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

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ABSTRACT

Among the major processes leading to tritium transport through Li ceramic breeders the percolation of gaseous tritium species through the connected porosity remains the least amenable to a satisfactory treatment. The combination of diffusion and reaction through the convoluted transport pathways prescribed by the system of pores poses a formidable challenge. The key issue is to make the fundamental connection between the tortuousity of the medium with the transport processes in terms of only basic parameters (e.g. molecular diffusion coefficient and porosity distribution) that are amenable to fundamental understanding and experimental determinations. This fundamental challenges is met within the following approaches. On the microscale the short range transport is modeled via a convection-diffusion-reaction approach. On a macro scale the long range transport is described within a matrix formalism. The convoluted microstructure of the pore system as prescribed from experimental measurements is synthesized into the present approach via monte carlo simulation techniques. In this way the approach requires as inputs only physical-chemical parameters that are amenable to clear basic understanding and experimental determination. In this sense it provides predictive capability. Using this approach the concept of residence time has been analyzed in a critical manner. Implication for tritium release experiments was discussed.

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 acts 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 A°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.

The most important process 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 highlighted. The formalism would then be applied to address the issue of residence time which has become an increasingly popular concept to analyze experimental data[12]. The analysis would clarify the physical meaning of the idea of residence time as well as the potential pit-fall of utilizing the concept.

2. Theory

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 discusses in the following 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:

$$r_c = \frac{2\phi}{S_g\rho}\frac{P}{p}$$ (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:

$$\frac{\partial C_g}{\partial t} + U\frac{\partial C_g}{\partial x} = D_g\frac{\partial^2 C_g}{\partial x^2} + k_dC_s - k_aC_g$$ (2)

and
$$\frac{\partial C_s}{\partial t} = g - k_d C_s + k_a \langle C_g \rangle \tag{3}$$

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. In fact for D_g the Bosanquet representation has been adopted in the present work[8].

$$\frac{1}{D_g} = \frac{1}{D_k} + \frac{1}{D_{AB}} \tag{4}$$

D_k is the Knudsen diffusion coefficient valid when the mean free path of the gas becomes of the same order or larger than r_c, the radius of pore channel.

D_{AB} is the molecular diffusion coefficient of a gas mixture A and B[14]. Here A may be HT and B would represent He which is the principal component of the mixture. D_{AB} would be the correct transport coefficient to be used when the mean free path of the gas is much smaller than r_c. Equation 4 would give a good description of D_g over the entire range of the ratio (mean free path)/r_c that is of interest to the present analysis. There are some corrections to equation 4 but they are unimportant due to the dilute nature of HT or HTO in He ($\leq 10^{-4}$)[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 $C_g(o)$ 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].

$$I(x) = \frac{(uC_g - D\partial C_g)\, A}{\partial x} \qquad (5)$$

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 ith node of the random pore network:

$$\sum_j I_{ij} = 0 \qquad (6)$$

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

$$\tilde{A}\ \vec{c} = \vec{G} \qquad (7)$$

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 7 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. Due to the two dimensional nature of the calculation and the limited size of the network (11 x 11 representing approximately 10^2 grains) the results of the analysis cannot yet be compared directly with experiment. Much larger size calculations together with scaling analysis would be part of the next stage of our work.

However very illuminating analysis can be performed on concepts central to the understanding of tritium percolation processes. Residence time is one such concept that would be examined in some detail in the next section.

3. Application to residence time analysis

In recent years the concept of residence time, τ has been increasingly employed to analyze and interpret in-pile measurements on tritium release rate. The concept has been quantified (somewhat arbitrarily) as the time necessary to attain a certain fraction of the steady state tritium release rate. Typically that fraction is around 2/3. Other applications involve estimating τ in terms of the ratio of the steady state inventory to the steady state release rate. In order for this kind of approach to be useful for analyzing release data it is necessary to understand the physical basis of this concept and the degree of usefulness in using a single number (i.e. τ) to characterize the data. The random network model presented here offers an excellent tool with which to address this issue. In the following analysis all calculation has been carried out in dimensionless unit. For example temporal unit has been expressed in terms of typical transit time across one single channel.

If one injects a sharp pulse at the center node of the system then one can calculate using the present model the output flux P(t) at the outlet node through the four corners. In fact P(t) represents the probability distribution of the first passage time. This is the first time at which the tritium-bearing species arrive at the outlet node after it has been injected

In a δ-function form (i.e. a sharp pule) at the central node. Note that even through the input is a sharp pulse, there is no unique first passage time. Fig. 1 shows the result of the simulation. Note the broad structure and the long tail of the distribution. This broad and highly skewed behavior arises from several sources. There are many different pathways through which the gas molecule can reach the outlet from the source. Because of the distribution in pore sizes the transit time for each pathway can be significantly different. This is so even for two pathways which may have nominally the "same" geometrical path lengths. This then results in a broad distribution of transit time. The long tail is characteristic of the complex structure of the pathways and the diminished concentration gradient in the long time limit. An important consequence of these findings is that the most probable transit time τ_{max} (as represented by the peak of the distribution) can be significantly different from the average transit time τ_{avg} (as computed from the probability distribution $P(t)$). In the case of the results of Fig. 1 τ_{avg} can be as much as a fraction of 2 above that of τ_{max}. If τ is to be interpreted as the residence time then a single value for it may lead to a misleading interpretation of the experimental data. In fact τ_{avg} is simply the first moment $\langle t \rangle$ of $P(t)$. What the present result indicates is that higher order moments $\langle t^k \rangle$ (k = 2,3,..) may be necessary to properly characterize $P(t)$ and the experimental release data.

Figs. 2-4 illustrate the concentration profile at various times. Fig. 2 represent the profile at earlier time at which very little has been exited from the outlet. Fig. 3 gives the profile at a time τ_{max}, the maximum $P(t)$ (i.e. the most probable). Here the structure is much more spread out. There are rapid fall off in the profile near the four corners connected to the outlet node. This is consistent with the maximal behavior of the output flux at that time. Fig. 4 represents the concentration profile at very late time (t~400) (i.e. at the long tail region) which represents a temporal regime where most of the initial pulse has exited from our network. This physical visualization of the dynamics is in agreement with the long tail region of Fig. 1.

This skewness in the distribution of residence times is expected to be further enhanced if there is a spatial distribution of tritium generation sources. To illustrate this point simulations have been performed for a two pulses case in which one pulse is introduced at the center (as before) and the second pulse next to one of the corners. Another simulation has been performed in which one pulse is introduced at t≥0 at every node. The resulting output fluxes as a function of time is shown in Fig. 5. The increasing skewness of the distribution with various distribution of sources is evident. In fact in the many-pulse case the rise occurs in an extremely short time scale. Table 1 indicates the increasing deviation of the mean residence time from the most probable as the number of pulses increases from one to two to about 120. The location of the pulse sources relative to outlet nodes are also of crucial importance.

The physical process of tritium generation throughout the interior of the Li ceramic materials can be represented as a superposition of a large number of such sharp pulses over time. Thus the characterization of experimental tritium release rates with a single residence time needs to be treated with caution. Higher order moments such as $\langle t^2 \rangle$ may be necessary to provide an adequate description of the experimental situations.

4. Conclusion

We have analyzed the problem of tritium percolation through a porous Li ceramic material. The technique that we have employed is a random network percolation model. Local transport in each individual 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 medium is accounted for via Monte Carlo methods. The approach has been applied to an analysis of the concept of tritium residence time which is associated with the first passage time, a direct output of our analysis. It was shown that the distribution of first passage time has a significantly skewed structure with a long time tail. An adequate description of such a distribution requires higher order moments such as $\langle t^2 \rangle$ besides the mean. Therefore analysis of experimental tritium release rates with some average

residence time needs to be treated with caution. In the next stage of our work the tool that we have developed would be employed to investigate the issues of very large networks, realistic microstructural information and the effect of varying pressure gradient along the purge channels. We have demonstrated that the approach that has been adopted can be utilized to analyze in a very illuminating way the underlying issues of the concept of residence time. We believe that the present approach is ideally suited to tackle these very important yet difficult issues.
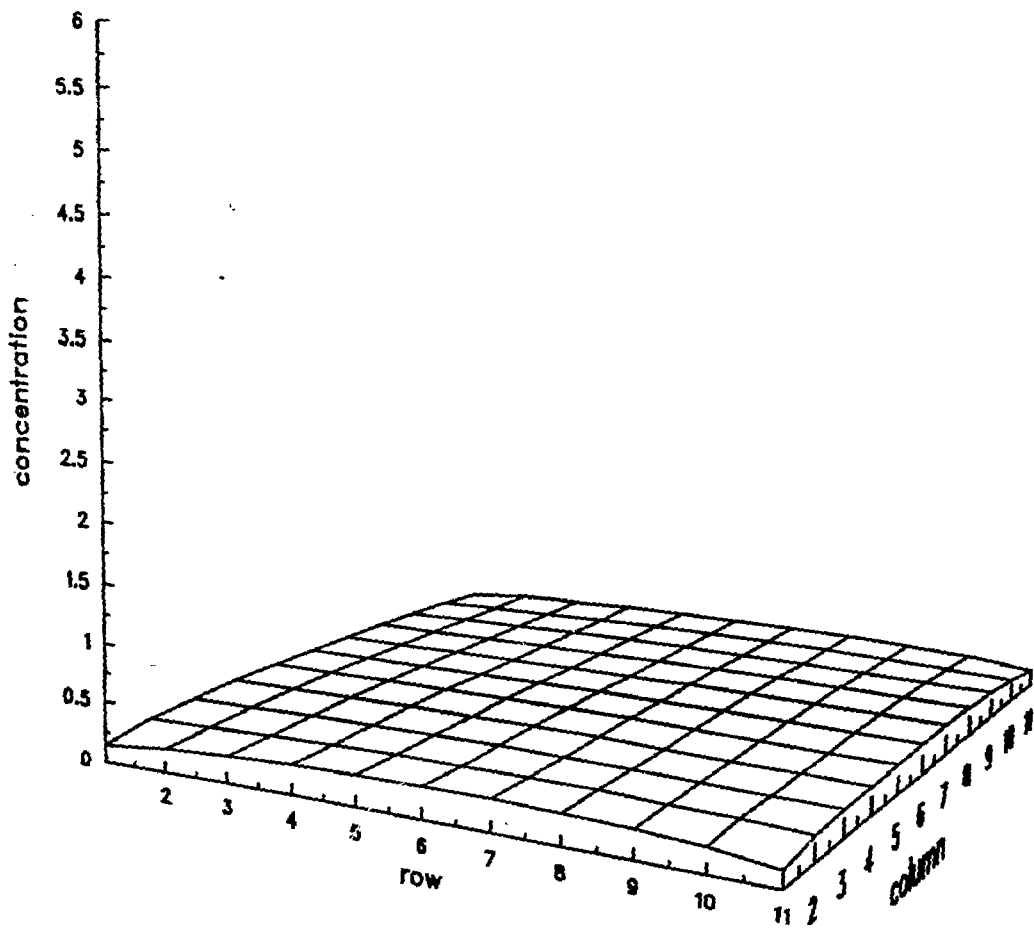
Table 1. Comparison of $\langle t \rangle$ to τ_{max}

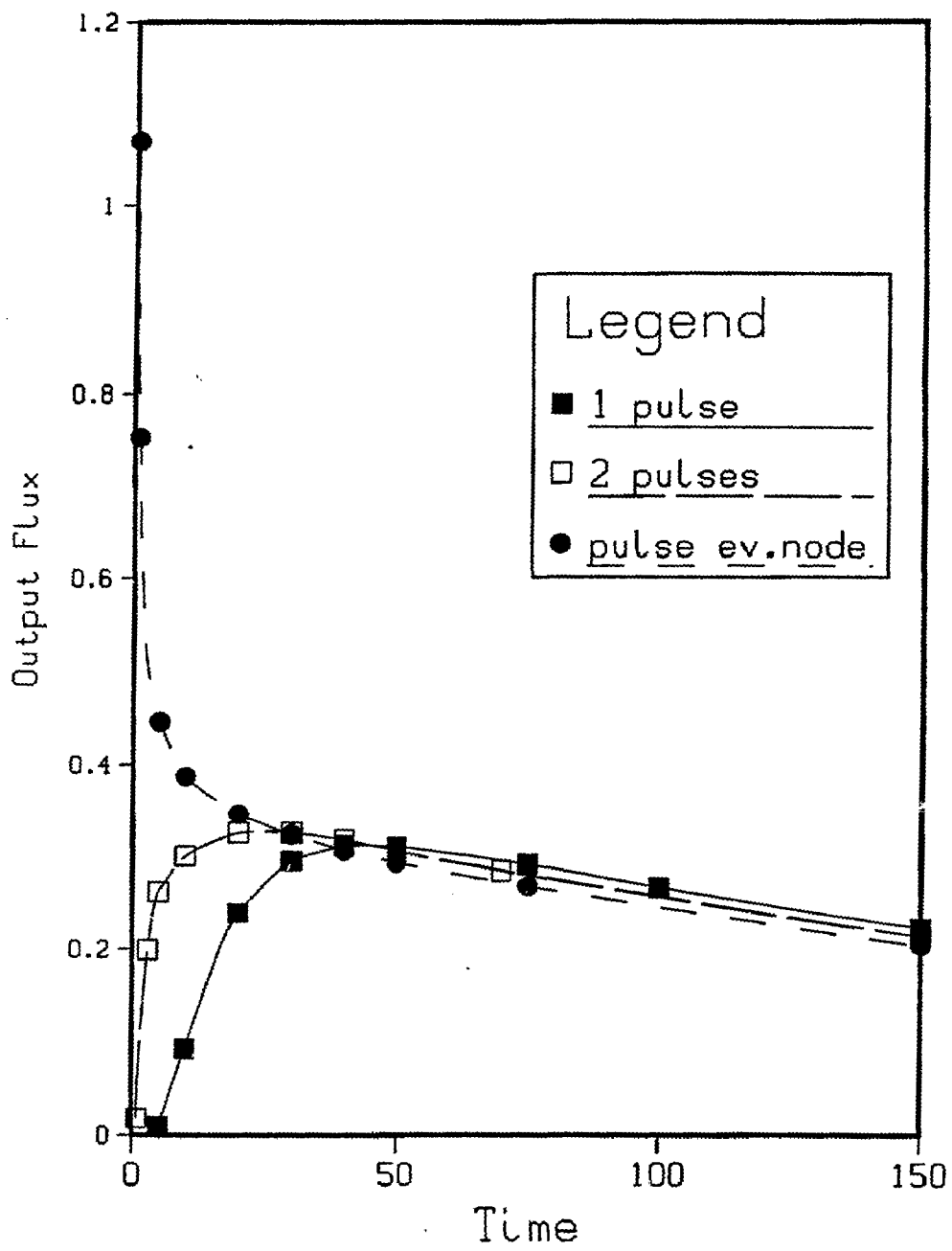| Pulse #	$\langle t \rangle$	τ_{max}	% Deviation
1	85	40	53
2	55	20	64
>100	30	<3	>90

Single pulse
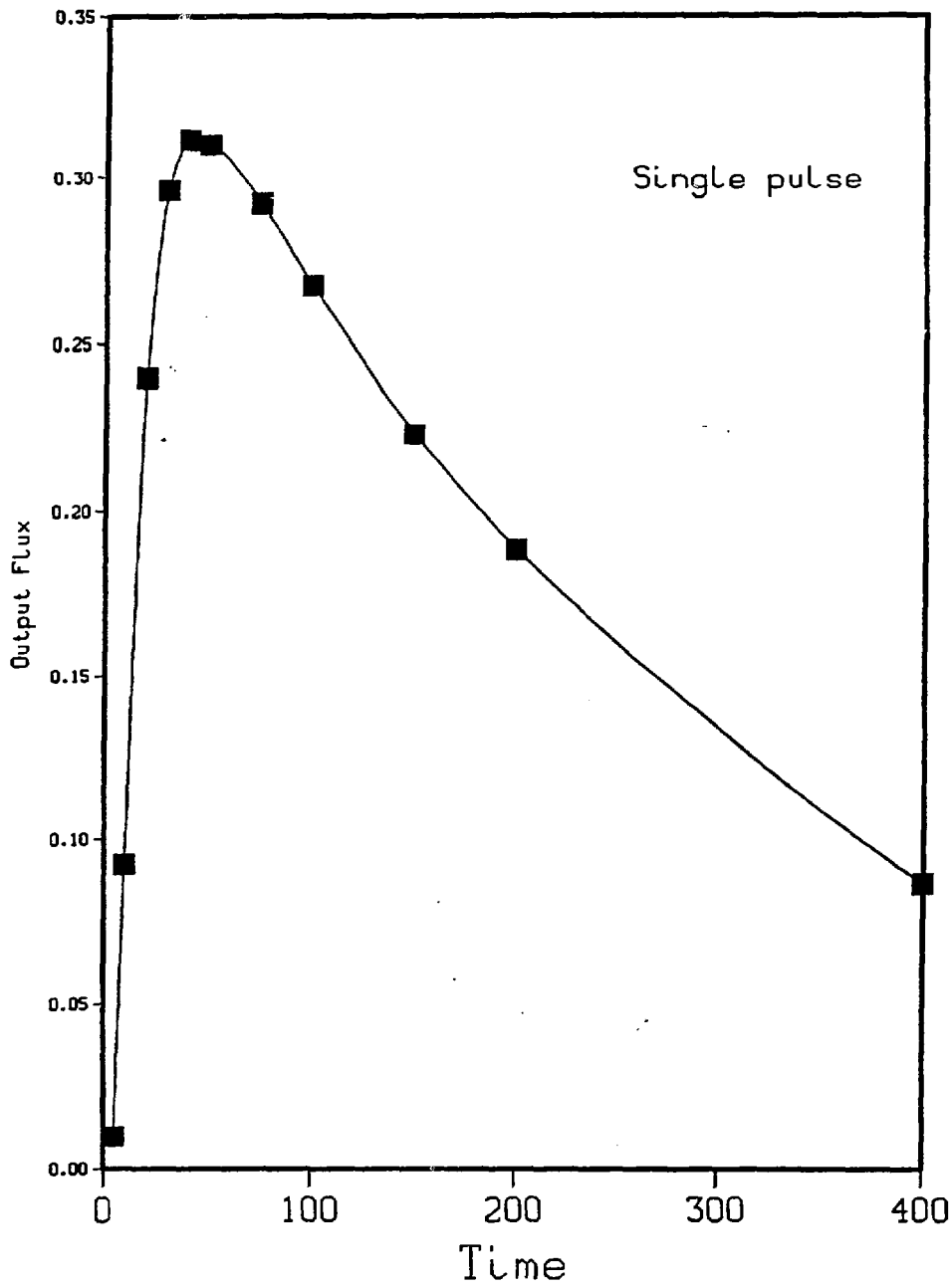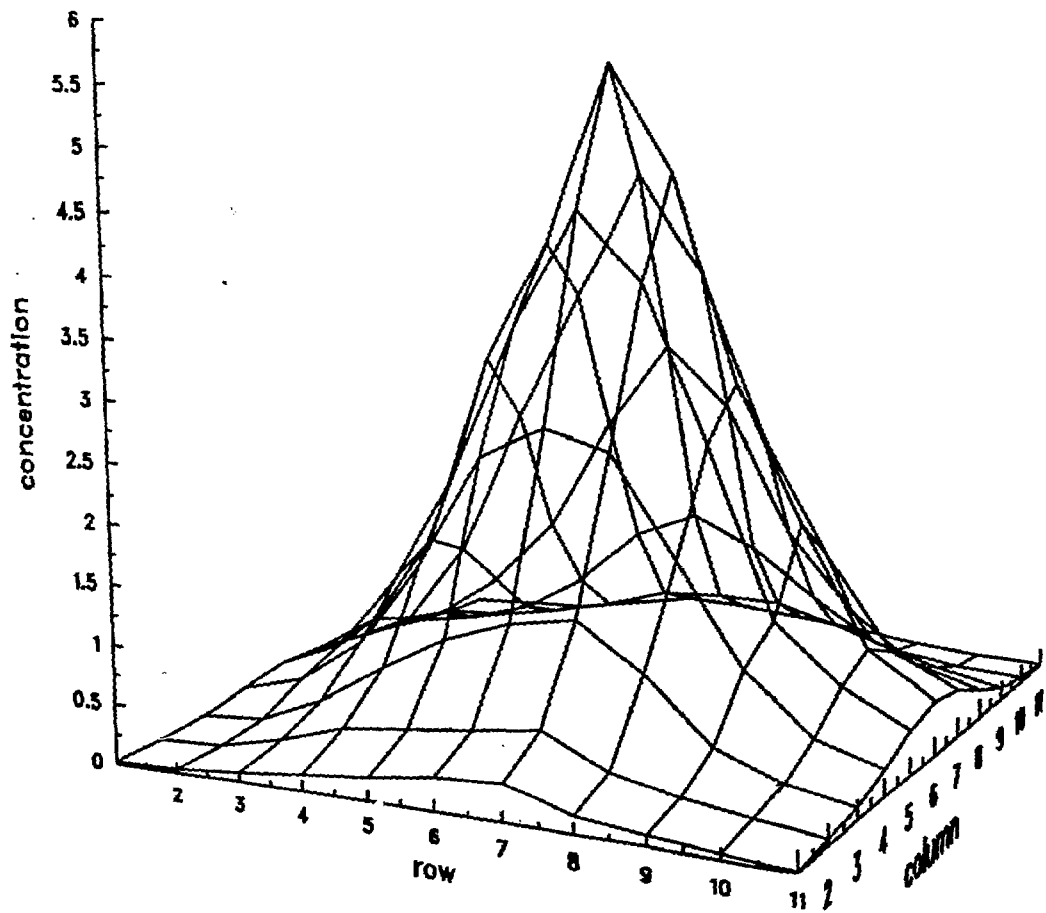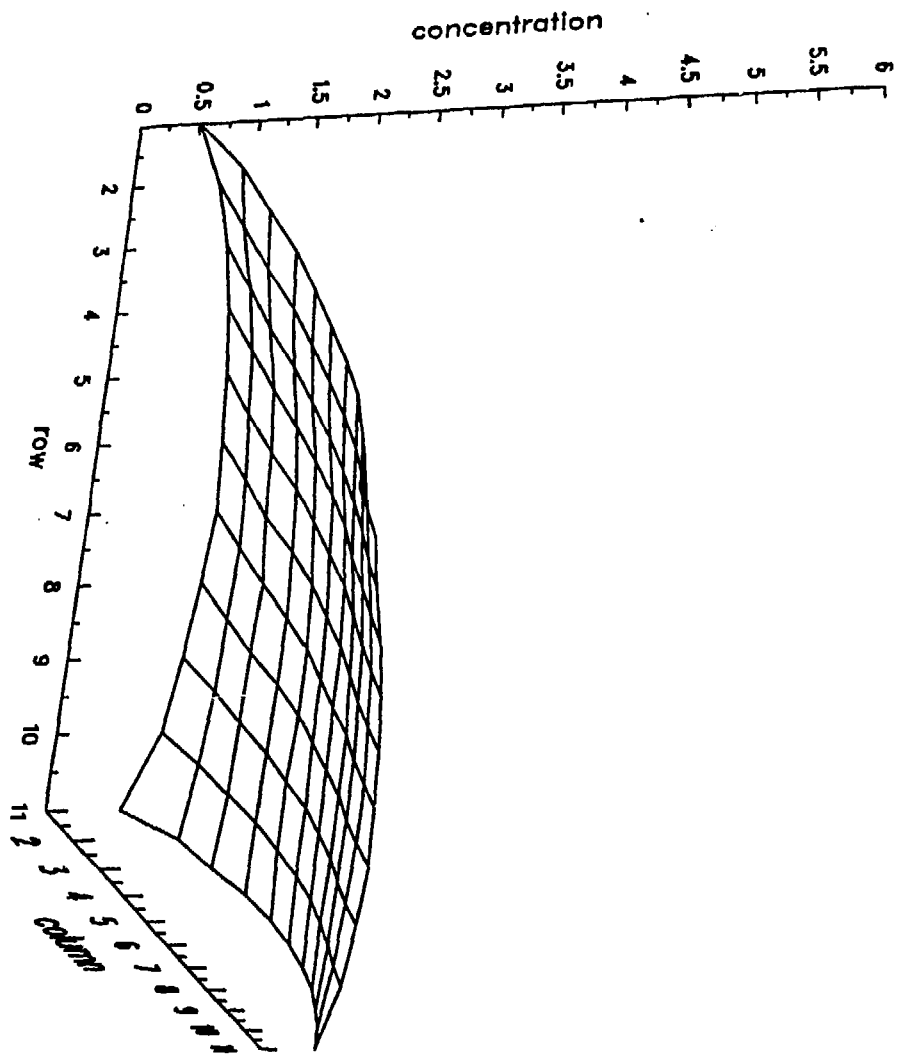
FIGURE CAPTIONS:

Figure 1. Output flux versus time for one pulse

Figure 2. Concentration profile at early time for one pulse

Figure 3. Concentration profile at intermediate time for one pulse

Figure 4. Concentration profile at late time for one pulse

Figure 5. Output fluxes versus time for one, two, and many pulses

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