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ABSTRACT

A random network model has been utilized to analyze the problem of tritium percolation through porous Li ceramic breeders. Local transport in each pore channel is described by a set of convection-diffusion-reaction equations. Long range transport is described by a matrix technique. The heterogeneous structure of the porous medium is accounted for via Monte Carlo methods. The model was then applied to an analysis of the relative contribution of diffusion and convective flow to tritium transport in porous lithium ceramics.

Tritium Percolation Through Porous Ceramic Breeders - a Random-Lattice Approach

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1. Introduction

The problem of describing tritium transport and release from Li ceramic breeder materials in a realistic and comprehensive manner is an important issue for fusion reactor design. A model for tritium transport with predictive capability is necessary to provide a coherent basis for estimating tritium inventory and other related issues. There are many mechanisms that act in concert in driving the transport of tritium. They have been treated with different emphasis by the ceramic breeder modeling community[1-5]. In general one can divide the various mechanisms into two broad groups depending on the length scales through which they act. The first group of processes is active through a length scale of $\text{\AA}$ s up to the size of an individual grain which for ceramic breeder materials typically range from a fraction of a μm to about 10 μm . They represent processes that take place either within the grain (i.e. bulk) or on grain surfaces. The bulk processes include intergranular diffusion, interaction with impurities and defects within the grain, and precipitation. Grain surface processes include adsorption/desorption and resolution.

The second group of processes involve mechanism that acts from a length scale of magnitude at least comparable to a single grain up to the size of the whole system. This latter scale for the purpose of understanding tritium release is represented by the average distance between purge channels (typically of the order of a centimeter)[6]. Purge channels are pathways introduced into the ceramic breeder materials by design to facilitate the extraction of tritium-bearing species from the interior of bulk ceramic breeder materials via inert gas (usually He) purge flow technique. For consideration of purge flow along purge channels the length scale could even be measured in meters. The important point is that the upper characteristic length scales (whether they be in the centimeters or meters range) are in the macroscopic regimes.

One of the most important processes in this later class is the gas transport through the interconnected porosity from pores interior to the breeder to the purge channel. Compared to bulk diffusion and surface processes gas transport through porous breeder ceramics has been subjected to much less thorough analysis. The difficulties in a realistic treatment of tritium-bearing gas percolation are different from that of (for example) analysis of bulk diffusion. Firstly, there is a statistical element to the process arising from the heterogeneous nature of the pore structure and channels that needs to be taken into account. Traditionally this has been subsumed into a so-called tortuosity factor which is essentially a fudge factor[7-8]. A more satisfactory approach should be based upon experimentally determined pore size distribution as input formations. Detailed data on pore

size distributions are beginning to be available for Li ceramic breeders[9]. Utilization of such statistical structural information would render the Monte Carlo[10] method a natural approach to describe tritium percolation through the porous ceramic medium.

Secondly as discussed already the length scales through which the percolation process works can range over several order of magnitudes. Consequently in many cases gradient of external parameters such as pressure and temperature cannot be neglected. Furthermore such gradients (e.g. temperature) are often anisotropic due to specific ceramic breeder configurations (e.g., thin slabs, cylindrical pellets, etc.). These constraints would imply that a one dimensional analysis of tritium pore percolation may be inadequate. In the following a formalism would be described that would address explicitly the statistical nature of the pore microstructure and the multi-dimensional character of the transport process. This formalism is adapted from the theory of random transport modified to treat the problem of gas percolation including issues such as generation source and desorption processes which are central to tritium transport processes[11]. Recent analysis of annealing experiment performed on irradiated ceramic breeder seems to indicate that bulk diffusion is not the rate-limiting process[5]. Consequently in the present treatment intragranular diffusion is not included. In the following discussion the physical basis of the approach and its implementation would be reviewed. The formalism basically starts at describing the process at the level of individual pore channels ($\sim 1\text{-}10\ \mu\text{m}$). Thus, it is able to utilize fundamental physical properties such as molecular gas diffusion coefficient D_g without any ad hoc

parameters. The actual mechanisms that lead to tritium mass transport in the pore channel are diffusion and convection. Convective mechanism may arise due to the pressure difference generated between the interior of the breeders and the outer region adjacent to the purge channels due to purge flow. When the pressure gradient is small the tritium transport through the pore network would be dominated by gas diffusion. Conversely convective flow may become important if the externally imposed pressure gradient becomes sufficiently large. The relative importance of diffusion versus convective processes towards tritium transport would be examined using the present formalism.

2. Theory

The theoretical basis of the approach has been addressed previously[15]. For completeness the formalized and its physical basis would be summarized as follows. The interconnected (i.e. open) porosity is likely to be intragranular. They lie on grain boundaries and grain edges. In the present analysis the intragranular porosity is modeled as a network of interconnected pores. A simple cubic network structure has been selected. Only two dimensional calculations will be presented in this work with the square network being the corresponding structure. However the formalism is completely general and is not limited in principle to any particular spatial discussion. The bonds (i.e. links) between nodes of the network represent the pore channels. If a fraction p of these channels are open and if P represents the fraction of open channels that are interconnected all the way to the

exterior then the average radius r_c of the pore channel is given by:

$$r_c = \frac{2\phi}{S_g \rho} \frac{P}{p} \quad (1)$$

Here ϕ is the porosity, ρ the theoretical density of the breeder and S_g the specific surface area. The relationship between P and p is governed by percolation theory[13]. In the limiting case of all the channels being open (i.e. $p=1$) P also assumes the value of unity and equation 1 reduces to the traditional formula[8]. For the present work we would largely concentrate on this case.

Equation 1 represents a mean radius r_c whereas in reality there would be a distribution of pore sizes that could be supplied from empirical microstructural information on the particular ceramic breeders that is of interest. A uniform pore size distribution with r_c given by equation 1 as the mean radius has been adopted as an illustrative representation in the present analysis. However the formalism can treat as input a wide class of pore size distribution including mono and bimodal ones. Physically structural disorder (in the form of variation of pore sizes) would lead to complicated flow processes. Acceleration or deceleration would occur as the tritium-bearing species (such as HTO or HT) migrate along pore channels of differing sizes and along different directions in our two dimensional simulations. The migration process is governed by convective transport and diffusion. The tritium-bearing species is introduced into the channels via generation from the grain interiors and desorption from the grain surfaces. The tritium-bearing species can also be removed from the vapor phase in the pores via readsorption onto

the pore surfaces. For a particular tritium species such as HT these mechanisms are represented by the following equations:

$$\frac{\partial C_g}{\partial t} + u \frac{\partial C_g}{\partial x} = D_g \frac{\partial^2 C_g}{\partial x^2} + k_d C_s - k_a C_g \quad (2)$$

and

$$\frac{\partial C_s}{\partial t} = g - k_d C_s + k_a \langle C_g \rangle \quad (3)$$

Here C_g = gas phase concentration
 C_s = concentration on grain surfaces
 u = velocity of tritium species in the pore channel
 D_g = gas phase diffusion coefficient
 k_d = desorption rate constant
 k_a = adsorption rate constant
 g = tritium generation rate
 $\langle C_g \rangle$ = average gas phase concentration

Equation 2 and 3 applies to both HT and HTO but with different transport coefficients (e.g. diffusion coefficient). For definiteness HT would be the representative species by this work. Note that these equations are assumed to be valid within one individual pore (i.e. over a length scale of the order of microns). No assumption has been made on the applicability of the equations (particularly equation 2) over macroscopic length scales (i.e. over many pores). Thus D_g in equation 2 is the molecular diffusion coefficient with no unknown fudge factors such as tortuosity included[8,14].

The equations 2 and 3 are solved by Laplace transform and direct quadrature. The resulting concentration C_g can be expressed in terms of the $C_g(0)$ and $C_g(1)$, the concentrations at the two ends (i.e. nodes) of the pore channel. The current $I(x)$ along each channel can then be evaluated using the expression (A being the channel area)[11].

$$I(x) = (uC_g - \frac{D\partial C_g}{\partial x}) A \quad (4)$$

If one assumes that at each node there is no net accumulation by the species represented by C_g then the following holds true for the i^{th} node of the random pore network:

$$\sum_j I_{ij} = 0 \quad (5)$$

Here I_{ij} is the current in the channel with the i^{th} and j^{th} nodes as its two end-points. The summation is over all the nearest neighbor pore channels to the i^{th} node. Equation 6 is equivalent to a matrix equation:

$$\tilde{A} \vec{C} = \vec{G} \quad (6)$$

Here $\vec{C}$ is a vector representing the node concentrations of all the nodes in the network. $\vec{G}$ is a vector that would incorporate the initial and boundary conditions. $\tilde{A}$ is a matrix that incorporate the dynamical parameters (such as diffusion, convection, etc.) of the network. Direct solution of equation 6 enable the concentration and hence the output flux to be evaluated.

To test this approach we have applied it to a two dimensional square network of pore channels whose cross-section radius is distributed in a random manner over a range such that the mean radius is given by equation 1. The analysis in the next section is based upon materials data (such as S_g and porosity ϕ) on Li_2O taken from the Mozart experiment[12]. The square network is considered to be a cross-sectional slice of a three dimensional piece of solid breeders. The four corners node are connected directly to an output node which represents basically one location of the purge channel.

3. Application to diffusion/convection analysis

In order to solve the matrix equation(6) in an efficient manner it is advantageous to transform the basic variables into dimensionless form. The key is to utilize the characteristic length scale l of the problem which is the length of an individual pore channel. All lengths are scaled with respect to l . The characteristic time scale τ is chosen such that

$$\frac{D_T}{l^2} = 1.$$

Physically τ is characteristic diffusion time across an individual channel. All temporal quantities are scaled relative to τ . In this way all quantities are in dimensionless units and with orders of magnitudes that are convenient for solving the matrix equation.

Utilizing the model that we have constructed as described above we have carried out an analysis of the comparative contribution of diffusion versus convection to tritium pore transport. The physical parameters/materials data for Li_2O are based on data from in-pile experiments in the literature. This includes the specific surface area S_g ($= 0.05 \text{ m}^2/\text{g}$) and porosity ϕ ($=0.2$) and the tritium generation rate of $0.627 = \mu\text{Ci/cc/sec}$.

As we have discussed in the introduction the primary transport mechanism is diffusion and convection. The relative importance of these two processes can be analyzed using the present random network model. A pressure gradient of 1 atmosphere/m was applied between the central node and the 4 corner

outlet nodes of the network. Pressure gradients of comparable magnitude along the purge channel are expected to be applied in realistic breeder/blanket configurations. Recall that the corner nodes are connected via a pore channel to the purge gas channel. The pressure gradient used here is expected to be comparable or greater than those gradients that are likely to exist between the solid breeder interior pores and those pore channels in the outer region. A pulse is injected at the center node of the network and the output flux is monitored at the corner outlet node. A similar calculation is carried out with the pressure gradient set to zero (i.e. pure diffusion). The output flux as a function of time was found to be indistinguishable. This seems to indicate that the moderate pressure gradient used here gas diffusion is much more important than convective flow. However, at higher pressure gradient convective flow would become more important. In fact the interplay between convection and diffusion can become quite involved with sometimes unexpected behavior. To illustrate this point we have compared the pure diffusion case which we have just considered to a case where convection becomes much more important (pressure gradient ~ 150 atmosphere/m). Fig. 1 shows the output flux as a function of time for the two cases. The convective flow dominated case shows a sharply peaked behavior at relatively early times with a sharp rise and a comparable sharp decline. For the pure diffusion case the structure is much lower in magnitude but much broader with a long time tail. This means that with a large enough pressure gradient driving force transport driven by convection can be much faster than that due to diffusion.

Recall that the flux along a pore channel is given by a convective term uc and a diffusive term $-D \frac{\partial c}{\partial x}$. Under certain circumstances it is possible that the diffusive flux is opposite to the convective flux and yet the overall flux is still directed outwards (i.e. out of the network). This would take place if the convective component is sufficiently large such that the outlet pore channels would become bottleneck (i.e. rate-limiting) to the outward transport. This would give rise to a concentration profile that may be higher near the outlet nodes than regions further towards the interior of the breeder. Yet the overall tritium flux is still outwards leaving the breeder. This seemingly unusual situation are depicted in Figs. 2, 3, and 4. The two-dimensional concentration profiles at three different times for the large pressure gradient case (represented in Fig. 1) are shown in those figures. Figure 2 shows the profile at a time shortly after the pulse has been introduced. The large peaked structure near the center depicting the pulse is very visible. But already one notes that the concentration gradient near the corner (i.e. outlet) nodes are already showing the opposite trend. Fig. 3 shows the concentration profile at a time when the output flux (according to Fig. 1) is at a maximum. Note the high concentration near the corner (outlet) nodes and the relatively low and flat profile over much of the network interior. Physically, this implies that diffusion is not contributing much towards (or even impeding) the outward flux. Instead convection is the dominant mechanism for outwards mass transport. Fig. 4 shows the concentration profile at much later time at which the output flux has declined to a low value according to Fig. 1. The concentration profile is practically flat over most of the network with small rise towards the corner. From these discussions one can see that in tritium percolation there

can be complicated interplay between convection and diffusion due to the convoluted structure of the transport pathways. Nevertheless these behaviors can be understood from a sound physical basis as the above discussion has shown. Here we have analyzed the case where local concentration gradients can oppose overall mass flow due to outlet pore channels developing bottlenecks under the action of large pressure gradient driving force. There can be other physically interesting cases (which we have not discussed) where geometrical factors such as local dead ends in transport pathways can lead to local backflow in opposition to the overall mass transport. All of these reaffirm the idea that porous media gas percolation due to interplay of diffusion and convection can lead to complex behavior of which the present work provide an example.

4. Conclusion

The issues of the relative contribution of diffusion versus convection has been addressed. At the moderate pressure gradient of 1 atmos/m diffusion has been found to be the predominant process. At larger pressure gradient convection becomes increasingly important. In fact when convection flow becomes dominant it is possible under some circumstances to find the local concentration profile to be in an unusual configuration such that it may tend to oppose the overall mass flow in the local region. This kind of detailed understanding and analysis is possible with the present random network model due to its ability to treat diffusion-convective transport in a multi-dimensional network of complex pathways in a fundamental manner. In the next stage we would utilize the model to evaluate in a more basic way the central concept of tortuosity and the dependence of various transport characteristics on system sizes.

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Figure 1. Output flux as a function of time. Solid square: pressure gradient = 150 atmosphere/m; empty square: no pressure gradient (i.e. pure diffusion) time in units of T .

Figure 2. Concentration profile for large pressure gradient at time = 3 (in units of T).

Figure 3. Concentration profile for large pressure gradient at time = 10.

Figure 4. Concentration profile for large pressure gradient at time = 50.

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