavior of candidate graphites are being intensely investigated. Measurements of diffusion coefficients for fission products in graphite are required for source term estimations and reactor safety.

We have previously measured diffusion coefficients for Cs in IG-110 graphite using the release method, in which graphite spheres were infused with Cs and subsequent release of Cs measured by ICP-MS [2], and we have illustrated infusion procedures and instrument calibration for Cs in NBG-18 graphite [3]. In this paper we apply the technique to diffusion of Cs in NBG-18 graphite, and focus on the results for NBG-18 and comparisons with IG-110.

We note that IG-110 graphite is a very fine-grained petroleum coke filler-based graphite produced by Toyo Tanso in Japan using an isostatic rubber press process. NBG-18 is manufactured using a vibrational molding process by SGL Carbon GmbH in Germany, using a much larger grain size and coal coke filler. Differences in manufacturing techniques and materials impart wide variation among the properties of nuclear graphites, including pore size distribution, concentration of impurities, density, and grain sizes. These characteristics are expected to have an effect on fission product diffusion coefficients in graphite. A summary of relevant characteristics for IG-110 and NBG-18 is given in Ref. [5].

2. Theory

Transport of Cs in certain graphites has been shown to occur via a pore surface diffusion mechanism which consists of series of random “jumps” of Cs atoms between diffusion sites [6-11]. The permeability of a material to a particular diffusant is characterized by the diffusion coefficient. The diffusion coefficient generally follows an Arrhenius type dependence on temperature, specifically:

$$D = D_0 \exp\left(\frac{-E_a}{RT}\right) \quad (1)$$

where D is the diffusion coefficient (m^2/s), D_0 is the diffusion coefficient at infinite temperature, E_a is the activation energy (J/mol), R the gas constant ($\text{J/mol}\cdot\text{K}$), and T the temperature (K). In graphite, the diffusion coefficient may be a function of other factors in addition to temperature, including pore size distribution, oxidation, irradiation, and concentration of contaminants.

Here we consider a spherical graphite sample of radius $r=R$ which has been infused with a particular fission product (FP). As the sample is heated, the concentration of the FP changes at a time dependent rate governed by the diffusion equation, as the FP atoms diffuse through and out of the sphere through its surface. Under the assumption that the mass distribution of the FP is spherically symmetric, we have [2,9,12,13]:

$$\frac{\partial C(r,t)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D r^2 \frac{\partial C(r,t)}{\partial r} \right) \quad (2)$$

With boundary condition:

$$C(R,t) = 0 \quad (3)$$

Here, $C(r,t)$ is the concentration of the FP (g/cm^3), and t is the time (s). Note that $C(r,t)$ is non-negative and is finite everywhere. This mass transfer equation is well known, and may be solved using separation of variables, transform techniques, or numerical methods.

The series solution of Eqns. (1-2) is known to be:

$$C(r,t) = \sum_{n=1}^{\infty} A_n \psi_n(r) \text{Exp}(-\lambda_n^2 Dt) \quad (4)$$

Where,

$$\begin{aligned} \lambda_n &= n\pi / R \\ \psi_n(r) &= \sin(\lambda_n r) / r \\ A_n &= \frac{2}{R} \int_0^R r^2 C(r,0) \psi_n(r) dr \end{aligned} \quad (5)$$

Where $C(r,0)$ is the initial condition, the concentration profile in the sphere, at $t=0$.

The mass loss rate (g/s) of FP from the sphere is expressed as:

$$\dot{m}(t) = -4\pi R^2 D \frac{\partial}{\partial r} C(r,t) \Big|_{r=R} = 4\pi R D \sum_{n=1}^{\infty} A_n (-1)^{n-1} \lambda_n \text{Exp}(-\lambda_n^2 Dt) \quad (6)$$

And, the cumulative fractional release $F(t)$, defined as the ratio of mass of FP released from the sphere (up to time t) to the total initial FP mass, is thus:

$$F(t) = \frac{1}{m_0} \int_0^t \dot{m}(t') dt' = \frac{4\pi RD}{m_0} \sum_{n=1}^{\infty} A_n (-1)^{n-1} \frac{1}{\lambda_n D} \left[1 - \text{Exp}(-\lambda_n^2 Dt) \right] \quad (7)$$

Where m_0 is the total initial total mass of the FP in the sphere,

$$m_0 = 4\pi \int_0^R r^2 C(r, 0) dr \quad (8)$$

If the initial distribution of FP, $C(r, 0)$ is known, (6) or (7) may be fit to experimental release data to determine the diffusion coefficient. In particular, if we take,

$$C(r, 0) = \alpha + \beta (r/R) \quad (9)$$

Where α and β are some constants, then we find:

$$A_n = -\frac{2R}{n^3 \pi^3} \left\{ 2\beta + (-1)^n \left[-2\beta + n^2 \pi^2 (\alpha + \beta) \right] \right\} \quad (10)$$

And, Eqn. (7) can be written as:

$$F(t) = \frac{8R^3}{m_0 \pi^3} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^4} \left[1 - e^{-\left(\frac{n\pi}{R}\right)^2 Dt} \right] \left\{ 2\beta + (-1)^n \left[-2\beta + n^2 \pi^2 (\alpha + \beta) \right] \right\} \quad (11)$$

An alternative and more convenient expression for $F(t)$ corresponding to Eqn. (11), valid for short time, can be found using the Laplace Transform technique. We have found this solution, to order t to be (we call it, $F_{short}(t)$ to distinguish it from the above series solution)

$$F_{short}(t) = \frac{4\pi R^3}{m_0} \left[\alpha (2\sqrt{\tau/\pi} - \tau) + 2\beta (\sqrt{\tau/\pi} - \tau) \right] \quad (12)$$

Where, the non-dimensional quantity τ is defined as (this combination appears in Eqn. (11) above also):

$$\tau = \frac{Dt}{R^2} \quad (13)$$

For the case of flat initial profile, $\beta = 0$, and Eqn. (12) is then the same as we had used in our previous work on IG-110. Also, as for the flat profile, we have found that Eqn. (12) is surprisingly accurate even for fairly large times (we have compared $F(t)$ and $F_{short}(t)$ for a range of parameter;

generally for good accuracy, it is necessary to retain about 100 or more terms in the series as it converges very slowly for short times).

We have explored use of both Eqns. (11) and (12) in our analysis, and have found that for the time periods (about 5 hours) of the release measurements in our experiments, results obtained from the two (we used 100 terms in the series) are indistinguishable.

3. Experimental

3.1. Instrumentation

A scanning quadrupole ICP-MS instrument (Perkin Elmer Nexion 300X) with a dual port quartz spray chamber was used for quantification. In order to correct for instrument variation during the measurements, a nebulizer continuously introduced a 1.00 pbb In internal standard solution in 2% aqueous HNO_3 at 200 $\mu\text{L}/\text{min}$ into one port of the spray chamber. A carbon aerosol helium jet system was used for transport of diffusing FPs to the other port of the dual port spray chamber. The gas jet system consisted of a helium source and a Palas GFG-1000 carbon aerosol generator specially fabricated by Palas for use with helium carrier gas. The gas jet was routed through a custom SiC cell designed to hold the graphite samples under simulated VHTR conditions (high temperature, flowing helium environment). The cell was housed in a Lindberg M Series hinged tube furnace and connected to the spray chamber with stainless steel capillary tubing, Swagelok stainless steel connectors, and Plasmatech polymer connectors. A complete description of the instrumentation and calibration procedures for release measurements is given in references [2] and [3].

We should note that transport of atoms and molecules in pure helium has been shown to occur only for distances on the order of centimeters [14] due to high diffusion rates of gas phase atoms and molecules, and subsequent deposition onto tubing walls. The addition of carbon aerosol particles to the flowing helium stream increases the transport efficiency of our measurement by greater than three orders of magnitude. The transport efficiency is also demonstrated to be sensitive to increased carbon particle density in the He stream which results from changes in the spark frequency in the aerosol generator (Fig. 2). This suggests that transport of FPs in VHTR cooling circuits may be greatly enhanced by the presence of graphite dust or other particulates present, and may contribute to release of FPs especially in a cooling circuit breach accident scenario.

Figure 1: ICP-MS sensitivity as a function of carbon aerosol generator spark frequency (Hz) or carbon particle aerosol density in the He carrier gas.

Further, we used a Photon Machines Analyte excimer laser in combination with the Nexion 300X ICP-MS for measurements of the Cs concentration profile in the NBG-18 carbon sphere via laser ablation. The laser uses an argon/fluoride/trace neon cell and operates at 192 nm.

3.2. Materials and Methods

3.2.1. Sample preparation

Spherical samples of 0.32 cm radius were milled from as-received NBG-18 stock material by the MURR Science Instrument shop. The spheres were added to a cylindrical quartz vial along with solid CsNO_3 (as-received from Alfa Aesar). The vial was sealed under 90 mtorr vacuum with a flame sealing torch. The vial was heated to 500°C for one hour to convert the nitrate salt to elemental cesium [8-10, 15-16].

The vial was then heated to 1100°C and maintained at this temperature for 8 days in an attempt to uniformly distribute cesium within the spheres. The spheres were machined down to a diameter of 0.30 cm using SiC sandpaper. Contamination and dust was removed from the surfaces of the spheres using compressed air.

3.2.2. Initial Cs content analysis

The cesium content of each sphere was measured using standard comparator neutron activation analysis at the MURR facility. Comparator standards were prepared from a certified solution of CsNO_3 purchased from High Purity standards. The spheres and standards were irradiated in the row 2

pneumatic tube irradiation position for ten seconds at a thermal flux of 5.0×10^{13} n/cm²/s to produce trace ^{134m}Cs via the reaction ¹³³Cs(n,γ)^{134m}Cs. The 127.5 keV gamma ray from decay of ^{134m}Cs was measured using a HPGe detector; samples were counted until at least 10,000 counts were acquired in the 127.5 keV peak. The initial cesium mass present in each sphere ranged from 14.3 to 15.7 μg.

The distribution of Cs in the spheres was measured by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) using a Photon Machines Analyte 193 excimer laser and Nexion 300X ICP-MS. Two of the spheres prepared as described in 3.2.1 were sectioned into hemispheres with a razor blade. The Cs concentration profile was analyzed by making 40 μm line scans using a 40 μm laser spot size at distance intervals of 200 μm along the radii of the flat surface of the hemispheres. The laser was operated at a power density of 2 mJ/cm² and a pulse frequency of 10 Hz.

3.2.3. Diffusion measurements

Cs release from the graphite spheres was measured isothermally at temperatures in the range of 1090K to 1395K. Release was measured for a period of approximately five hours at all temperatures. At the start of the experiment, the SiC cell is heated to target temperature and the ICP-MS is tuned. The Cs signal is monitored for approximately one hour before a sphere is introduced into the cell to allow for correction due to instrument Cs background. A sphere is introduced into the cell by disconnection of the gas-jet system at the aerosol outlet of the SiC cell; the sphere is dropped in and descends into the heated sample holder of the cell. Due to the high thermal diffusivity of the graphite, small size, and small heat capacity, we assume the sphere heats instantaneously to the experimental temperature and that diffusion is measured isothermally. We have conducted thermal diffusivity calculations to investigate the rate of change of temperature of the spheres; these calculations indicate this is a valid approximation.

3.2.4. Final Cs content analysis

After release measurements, the Cs content of each sphere is quantified again using standard comparator INAA as described in section 3.2.2. The difference in Cs mass from before and after release measurements is used to determine the ICP-MS calibration factor. The calibration factor scales the real time ICP-MS count rate or cumulative count total to actual mass transfer units (grams Cs/s or grams Cs, respectively).

4. Results

The initial distribution of Cs in the spheres after the loading procedure (infusion) was determined by LA-ICP-MS and is given in Fig. 3:

Figure 3: Initial Cs concentration profile measured by LA-ICP-MS

This profiles appears to be approximately linear, and therefore we have fit it with $\alpha + \beta(r/R)$, where α and β are constants (theoretically the profile should be flat at the center. We have discussed the infusion problem in appendix A, and estimated that this approximation is reasonable). We have found:

$$\alpha = 4.21 m_0 \quad (g \text{ cm}^{-3}) \quad (14)$$

$$\beta = 6.18 m_0 \quad (g \text{ cm}^{-3}) \quad (15)$$

We have obtained diffusion coefficients for Cs in NBG-18 by fitting both Eqn. (11) and Eqn. (12) to the fractional release data via least squares regression analysis, described previously in [2]. The infinite series given by (11) has been approximated using the first 100 terms. The results obtained via the use of either equation are indistinguishable. Our results are reported in Table 1.

Table 1. Cs diffusion coefficients in NBG-18 graphite in the temperature range of 1090K to 1395K.

Initial Cs Content (μg)	Total Cs Release (μg)	Analysis Time (hr)	Temperature (K)	D (m^2/s)
14.3	0.80	5	1090	1.5×10^{-13}
15.1	1.2	5	1140	2.4×10^{-13}
15.0	1.3	5	1185	3.3×10^{-13}
14.3	1.1	5	1238	3.2×10^{-13}
15.7	2.8	5	1290	1.5×10^{-12}

Figure 4: Fractional release curves for six $R=0.3$ cm NBG-18 graphite spheres as measured by ICP-MS.

Figure 5: Fractional release curves and respective fit of Eqn. 11 for $R=0.30$ cm NBG-18 graphite spheres at 1290 and 1185 K.

The temperature dependence of the diffusion coefficient is reported in the Arrhenius form (Eqn. 1). The values of the pre-exponential factor D_0 and activation energy E_a over the temperature range of 1090-1395 K are reported in Table 3.

Table 4. Pre-exponential and activation parameters for diffusion of Cs in NBG-18 graphite between 1090K and 1395K.

Material	Diffusant	D_0 (m ² /s)	$\pm\Delta\ln D_0$	E_a (J/mol)	$\pm\Delta E_a$ (J/mol)
NBG-18	Cs	1.0×10^{-7}	2.10	1.23×10^5	2.1×10^4

5. Discussion

We have used classical diffusion theory for describing Cs transport in NBG-18 graphite using an effective diffusion coefficient and corresponding transport equation, (2). In doing so, we assume the transport of Cs obeys classical Fickian diffusion kinetics and diffusing material is continuously removed from the sphere surface. Our results suggest these assumptions are valid for the temperature range and experimental conditions tested here. Cs release during some trials showed an initially larger diffusant release rate than would be expected considering ideal transport behavior, as evidenced by the 1290 K plot in Fig. 5. Initial rapid release of volatile diffusants is common in release experiments [12] but may indicate time dependence of the diffusion coefficient or multichannel transport processes. Additionally, initial rapid release may be a consequence of the pore structure of the particular graphite analyzed, where for some samples a larger “exposed” surface area may be present due to very large pores on the sample surface. Some variance is evident in the measured initial concentration profile in Fig. 3, which reflects the well-documented tendency of Cs to concentrate in the binder components of certain graphites [7-8,10].

It is common to perform the initial FP loading procedure for sufficient time for a macroscopically uniform distribution of FP to be achieved, as a uniform initial distribution simplifies extraction of diffusion coefficients [2,9,12-13]. It is sometimes possible to assume an initially uniform distribution *a priori* and extract diffusion coefficients from release data. The validity of this assumption may be checked by using the diffusion coefficients obtained to calculate the theoretical concentration profile that should result based on the temperature, initial, and boundary conditions present during the loading procedure. In some experiments, it may be necessary to assume a uniform initial distribution or approximate the actual distribution by a uniform one; in the present case, such an assumption would result in an overestimate of the reported diffusion coefficient by approximately 10%.

Selected data for Cs diffusion in various graphites are presented in Fig. 6 for comparison with the NBG-18 data from this work.

Figure 6: The measured diffusion coefficients from this experiment plotted versus reciprocal temperature with other values for various graphites reported in the literature [2,8-10,15-18].

Measured diffusion coefficients for Cs in NBG-18 appear lower than those for Cs in IG-110 graphite. This difference may be attributable to differences in pore structure or differences in the identity and concentration of impurities present in the graphites. Hayashi et. al.'s series A and B, which differ by up to two orders of magnitude (see figure 6) were reported to be from different manufacturing lots of IG-110 [16]. It is not known why the Cs diffusion coefficient in IG-110 graphite for series A and B are so different from other Cs diffusion coefficient measurements in IG-110 or other graphites. Hayashi et al. made the diffusion coefficient measurements using a profile technique similar to what other groups have used, wherein a disc of graphite impregnated with Cs is placed in contact with an initially clean acceptor specimen and annealed at a specific temperature. The resulting concentration profile in the acceptor graphite was measured after sectioning. The authors do not report the initial Cs concentration used in the experiments and it is possible that concentration dependence causes observed deviation from other results. Hayashi et al. also suggest that structural differences in the IG-110 graphite introduced during manufacturing account for the large observed difference between their reported Cs diffusion coefficients. It is also possible that trace element differences in the IG-110 graphite that arise between manufacturing lots contributed to the observed difference between their reported Cs diffusion coefficients. There may be similar material variation in NBG-18 graphite. It may

therefore be beneficial to test multiple manufacturing lots of NBG-18 to determine if manufacturing variation has an effect on Cs diffusion.

Diffusion of Cs in certain graphites has been shown to be dominated by surface diffusion mechanism wherein Cs migrates via transport along interior pore surfaces [6-10], as opposed to gas-phase diffusion through the bulk pore volume. This is consistent with the diffusion activation energies we have determined for IG-110 and NBG-18 graphites of 110 kJ/mol and 123 kJ/mol respectively, both of which are larger than the enthalpy of vaporization of cesium of 65 kJ/mol. Thus, transport of Cs in IG-110 and NBG-18 should occur primarily via a similar pore surface diffusion mechanism. IG-110 is a very fine-grained graphite and has a correspondingly large Brunauer-Emmett-Teller (BET) surface area in comparison to NBG-18. The larger surface area available for Cs transport in IG-110 may partially explain the larger observed diffusion coefficients in the material.

The presence of impurities in graphite has also been shown to affect diffusion coefficients of fission products in graphite. Impurities may sorb or dissolve diffusant atoms, lowering the diffusant vapor pressure and therefore lower the rate of transport [11]. Solid impurities may immobilize diffusant atoms if the activation energy for desorption from the impurity site is large. These effects have been shown to have a negligible effect on Cs diffusion in certain graphites [11]. While NBG-18 has a much higher concentration of impurities than IG-110, it is unknown what effect this difference has on the differences observed in the current work. As the concentration of certain impurities may vary (whether the impurities are present in the graphite naturally, through production or machining processes, or those produced by fission) the present system was designed to be capable of studying multicomponent transport in graphite. Further investigation of the effects multiple components may have on the diffusion of one another will be undertaken in the future.

6. Conclusion

We have measured diffusion coefficients of Cs in NBG-18 graphite using the release method and ICP-MS coupled with a carbon aerosol helium gas-jet system. We have obtained:

$$D_{Cs/NBG-18} = (1.0 \times 10^{-7} \text{ m}^2/\text{s}) \exp\left(\frac{-123 \text{ kJ/mol}}{RT}\right) \quad (14)$$

This appears to be the first measurement of Cs diffusion coefficients in NBG-18 graphite, and therefore there are no data for direct comparison at this point. However, the results are in agreement with measurements Cs diffusion coefficients in similar graphites reported in the literature. The diffusion coefficients for Cs in NBG-18 are lower than those we have measured in IG-110, and by extrapolation may remain so up to temperatures exceeding the loss of coolant scenario maximum attainable core temperature of the VHTR.

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Appendix A: The Infusion Profile of Cs in NBG-18

Our measurements indicated that the final infusion profile of Cs in the graphite sphere was approximately linear, and we used this linear profile to obtain the diffusion coefficients from the release data. Theoretical considerations would indicate that the profile should have some flatness (zero gradient) at the center of the sphere. To clarify it further, we note that the solution of the infusion problem is closely related to the solution of the release problem (particularly when the initial concentration profile $C(r,0)$ is a constant). Thus for infusion, one considers the problem (we have put a tilde to distinguish it from the release problem; note that $\tilde{C}(r,t)$ is finite everywhere),

$$\frac{\partial \tilde{C}(r,t)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D r^2 \frac{\partial \tilde{C}(r,t)}{\partial r} \right) \quad (\text{A.1})$$

With boundary condition: (A.2)

$$\tilde{C}(R,t) = \tilde{C}_\infty \quad (\text{A.3})$$

And the initial condition:

$$\tilde{C}(r,0) = 0 \quad (\text{A.4})$$

Then we can show that,

$$\tilde{C}(r, t) = C(r, t) |_{C(r, 0) = -\tilde{C}_\infty} + \tilde{C}_\infty \quad (\text{A.5})$$

And, assuming $\tilde{C}_\infty$ is known (vapor pressure of FP at the infusion temperature), it is possible to extract the diffusion coefficient from the measurements of concentration profile (or the total mass infusion) in the infusion part of the experiments also.

We note that the infusion problem has the solution:

$$\tilde{C}(r, t) = \sum_{n=1}^{\infty} A_n \psi_n(r) \text{Exp}(-\lambda_n^2 Dt) |_{C(r, 0) = -\tilde{C}_\infty} + \tilde{C}_\infty \quad (\text{A.6})$$

Where,

$$A_n = \frac{2}{R} \int_0^R r^2 C(r, 0) \psi_n(r) dr = - \left(\frac{2}{R} \int_0^R r^2 \psi_n(r) dr \right) \tilde{C}_\infty = - \frac{2}{\lambda_n} (-1)^{n-1} \tilde{C}_\infty \quad (\text{A.7})$$

Which gives

$$\tilde{C}(r, t) = \left(1 - \sum_{n=1}^{\infty} \frac{2}{\lambda_n} (-1)^{n-1} \psi_n(r) \text{Exp}(-\lambda_n^2 Dt) \right) \tilde{C}_\infty \quad (\text{A.8})$$

Indicating that for a large time t , the infusion profile should be:

$$\tilde{C}(r, t) = \left(1 - \frac{2}{\lambda_1} \psi_1(r) \text{Exp}(-\lambda_1^2 Dt) \right) \tilde{C}_\infty = \left(1 - 2 \frac{\sin(\pi r / R)}{(\pi r / R)} \text{Exp}(-\pi^2 Dt / R^2) \right) \tilde{C}_\infty \quad (\text{A.9})$$

Our computations confirm that for the case at hand the above expression is both useful and adequate (it gives results that agree with those obtained by using more terms in the series). We have therefore fit the normalized infusion profile (temperature of 1373 K, for $t=8$ hours) with the above (A.9), and we obtain approximately:

$$D = 1.90 \times 10^{-12} \quad m^2 / s \quad (\text{A.10})$$

Which agrees well with the value ($D = 2.7 \times 10^{-12} \quad m^2 / s$) obtained from the release measurements (at 1395 K).

One can estimate $\tilde{C}_\infty$ in several ways (using the infusion profile, the vapor pressure for Cs, or by the INAA mass measurements). Considering the INAA data, one would have:

$$\tilde{C}_{\infty} = \frac{m_0}{4\pi \int_0^R r^2 \left(1 - 2 \frac{\sin(\pi r / R)}{(\pi r / R)} \text{Exp}(-\pi^2 D t / R^2) \right) dr} = \frac{m_0}{\frac{4\pi R^3}{3} \left(1 - \frac{6}{\pi^2} \text{Exp}(-\pi^2 D t / R^2) \right)} \quad (\text{A.11})$$

Thus, the initial profile for each sphere can be approximated by (the subscript *inf* indicates values corresponding to infusion conditions):

$$C(r, 0) = \frac{m_{0, \text{INAA}, j}}{\frac{4\pi R^3}{3} \left(1 - \frac{6}{\pi^2} \text{Exp}(-\pi^2 D_{\text{inf}} t_{\text{inf}} / R^2) \right)} \left(1 - 2 \frac{\sin(\pi r / R)}{(\pi r / R)} \text{Exp}(-\pi^2 D_{\text{inf}} t_{\text{inf}} / R^2) \right) \quad (\text{A.12})$$

We can write this for convenience as:

$$C(r, 0) = \tilde{m}_0 \left(1 - b \frac{\sin(\pi r / R)}{(\pi r / R)} \right) \quad (\text{A.13})$$

And, calculate release rates based on this expression rather than a linear profile. In our infusion part of the experiments, however, $\tilde{C}_{\infty}$ was not kept constant. It decreased with time as Cs was infused in the sphere(s), and hence we concluded that it was better to use the experimentally measured infusion profile rather than the above (the linear profile matches well with the above up to more than half way in the sphere as seen below). We have shown fits to the infusion data with Eqn. (A.9) in the Fig. 8 below. We also note that in Ref. [19] a numerical technique was applied to compute time dependent fission product release from irradiated nuclear fuels heated at increasing temperatures (temperature ramp) in a furnace at very high temperatures. This technique would be suitable for further analysis of the infusion part also and coupling of the time dependent infusion chamber Cs concentration with the Cs concentration in the graphite sphere. Future numerical analysis on these lines, and comparisons with experiments would be of interest.

Figure 8: The normalized infusion profile (mass concentration vs radius), measurements and theory.