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MATHEMATICAL DESCRIPTION OF FISSION
PRODUCT TRANSPORT IN COATED PARTICLES
DURING POSTIRRADIATION ANNEALS

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R. B. Evans III M. T. Morgan

JUNE 1974

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CONTENTS

Abstract	1
1. Introduction	i
2. Basic Considerations	3
2.1 Experimental	3
2.1.1 The Diffusion Experiment	3
2.1.2 Some Diffusion Results	3
2.1.3 Qualitative Interpretations	3
2.2 Initial and Boundary Conditions	5
2.2.1 Preliminary Remarks	5
2.2.2 Objectives	5
2.2.3 Description of the Diffusion Specimen	6
2.2.4 Zone 1 - The Source	7
2.2.5 Zone 2 - The Pyrocarbon Coating	10
3. Release Equations	12
3.1 Continuous Depletion of Source Potential	12
3.1.1 Radial Flow in Spherical Coordinates	12
3.1.2 Linear Flow in Slab Geometry	18
3.1.3 Discussion	20
3.2 Constant Potential at the Source Boundary	22
3.2.1 The Complete Solution	22
3.2.2 General Release Equation	25
3.2.3 Diffusion Control - No Film	27
3.2.4 Diffusion with Film Effects	29
3.2.5 Approximation of Depletion Curves	29
3.3 Depletion After Constant-Potential Operation	31
3.3.1 Linear Flow Solution	31
3.3.2 Discussion	33
4. Auxiliary Determinations	35
4.1 Experiments with Separated Particle Components	35
4.2 Concentration Profiles by Grinding	36
4.3 Summary	39
5. Closure	40
6. Acknowledgments	41
7. Nomenclature	41
8. References	43

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ABSTRACT

This report is concerned with several integrated forms of the diffusion equation that might be used to interpret and correlate cesium (and perhaps strontium) release data obtained from postirradiation anneals of pyrocarbon-coated fuel particles. Emphasis is placed on the role of the initial and boundary conditions as influenced by source concentration levels, permanent trapping in the source, and partition coefficients between the source and coating. It is assumed that release rates are controlled by the source potential and the diffusivity of the coating (with and without an external film or evaporation coefficient). A review of the equations, coupled with considerations of correlation procedures, indicates the need for complementary experiments that will give independent measurements of the trapped fraction and boundary concentrations.

1. INTRODUCTION

Deposited cesium isotopes are responsible for most of the gamma activity in HTGR primary coolant circuits examined to date;^{1,2} moreover, it is clear that release of cesium into the primary circuit should be controlled for the following reasons:

- (1) The extent of internal cesium contamination will govern access limitations which, in turn, will determine the feasibility and/or costs of maintenance following shutdown.
- (2) Loss of the helium coolant, which contains traces of cesium, during a blowdown accident could influence subsequent cleanup and land use costs, even through short-term doses to individuals at site boundaries are of little significance.

Cesium released from fuel particles is delayed to a certain extent in structural graphite components supporting and surrounding the fuel compacts, but our knowledge about the mobility of cesium under such circumstances is limited. Given a rate of release from the fuel, one would be hard pressed to make a reliable estimate of the amount of cesium that would permeate the fuel sleeve during a four-year fuel cycle. Any benefits of delay might even vanish when one considers gas turbine HTGRs at very high temperatures. Therefore, cesium control must rely on the retention efficiencies of the fuel particles. A prime objective of this study has been collection of information which will aid in determination of the degree of control to be expected from particles comprising the fertile component of the current reference fuel.³ Aside from these broad considerations, our immediate areas of concern may be introduced by tracing fuel particle development over the last decade from the standpoint of the authors' involvement.

Early reference designs for fuel particles were based on UC_2 particles coated with either lamellar or columnar pyrocarbons (PyC). Coating technology advanced rapidly from this point to duplex, then triplex, and finally to various arrangements including buffer layers. For the initial configurations, it was found that noble gases were well contained but that metals such as barium, cesium, and others would leak through the coatings to create new and unexpected problems. Even fissile and fertile fuels were found to be mobile which prompted intense studies of actinide diffusion in pyrocarbons. Continued development activities, however, revealed that actinide migration could be effectively eliminated by using oxide, rather than carbide, kernels. The problem of migration of fission products of intermediate volatility (e.g. cesium) remained, and this could only be eliminated by the use of improved silicon carbide coatings, which also held up actinides.

Current reactors in the United States) fissile particles are UC_2 kernels with Buffer/PyC/SiC/PyC coating layers. On one concept, the fertile particles might be ThO_2 with Buffer/PyC layers (called oxide-BISOs). It is postulated that the BISO coating could be used to enhance fuel fabrication and reprocessing economy. If this concept proves inadequate, one could always revert to the coating array on fissile particles. Our present problem involves evaluation of the retention performance of the oxide-BISO concept as it applies to fertile particles.

Considerable research effort has been expended both at ORNL and GAC on studies of cesium migration through coatings on BISO-oxide particles. The initial philosophy behind local efforts centered on relative retention efficiencies of various coatings. Five years ago it was sufficient to perform a release experiment, determine a coating diffusion coefficient, and then state whether material A had better retention properties than material B (i.e., a lower coefficient). However, extensions of this work have forced the realization that more than a diffusion coefficient is required to specify release or retention properties. In fact, it now appears that, although cesium release might be predicted in terms of classical diffusion (heat transfer) models, additional considerations relating to irreversible trapping may be required. This is of considerable importance since a large portion of the BISO effort can be salvaged in the event that we are forced to abandon the BISO concept in lieu of the less imaginative, more conservative TRISO concept; the latter includes, of course, the SiC layer.⁴ The portion that can be salvaged includes the careful delineation of various effects relative to kernels, buffer layers, and outer coatings that might permit translation of present results to more "advanced" concepts.

This report is one of two concerned with the collection of theoretical and experimental material relative to cesium release from BISO-coated oxide particles. Specifically, this report deals with the various equations derived as boundary-value problems applicable to cesium release experiments. For a first application, some of these equations will be applied to completed experiments in order to extract a maximum amount of information from available data. For a second application, they will be used for the design of supplementary experiments with materials studied to date. The success of these applications will be detailed in subsequent reports.

Several excellent reviews of equations that describe release rates of fission products from irradiated fuels are given in the literature. The most definitive of these relate to noble gases. When one seeks mathematical descriptions of the mechanisms controlling cesium release from intact BISO particles, the amount of available information is very limited. Theoreticians move rapidly to extensions covering reactor operating conditions, where production and decay phenomena must be accounted for at the expense of other, seemingly less dominant, effects. Conditions applicable to postirradiation anneals of the type we perform are quickly passed over in a search for generality. A report most pertinent in application to present goals is that by Raines *et al.*⁵ Unfortunately, after this effort, emphasis passed from writing specific equations in closed form to computerized numerical solutions of heat equations that take into account numerous possible complexities. Examples of this new approach are given by Dunlap and Gulden,⁶ Walther,⁷ and Norman *et al.*⁸ The latter are so sophisticated that they require detailed understanding of input programs that may or may not apply to our problems. To avoid a review of computer techniques, we decided to use a direct approach to solving the problems. We would try to select well-known equations that have worked well in the past for correlation of transport behavior. This report deals with a discussion of the selections and the significance of the initial and boundary conditions involved from an experimental point of view.

2. BASIC CONSIDERATIONS

2.1 Experimental

2.1.1 The Diffusion Experiment

Several kinds of laboratory determinations and auxiliary experiments are employed in studies of fission product release from coated fuel particles, but postirradiation anneals of intact particles constitute the heart of the entire experimental program. If the irradiations are conducted at low temperatures ($<800^{\circ}\text{C}$) and the isothermal anneals are conducted at high temperatures (1000 to 1600°C), cumulative release data obtained during the anneals provide definitive information concerning the release mechanism because some measure of control will have been exercised over the initial and boundary concentrations within the particles.

The diffusion anneal experiments conducted to date have specialized in studies of ^{137}Cs release, with particular emphasis on BISO-coated oxide fuel particles. In these experiments, irradiated particles are analyzed for initial ^{137}Cs content by gamma-ray spectrometry (total cesium, including ^{133}Cs and ^{135}Cs , can be estimated); then they are heated for predetermined time intervals at an assigned constant temperature. The configurations and environment within the high-temperature containment envelope are arranged and adjusted such that all the cesium released as a vapor during an anneal interval will condense on cool collection surfaces adjacent to the hot zone about the particles.

To separate gamma-ray contributions from released and retained cesium, the furnace is shut down after each anneal interval, and individual gamma analyses are performed on all components of interest. The cumulative buildup of cesium on collection surfaces is utilized as a measure of the time-integrated release rates because release values are much smaller than retained values. Additional details are available elsewhere.⁹

2.1.2 Some Diffusion Results

The 1600°C release behavior observed during anneals of two types of BISO-coated ThO_2 particles is illustrated in Fig. 1. Here the cumulative cesium release data are plotted as a function of time, and the release values are expressed as fractions of the total cesium present at the beginning of the experiment. Such plots are often designated as fractional release curves. Both curves illustrate one of the more impressive aspects of the experiments in that a period of well over two months was required for their completion. (This includes shutdown times to perform the gamma analyses.)

Curve II is typical in the sense that the experiment was terminated before a fractional release of 0.20 was attained. Curve I is atypical, and in fact unique, because these are the only ORNL intact particle results demonstrating that the ultimate release values could be considerably less than 100% of the initial content. Similar data probably could have been obtained for particles of curve II, but an additional six months of experimentation might have been required. Aside from indications of an ultimate release value, both curves reveal common features which would have been more apparent if the ordinate values for curve II had been plotted on an expanded scale.

2.1.3 Qualitative Interpretations

Most sets of data involving extended anneal times have features common to regions A and B; several show region C characteristics. Regions A and C correspond to time regimes wherein transient conditions prevail within the particle. Throughout region A, the coating is loading up with cesium; over C, it would appear that the driving force at the source boundary is falling which, in turn, permits the coating to unload.

Fig. 1. Postirradiation Cesium Release Behavior of Two Pairs of Bi₅O-Coated Thoria Particles. The results show the relative retention effectiveness of LTI coatings derived from propylene (Curve I) and HTI coatings derived from methane (Curve II).

The intermediate region, B, seems to represent a quasi-steady state regime in which release rates are nearly constant with time. Linear extrapolation of the region B segment to the time axis gives a "breakthrough time," which can be described as the time that cesium would first appear outside the coating if the material had moved through the coating uniformly without dispersion. It is standard practice to evaluate an admittance parameter on the basis of the breakthrough time and, in the absence of auxiliary information, to call it a diffusion coefficient. Although the validity of this approach seems questionable, we will show that it gives surprisingly good approximations in many nonideal cases.

Another important feature of the release curves relates to the slope in region B. Since this slope is nearly constant, it should reflect the influence of a steady-state rate equation that carries contributions of a driving potential, the diffusion coefficient, and (unfortunately in some cases) additional parameters representing subtle side effects. If the latter were negligible, one could — in principle — extract two values of importance from data in region B, namely, a diffusion coefficient and a driving potential. This is precisely the approach one would take for systems exhibiting a time-constant potential at the source boundary and a zero potential at the outer boundary.

The crux of the matter reduces to whether: (1) all three regions are governed by three distinctly different mechanisms, (2) one mechanism applies for regions A and B and a second for region C, or (3) a

single mechanism controls all regions. The last possibility must be included because the curve for this case will exhibit manifestations of all three regions. An examination of the curves on Fig. 1 reveals that a mechanistic resolution cannot be obtained through a cursory inspection of a release curve; the time boundaries cannot be distinguished. To accomplish this, one must compare either the entire curve or expanded portions of the curve to solutions of the diffusion equations derived under various conditions. These conditions should represent reasonable limiting cases. The selection and discussion of such equations are prime objectives of this report. We shall start with a generalized discussion of the conditions that set the form of the equations.

2.2 Initial and Boundary Conditions

2.2.1 Preliminary Remarks

For purposes of orientation we shall briefly describe a fuel particle and its components. A BISO-coated oxide particle has three major components: a thorium or uranium oxide kernel, a buffer layer, and an outer pyrolytic carbon coating. The kernel is usually a high-density material; the buffer is a very porous carbonaceous material designed to accommodate dimensional changes and absorb recoil damage; the outer coating is a moderate-density isotropic pyrocarbon designed to serve as a tiny leakproof pressure vessel. In addition, earlier specifications required the presence of a thin external coating (columnar PyC) ostensibly to avoid fabrication damage when a large number of particles were bonded together to form a fuel stick. Most of the ORNL experiments have involved particles with such "sacrificial layers" simply because they were available as large batches of identical materials.

Since many of the particles have been subjected to high burnup levels prior to diffusion anneals, it is pertinent to describe the physical condition of the particles after irradiation. It turns out that diffusion annealing at moderately high temperatures does not alter the appearance of the particle. Therefore, we have elected to discuss one that was irradiated to 20% burnup (FIMA) and then annealed at 1250°C for 2500 hr to obtain a fractional release of 0.25. Figure 2 gives a pictorial representation of a photomicrograph of a water-polished section, along with two microprobe scans of the same section.

Two interpretive restrictions on microprobe results should be mentioned here. First, ratios of average scan-recorder readings for two different matrices are not equivalent to the actual average concentration ratio. The scan values on the ordinates of Figs. 2(b) and 2(c) only reflect relative cesium concentrations within a given region. Fortunately, total cesium, as seen by the probe in a given region, is directly proportional to the tracer isotope ^{137}Cs , which forms the basis for our diffusion data. Total cesium is present as ^{133}Cs , ^{135}Cs , and ^{137}Cs . The first two are stable; the tracer is long-lived. Thus the ratio of ^{137}Cs to total cesium remains constant at $\sim 1/2$. This is one of the favorable features of cesium experiments.

The second restriction on microprobe results involves false concentration decreases, or sudden "dips" in the scan readings. These occur when the probe encounters deep voids. Probe emissions are lost at these points, and the detector will interpret such losses as decreases in cesium concentration. Some perspective regarding the interpretation of scans may be gained by noting the probe reactions to the mounting plastic beyond specimen edges, as shown in Figs. 2(a) and 2(c).

2.2.2 Objectives

One might question the wisdom of placing emphasis on limited microprobe data which are only qualitative at the present stage of development. A response would be to point out that the selection of appropriate release equations requires knowledge about internal concentration profiles, as well as internal conditions governing the shape of the profiles. Such information cannot be extracted from current ORNL

Fig. 2. Microprobe Data Obtained by Scanning Components of a BISO-Coated UO_2 Particle. Prior to scanning, this particle was irradiated to 20% burnup, annealed at 1250°C for 2500 hr to 25% fractional release, and then sectioned and polished.

data. The latter relate to external measurements of cumulative release; there is no way to backtrack and acquire the required information. For the time being, the only recourse is to use the microprobe data, with some degree of skepticism, for resolution of the following points: (1) location and definition of a source zone as it appears after an appreciable diffusion-anneal time; (2) examination of diffusion resistances within this zone; and (3) extrapolation of information for (1) and (2) from extended times to earlier periods, in order to obtain estimates of the initial conditions.

Considerations of point (3) require heuristic speculations and will be discussed in more detail in a subsequent section concerning phenomena in the source zone. It should be remarked here that considerable attention is given to boundary conditions but that queries relative to initial conditions are often ignored. This is understandable since experiments designed to establish initial conditions tend to identify all the weaknesses in laboratory procedures.

2.2.3 Description of the Diffusion Specimen

The Kernel. Irradiations to high burnup levels produce dramatic effects in both the kernel and buffer regions. Large voids appear in the initially dense oxide kernels. Exhaustive microscopic examinations reveal

that void sizes increase as burnup increases, and that voids tend to merge during growth. Since significant amounts of cesium moved out of the kernel during migration, it must be assumed that many voids are interconnected. We note that flow is the only criterion available for the degree of connection. Pore connections can never be pinpointed via two-dimensional microscopy.

Based on the microprobe results, long-term cesium drainage *did not* produce a concentration decrease over the kernel region. Resistances in the kernel *did not* control release rates. However, an appreciable fraction of the fission products was immobilized in some mysterious fashion. In view of the damage suffered by the kernel, it seems logical to assign microscopic volumes within the kernel as the region of residence for trapped fission products.

The Buffer Layer. -- The original featureless structure of buffer material (actually a cheap soot, produced by a sophisticated process) has been converted to a duplex structure. In the region adjacent to the kernel, severe alterations resulting from recoil and knock-on phenomena have occurred. In simpler terminology, the buffer here is "cramped full" with heavy fuel and solid fission products. The microprobe detects high cesium concentrations at the outer, more porous, buffer region. This segregation probably resulted from an overpopulation syndrome -- the cesium had nowhere else to wait before its transport out through the coating. A literal translation of microprobe data for the buffer region would suggest movement *into* the particle; an "honest interpretation" would yield a positive slope. The need for skepticism is hereby demonstrated; it is known that cesium moved out of the particle. We note also the formation of precipitates and of new voids in the buffer region. While it is difficult to assess their effects, they could have marked influences on the microprobe scans.

The Pyrolytic Carbon Coating. -- The condition of the outer coating is remarkably unchanged at the magnifications involved ($\sim 300\times$). Nearly all damage extending beyond the kernel is absorbed by the buffer. Voids in the coating are no more pronounced than they were prior to irradiation; they remain as isolated voids. As to cesium profiles, nothing definite can be attributed to the presence of the sacrificial layer. The first microprobe scan over the coating exhibits a definite concentration decrease; the second does not. An average of a large number of scans, however, would probably have a definite negative slope, verifying the coating's ability to act as a diffusion barrier.

Summary. -- The probe data support all natural impulses to fix the outer boundary of the source zone as the buffer layer-PyC coating interface, and to homogenize the kernel and buffer regions (lk) and (lb) into a single source zone. Although regional concentrations within the source zone are different when referred to bulk volumes, it will not be difficult to concoct an average concentration for the source because diffusion resistances in regions (lk) and (lb) appear small in comparison to those envisioned for the coating. Thus we have the advantageous situation in which we combine all unknown structural effects related to damage and trapping in the source zone and divorce them from the diffusion parts of the problem. The trapped fraction can be dumped in a negative potential well. Finally, we note that the shapes of microprobe traces are quite similar to hypothetical profiles used to derive the diffusion equations that will appear in subsequent sections.

2.2.4 Zone 1 -- The Source

Discussions of the experimental procedures emphasized the role of cesium vapor transport as a key factor in external release measurements. Since formation of reduced cesium vapor is favored at high temperature, it is felt that a gas transport mechanism also controls cesium migration in the porous regions of the source zone. We envision that the cesium will attain some partial or vapor pressure, $p' = n'RT'$, as dictated by chemical potentials within the kernel and/or buffer, where the primes denote values corresponding to mobile cesium. Then we can write for the initial content, using subscripts k and b for

kernel and buffer regions:

$$V_k [\epsilon_k n'_1(0)] + V_b [\epsilon_b n'_1(0)] = fM_1^0.$$

Gas densities are referred to pore volumes; the porosities, ϵ , convert these to bulk volumes, V . The fM_1^0 denotes the total amount of mobile cesium available initially. All pore volumes over k and b are assumed to be connected, and the gas density (pressure) is to be uniform throughout the source. The gas density is, therefore, given by:

$$n'_1(0) = \frac{fM_1^0}{\Sigma V_p}$$

where

$$\Sigma V_p = \epsilon_k V_k + \epsilon_b V_b,$$

and the summed quantity represents the total pore volume. At this point, one could define a volume-averaged porosity, then write down a source depletion equation such as

$$V_1 \langle \epsilon \rangle_v [n'_1(0) - n'_1(t)] = fM_1^0 - M_1^*(t).$$

The starred value represents the amount of active material remaining at any time, t , and the difference in active amounts is the same as that in total amounts. Both differences are equivalent to the cumulative loss $N_1(a,t)$ from the source at $r = a$. Notice that diffusion terms and coefficients are absent.

Some bookkeeping will be required to separate the active and total amounts. First, however, we shall consider changing concentrations to bulk values or pseudo-solid-state values. This must be done eventually since gas transport will not apply to the coating, and little information is available concerning p' , ϵ_k , and ϵ_b in the source zone. Consideration of the first equation for the initial quantity in terms of k and b region is adequate. Under the usual convention, we say that the bulk concentration for region j is $\epsilon_j n'_1(0)$, where $j = k$ or b . Then, using mobile or active notation,

$$V_k C_k^*(0) + V_b C_b^*(0) = fM_1^0.$$

Illustrative histograms depicting initial and boundary conditions as visualized for the source region are presented in Fig. 3.

In Figs. 3(a) and 3(b) we show the k and b profiles, with and without contributions of the trapped fraction. One may note that starred and unstarred bulk concentration (i.e., the active and actual) values are equivalent over b , but not over k . Consider the discontinuity at the $k - b$ interface and the concentration ratio

$$\frac{C_b(0)}{C_k(0)} = \frac{C_b^*(0)}{C_k^*(0)} = \frac{\epsilon_b n'_1(0)}{\epsilon_k n'_1(0) + \frac{(1-f)M_1^0}{V_k}} = \frac{\epsilon_b}{\epsilon_k + \frac{(1-f)\Sigma V_p}{fV_k}}$$

as it applies to Fig. 3(a). The second term in the denominator accounts for the trapped amount. The value

Fig. 3. Schematic Representation of Initial and Boundary Conditions Arranged to Account a Permanent Trapped Fraction and Partition Coefficients. Initial conditions are exhibited in (a) through (c); boundary conditions for a depleting system are shown at (d).

of this ratio is initially slightly greater than unity but, as drainage proceeds, shifts constantly toward zero. If, on the other hand, the concentration profile is constructed entirely in terms of active concentrations, as in Fig. 3(b), the ratio becomes meaningful; that is, it becomes a time-constant "partition coefficient," ϕ :

$$\phi_{kb} = \frac{C_b^*(0)}{C_k^*(0)} = \frac{C_b^*(t)}{C_k^*(t)} = \frac{\epsilon_b}{\epsilon_k}.$$

The concept of ϕ is very simple, almost trite, when applied to the source zone, nevertheless, it has considerable importance when applied to the source-coating interface where it reflects gas-solid solubilities.

The general shape of the profiles in Fig. 3(b) should be retained throughout the depletion if ϕ remains constant. Thus, the shape at any t is about the same as that at $t = 0$ and vice versa. Because there is no reason to carry two source concentrations from this point on, a volume average value of the form

$$V_1 \left[\frac{V_k}{V_1} C_k^*(0) + \frac{V_b}{V_1} C_b^*(0) \right] = V_1 C_1^*(0) = fM_1^0$$

will be used. Consider the concentration relationship:

$$C_1(t) = C_1^*(t) + (1 - f)C_1^0,$$

where

$$C_1^*(0) = fC_1^0.$$

With the above, one may write the following differences:

$$V_1 [C_1(0) - C_1(t)] = V_1 [fC_1^0 - C_1^*(t)].$$

Both are equivalent to

$$M_1^0 - M_1(t) = fM_1^0 - M_1^*(t) = N_1(a, t).$$

After very long periods of time, all differences and $N_1(a, t \rightarrow \infty) \rightarrow fC_1^0$.

The rate of release from the source zone is

$$-\frac{dC_1^*(t)}{dt} = -\frac{\epsilon_1}{RT} \frac{dp'}{dt} = +\frac{1}{V} \frac{dN_1(a, t)}{dt},$$

where the initial condition is $C_1^*(0) = fC_1^0$. It is desirable to express concentrations as active values in order to get a proper connection between zones 1 and 2 via the ϕ_1 as indicated in Fig. 3(d).

2.2.5 Zone 2 – The Pyrocarbon Coating

All of the diffusion effects for cesium migration are charged to zone 2, the pyrocarbon coating. The outer boundary at $r = b$ is always assumed to be zero for cesium transport, at least for the first round of

data correlations. Every experimental precaution is taken to ensure that this will be a good approximation; however, in some instances, a back pressure might exist if (1) the particles were buried in a matrix with a cesium concentration slightly above zero, or (2) if a film operated between $r = b$ and the gas about a freestanding particle. These effects are most severe for strontium; contributions of film or evaporation coefficients will be considered later.

Pyrocarbon matrices do not always have a uniform structure: properties in the initial deposits are different from those laid down at the end of the process. One author¹⁰ has detected connected voids in regions corresponding to $r = b$. Furthermore, we have some evidence to show that increased cesium concentrations in the coating increase the diffusion coefficients, but only by a factor of 2 or 3.

Aside from the above, the region corresponding to $r = a$ is of most interest. We consider the ratio

$$\frac{C_1^*(a,t)}{C_2(a,t)}$$

and a Henry's law relation

$$n_1(t) = K_c C_2(a,t)$$

or

$$p_1(t) = K_p C_2(a,t),$$

where

$$RT'K_c = K_p.$$

The latter states that there is an equilibrium relationship between the partial pressure of the gas and the concentration in the solid pyrocarbon. The $C_2(a,t)$ value follows the $p_1(t)$, up or down. As the pressure is increased, the K_p starts to increase; then there seems to be a limit (a saturation value) as to the amount of cesium that the pyrocarbon will accept. If $p_1(0)$ exceeds this limit, the $C_2(a,t)$ will remain constant until $p_1(t)$ decreases to a lower value where the equilibrium begins to take over again. The ratio will decrease, then assume a constant value such that

$$\frac{C_1^*(a,t)}{C_2(a,t)} = \frac{(\epsilon_1)n_1'(t)}{C_2(a,t)} = K_c(\epsilon_1) = \phi_{21}.$$

Since this is the only partition coefficient that will appear in the solutions, the subscript 21 may be eliminated.

Consider now the regions noted in Fig. 1, particularly regions A and B. It is not unreasonable to assume that particles subjected to high burnup levels ($>10\%$ FIMA) will have very high concentrations of untrapped cesium in zone I. Thus there may be many instances in which release throughout A, and into B, is controlled by a constant-potential process. Stated differently, $C_1^*(a,t)$ will be greater than the equilibrium $\phi C_2(a,t)$ value at the temperature of the experiment such that the coating about $r = a$ is "saturated," and the actual $C_2(a,t)$ will be a constant, $C_2(a)$. If this happens, a portion of B represents a constant release

rate regime. The only condition to be stated at $r = a$ is:

$$C_2(a,t) = C_2(a).$$

There is no zone I contribution in the equations. Of course, zone I depletion occurs and the rate can be computed, but the value will depend only on interactions in the coating.

On the other hand, there may be many cases where the release rates are so high (or the burnups are so low) that $C_2(a,t)$ will fall to an equilibrium value at some point in B or A. If this or any other $C_2(a,t)$ mode transition occurs in A, one would be hard pressed to interpret the data. However, equilibrium attainment in B can be handled, even though it might be difficult to determine the time, t'_0 , at which $C_2(a,t)$ starts to decrease in an orderly fashion. Here, one must specify $C_2(a,t)$ in terms of $C_1^*(t)/\phi$; as well as, a rate equation which gives zone I capacity contributions to the process. Thus

$$\phi C_2(a,t) = C_1^*(t).$$

and from the last part of the zone I discussion,

$$\frac{1}{V} \left| \frac{dN_1}{dt} \right|_{1 \text{ or } 2} = - \frac{dC_1^*(t)}{dt}.$$

or

$$\frac{1}{V} \left[-A \frac{\partial C_2(a,t)}{\partial r} \right] = - \frac{dC_1^*(t)}{dt}.$$

The initial condition for this rate boundary condition is

$$C_1^*(t'_0) = fC_1^0$$

is these derivations. We now turn to the development of diffusion equations, starting with this second set of conditions, for the case where t'_0 corresponds to real time zero. It is convenient to let $A/V = 1/a'$.

3. RELEASE EQUATIONS

3.1 Continuous Depletion of Source Potential

3.1.1 Radial Flow in Spherical Coordinates

Consideration is now given to the diffusion phenomena within the coating that govern the fission product retention properties of a fuel particle. We seek a fission product release rate equation, in time-integrated form, that can be used to prepare a set of "predicted" release curves. Comparisons with experimental curves should permit evaluation of the boundary and initial conditions used in the derivation and/or suggest the nature of the true conditions. The equations to be derived here represent an extreme limiting case. They will apply only to situations where values of f and/or burnup are relatively low. We shall assume that the highest (the initial) source potential will be less than any restrictive hypothetical saturation value. In other words, at time zero, the ϕ will "lock in" at a constant value and $C_2(a,t)$ will fall in proportion to $C_1^*(t)$ throughout the life of the experiment. Transient conditions will prevail at all times.

The form of the heat equation describing transient diffusion in the "zone-2" spherical shell between radii a and b is:

$$D \frac{\partial^2 C_2}{\partial r^2} + \frac{1}{r} D \frac{\partial C_2}{\partial r} = \frac{\partial C_2}{\partial t}, \quad (a < r \leq b, t > 0).$$

If we let $U_2 = rC_2$ and $U_1^* = rC_1^*$, then the Laplacian on the left side simplifies and the equation becomes linear in form; one then obtains

$$D \frac{\partial^2 U_2}{\partial r^2} = \frac{\partial U_2}{\partial t}.$$

A choice must be made here as to the method of approach. We can employ either formal methods or Laplace transformation techniques. A formal solution requires a search for a suitable set of properly normalized Eigenvalued functions that will converge, in series form, to the rather "sticky" boundary conditions associated with this particular problem. Since this search might prove more difficult than the original problem, the use of Laplace transforms seems more reasonable. These are defined by:

$$\mathcal{L}\{F(t)\} = \int_0^\infty F(t)e^{-st} dt = f(s).$$

Application of this operation to both sides of the "U" equation gives

$$D \frac{d^2 u_2}{dr^2} = su_2 \quad U_2(r, +0). \quad (1)$$

The $+0$ means that we consider the condition at some $t > 0$ and project it back to $t = 0$ "from the right." To summarize, we first changed from $C_2(r, t)$ to $U_2(r, t)$ in $r - t$ space. Next, we transformed to $u_2(r, s)$ in $r - s$ space, where the r contributions can be handled as ordinary differential equations and t contributions are arrived at automatically, in integral form, via inversion back to $U_2(r, t)$.

The initial and boundary conditions for Eq. (1) were discussed in detail in the previous section. We merely enumerate them here.

Initial conditions:

$$C_1^*(0) = fC_1^0, \quad U_1^*(+0) = afC_1^0, \quad (0 \leq r \leq a). \quad (2)$$

$$C_2(r, +0) = 0, \quad U_2(r, +0) = 0, \quad (0 \leq r \leq b). \quad (3)$$

Boundary conditions:

$$C_2(b, t) = 0, \quad bu_2(b, s) = 0, \quad (t \geq 0). \quad (4)$$

$$\phi C_2(a, t) = C_1^*(a, t), \quad \phi u_2(a, s) = u_1^*(s), \quad (t > 0). \quad (5)$$

The last boundary condition can be troublesome; it must be written down carefully:

$$\frac{\partial C_1^*(t)}{\partial t} = \frac{D}{a'} \frac{\partial C_2(a,t)}{\partial r}, \quad (t > 0).$$

But

$$U = rC,$$

and

$$\frac{\partial C_2}{\partial r} = \frac{1}{r} \frac{\partial U_2}{\partial r} - \frac{U_2}{r}.$$

Thus

$$\frac{\partial U_1^*(t)}{\partial t} = \frac{D}{a'} \left[\frac{\partial U_2(a,t)}{\partial r} - \frac{U_2(a,t)}{a} \right].$$

The transformed version is:

$$su_1^*(s) - U_1^*(+0) = \frac{D}{a'} \left[\frac{du_2(a,s)}{dr} - \frac{u_2(a,s)}{a} \right]. \quad (6)$$

We recall here that a' represents V/A . Now this boundary condition can be altered using IC(2) and BC(4) as follows:

$$\phi su_2(a,s) - afC_1^0 = \frac{D}{a'} \left[\frac{du_2(a,s)}{dr} - \frac{u_2(a,s)}{a} \right]. \quad (6a)$$

It turns out that the second term in the brackets introduces an inordinate amount of algebraic difficulty in the inversion procedures.

The next step is to solve Eq. (1) in light of IC(3). We have

$$\frac{d^2 u_2}{dx^2} - \frac{s}{D} u_2 = 0; \quad (7)$$

a solution is

$$u_2 = B_1(s)e^{+r(s/D)^{1/2}} + B_2(s)e^{-r(s/D)^{1/2}}.$$

To satisfy BC(4) and accommodate boundary conditions at $r = a$, we let

$$B_1(s) = \frac{A(s)}{2} e^{-b(s/D)^{1/2}},$$

and

$$B_2(s) = + \frac{A(s)}{2} e^{+b(s/D)^{1/2}} .$$

Then

$$u_2 = A(s) \sinh [(b - r)(s/D)^{1/2}] . \quad (7b)$$

and

$$\frac{du_2}{dr} = A(s) \{(s/D)^{1/2} \cosh [(b - r)(s/D)^{1/2}]\} .$$

When $r = a$, $b - r$ becomes $\ell = b - a$. Now information from Eq. (7b) can be inserted into Eq. (6a) to yield an expression for $A(s)$, which can then be applied in Eq. (7b). The result is:

$$u_2(x,s) = \frac{e^{-k} k f C_1^0 \sinh [(b - r)(s/D)^{1/2}]}{\left(s + \frac{Dk}{a^2}\right) \sinh [\ell(s/D)^{1/2}] + \frac{k}{a} (s/D)^{1/2} \cosh [\ell(s/D)^{1/2}]} ,$$

where $k = a/a' \phi$.

We now have the solution for $u_2(r,s)$ in $r-s$ space. An inversion formula is required for conversion to $r-t$ space. It is doubtful that the appropriate $F(t)$ -vs- $f(s)$ relationship has been tabulated for $u_2(r,s)$. The only recourse is to use the inversion integral of the product $e^{\lambda t} f(\lambda)$, where λ is the dummy variable of integration for s expressed as a complex variable and $f(\lambda)$ represents $u_2(x,s)$. The result we seek is an infinite series of residues $\sum_n \rho_n(t)$, $n = 1, 2, \dots$, of poles of $f(\lambda)$ which happen to be singularities of $e^{\lambda t} f(\lambda)$. These occur at poles of $u_2(r,s)$ positioned at s_n values that tend to make $u_2(r,s) \rightarrow \infty$.

First, we examine $u_2(x,s)$ to determine if it has a singularity at $s = 0$. This is done by expanding the hyperbolic functions in terms of series and taking the limit as $s \rightarrow 0$; because the limit has a finite value, there is no singularity at $s = 0$ for Eq. (9c). If a singularity were found, we would attempt to remove it by forming the product $(s - 0)u_2(x,s)$. Successful removal makes the $s = 0$ singular point a simple pole. The limit of the product, as $s \rightarrow 0$, would be the residue of the pole, and also part of our inverted solutions.

Nonzero singularities are found by setting the denominator of Eq. (7c) equal to zero, but first let us write:

$$u_2(x,s) = \frac{p(s)}{q(s)} .$$

and

$$\ell(s/D)^{1/2} = i\alpha .$$

One finds that

$$p(s) = i(a' k f C_1^0) \sin [(\alpha/\ell)(b - r)] . \quad (8)$$

and

$$q(s) = iD \left\{ \left| \frac{a^2}{\ell^2} + \frac{k}{a^2} \right| \sin \alpha + \left| \frac{\alpha k}{a\ell} \right| \cos \alpha \right\}.$$

The imaginary number i will cancel in the ratio, and $q(s)$ will be zero when

$$\cot \alpha_n = \frac{a\alpha_n}{\ell k} - \frac{\ell}{a\alpha_n} = \frac{R\alpha_n}{k} - \frac{1}{R\alpha_n}. \quad (9)$$

Intersection of the cotangent curves and a hyperbola locates the α_n in each $(0, \pi) + \dots + (n\pi) + (n+1)\pi$ interval. At high n , the values approach $n\pi$. Although there is an equivalent set of negative α_n 's, we can only use the positive ones [see Eq. (7)]. There are no repeated α_n values, and all are real. Equation (8) is called the auxiliary equation, and the α_n 's are found to be the roots of our final equations. Since

$$s_n = -\frac{\alpha_n^2 D}{\ell^2}, \quad n = 1, 2, 3, \dots \quad (10)$$

all poles will lie on the negative real axis in the complex s plane. The poles are "simple." In this case, the problem of inversion reduces to the application of:

$$F(t) = \sum_n \frac{p(s_n)}{[dq/ds]_{s_n}} e^{s_n t}. \quad (11)$$

Equation (11) gives a simple recipe for obtaining $U_2(r, t)$. We find $dq/d\alpha$, then dq/ds , and form the series indicated:

$$\frac{dq}{d\alpha} = -\frac{D}{\ell} \left[\left(\frac{a\alpha}{\ell} - \frac{k\alpha}{a} \right) \sin \alpha - \left(\frac{\alpha^2}{\ell} - \frac{k\ell}{a^2} - \frac{k}{a} \right) \cos \alpha \right],$$

$$\frac{dq}{ds} = \left(\frac{d\alpha}{ds} \right) \left(\frac{dq}{d\alpha} \right) = - \left(\frac{\ell^2}{2D\alpha} \right) \left(\frac{dq}{d\alpha} \right),$$

$$\left[\frac{dq}{ds} \right]_{\alpha_n} = \frac{\ell}{2} \left[\left(\frac{2}{\ell} + \frac{k}{a} \right) + \left(\frac{\alpha_n}{\ell} - \frac{k\ell}{\alpha_n a^2} - \frac{k}{\alpha_n a} \right) \left(\frac{a}{k} \right) \left(\frac{\alpha_n}{\ell} - \frac{k\ell}{\alpha_n a^2} \right) \right] \sin \alpha_n.$$

The auxiliary equation, Eq. (9), was used to factor out the $\sin \alpha_n$; for this reason, the subscript n appears on the α 's. Now let $\alpha_n = \alpha'_n \ell$. This is done because we seek a specific form for $(dq/ds)\alpha_n$ which will allow comparisons with other related solutions cataloged by Carslaw and Jaeger.¹¹ From these we can write an identity required in the present problem. Continued manipulations yield:

$$\left[\frac{dq}{ds} \right]_{\alpha'_n} = \frac{a}{2k} \left[\left(\frac{k}{a} + \frac{k^2 \ell}{a^2} + \frac{k^2}{a^3 \alpha_n'^2} \right) + \ell \left(\alpha'_n - \frac{k}{a^2 \alpha_n'} \right)^2 \right] \sin \alpha'_n \ell$$

The final result is obtained when one seeks out the various factors associated with

$$\frac{k^2}{a^2} \cot^2 (\alpha'_n \ell) ,$$

and

$$\left(2 \frac{k}{a} - \frac{k^2}{a^2 \alpha_n'^2} \right) \cot (\alpha'_n \ell) .$$

Thus,

$$\left. \frac{dq}{ds} \right|_{\alpha_n'} = \frac{2k(\alpha_n' \ell) + 4(\alpha_n' a) \sin^2 (\alpha_n' \ell) - k \sin (2\alpha_n' \ell)}{4(\alpha_n' a) \sin (\alpha_n' \ell)} . \quad (12)$$

We define $Q(a, k, \alpha_n', \ell)$ as the numerator of this expression.

A combination of Eqs. (8), (9), and (12), according to Eq. (11), completes the inversion:

$$U_2(r, t) = \sum_n \frac{4a\alpha_n'(a' k f C_1^0) \sin (\alpha_n' \ell) \sin [\alpha_n'(b - r)]}{Q(a, k, \alpha_n' \ell)} e^{-D\alpha_n'^2 t} , \quad (13)$$

where $U_2(r, t) = rC_2(r, t)$.

Expressions for the flux are:

$$J(r, t) = -D \frac{\partial C_2(r, t)}{\partial r} = -\frac{D}{r} \frac{\partial U_2(r, t)}{\partial r} + \frac{D}{r^2} U_2(r, t) .$$

At $r = b$, the last term on the right is zero, and the flux out of the particle is every term in Eq. (13) multiplied by the factor

$$(-D)(-\alpha_n'/b) \cos [\alpha_n'(b - b)] = D\alpha_n'/b .$$

The time-integrated flux is:

$$\int_0^{\bar{t}} J(b, t) dt = \sum_n \frac{4a(a' k f C_1^0) \sin (\alpha_n' \ell)}{b[Q(a, k, \alpha_n' \ell)]} \int_0^{\bar{t}} e^{-D\alpha_n'^2 t} d(D\alpha_n'^2 t) ,$$

and the integral is $(1 - e^{-D\alpha_n'^2 \bar{t}})$.

Consider now the cumulative fractional release written as:

$$FR = \frac{N(b, \bar{t})}{M_1^0} = \frac{N(b, \bar{t})}{V_1 C_1^0} .$$

where

$$N(b, \bar{t}) = 4\pi b^2 \int_0^{\bar{t}} J(b, t) dt$$

If one recalls that $a' = V_1/4\pi a^2$, the following equation can be obtained by appropriate substitutions and manipulations:

$$\frac{FR}{f} = \frac{4kb}{a} \sum_n \frac{(1 - e^{-D\alpha_n^2 \bar{t}}) \sin(\alpha_n' \ell)}{Q(a, k, \alpha_n' \ell)} \quad (14a)$$

Eq. (14a) can be expressed as two series: one without, and one with, an exponential term. With the aid of another solution given by Carslaw and Jaeger,^{1,2} it can be shown that the first series corresponding to $t = 0$ converges to unity. Thus, with $\alpha_n = \alpha_n' \ell$,

$$\frac{FR}{f} = 1 - \frac{4kb}{a} \sum_n \frac{e^{-\alpha_n^2 T} \sin \alpha_n}{[2k\alpha_n + (4a\alpha_n/\ell) \sin^2 \alpha_n - k \sin 2\alpha_n]} \quad (14b)$$

where

$$T = \frac{D\bar{t}}{(b-a)^2}, \quad k = \frac{a}{a'\phi} = \frac{3}{\phi}.$$

and α_n are the positive roots of

$$\cot \alpha_n = \frac{a\alpha_n}{k(b-a)} - \frac{(b-a)}{a\alpha_n}; \quad n = 1, 2, 3, \dots$$

3.1.2 Linear Flow in Slab Geometry

In view of the complexities of Eq. (14b), we explore the possibility of approximating radial flow with linear flow equations. The same initial and boundary conditions that were used previously will be applied here. The distinguishing feature is that we will pretend that $A(r)$ can be represented by a position constant average of $4\pi ab$. Then the "U" substitution can be eliminated, and one may write

$$D \frac{\partial^2 C_2}{\partial x^2} = \frac{\partial C_2}{\partial t}$$

Initial conditions:

$$C_1^*(0) = fC_1^0, \quad C_2(x, +0) = 0.$$

Boundary conditions:

$$C_2(b, t) = 0, \quad \phi C_2(a, t) = C_1^*(a, t).$$

and

$$\frac{\partial C_1^*(t)}{\partial t} = \frac{DA}{V} \frac{\partial C_2(a,t)}{\partial x}.$$

The procedure is exactly the same as outlined in Sect. 3.1.1. One obtains the transformed equation:

$$c_2(x,s) = \frac{ifC_1^0 \sin [\alpha/\ell(b-x)]}{\frac{i\phi D}{\ell} \left(\frac{\alpha^2}{\ell} \sin \alpha + h \cos \alpha \right)},$$

where $h = A/V\phi$.

The inverse is:

$$C_2(x,t) = \sum_n \frac{2hfC_1^0 e^{-D\alpha_n'^2 t} \sin [\alpha_n'(b-x)]}{\phi[\ell(\alpha_n'^2 + h^2) + h] \sin(\alpha_n' \ell)}. \quad (15)$$

A form of this kind is given by Carslaw and Jaeger.^{1,3} Converting to the flux and then integrating with respect to time gives:

$$\frac{FR}{\dot{q}} = 1 - \sum_n \frac{2he^{-D\alpha_n'^2 t}}{[\ell(\alpha_n'^2 + h^2) + h] \cos(\alpha_n' \ell)}. \quad (16)$$

Let $\alpha_n = \alpha_n' \ell$, $L = \ell h$, and $T = Dt/\ell^2$. Then Eq. (15) evaluated at $x = b$ can be written as:

$$\frac{C_1^*(a,t)}{C_1^*(0)} = \sum_n \frac{2Le^{-\alpha_n^2 T}}{[L(L+1) + \alpha_n^2]} = 1 - f_1(L,T). \quad (16a)$$

and

$$\frac{FR}{\dot{q}} = 1 - \sum_n \frac{2L(\sec \alpha_n) e^{-\alpha_n^2 T}}{[L(L+1) + \alpha_n^2]} = f_2(L,T). \quad (16b)$$

The α_n here are roots of:

$$\alpha_n \tan \alpha_n = L, \quad n = 1, 2, 3, \dots \quad (17)$$

A detailed derivation of Eq. (16b) is given by Raines *et al.*⁵ The $f(L,T)$ functions are discussed by Jaeger and Clarke^{1,4} and Carslaw and Jaeger.^{1,5}

3.1.3 Discussion

Inspection of the release relationships Eqs. (14b) and (16b) reveals that very little can be done regarding correlation of depletion data in the absence of an f value. All apparent fractional release values must be divided by f because the model is based on the fraction of mobile cesium initially present - not the total value. This adjustment tends to steepen the original curve in such a way that terminal values will approach unity in compliance with the $T \rightarrow \infty$ limit of the derived release functions. In many cases, the problem relates to conservation of experimental time; it is not feasible to run experiments for long times just to obtain f . The best approach for obtaining an accelerated determination would be to crack the particle, remove the coating, and anneal the remaining components at the temperature of interest. However, it may be possible to estimate f if the curves account for about half the mobile amount. Of course, this procedure is somewhat complicated because one must couple this estimate with estimates for L or k and D .

Plots of the two functions under discussion are shown in Fig. 4. For sample calculations covering the spherical case, it was necessary to select a particular R representing an average collection of particles. Considerations of a different collection would require another R value and computations of a *complete* new set of curves giving FR as a function of Dt/ℓ^2 at various k values. In the linear flow case, one set of curves is adequate. The objective of presenting the plots in Fig. 4 was to provide some indication as to the shapes of the curves on an FR -vs- $\log T$ basis, and also to demonstrate how effectively spherical results can be approximated with linear results. It is only necessary to select a set of L values which will correspond to the various k values. If we take $A = 4\pi ab$ in the expression for L , then

$$L = \frac{\ell A}{V\phi} = \frac{(b-a)(4\pi ab)}{\phi(4/3)\pi a^3} = \frac{3(b-a)b}{\phi a^2} = \frac{b(b-a)k}{a^2},$$

where $\phi = 3/k$.

What we have actually done is to "smear" the source volume out over an average area to define an effective source depth, and then to postulate that ϕ is the same in each system. Of course, if we start discussing concentration profiles, the problem should be approached in another way. The above result is adequate, however, for a rough correlation of release data. Figure 5 shows a plot of the curves in rectangular coordinates. Figure 6 gives a plot of Eq. (15), demonstrating the high initial source zone depletion rates. For example, at $L = 1.0$ and $T = 0.4$, the source zone has lost 46% of its initial active concentration [Fig. 6] the corrected release at $r = b$ is only 16% [Fig. 5].

Brief descriptions of the curve fitting and parameter extraction procedures are in order. We assume that the final measured cumulative release is high enough to permit at least a "ball park" estimate of f . If an estimate of maximum saturation concentration of the fission product in the coating of interest is also available, the constant-potential correlations (given in the next section) should be employed to ensure that this value was not exceeded during the experiment being analyzed. With the assurance that constant-potential behavior did not intrude into the results, one may correct the data to give FR/f values and plot these as a function of $\log$ [real time, t]. The experimental semilog plots can be lined up with theoretical semilog plots [see Fig. 4 - dotted curves] by parallel translations of the t and T axes. At this point, tentative values of f , D , and L may be selected. We assume that the data have already been plotted on rectangular paper and that an average slope, m , and t_0 have been determined. From the curves in Fig. 5, one may obtain a T_0 -vs- L^{-1} curve and an m' -(theoretical slopes)-vs- L^{-1} curve. All this information, along with the relationship

$$m = (Df/\ell^2)m',$$

Fig. 4. Depletion curves Predicted on the Basis of Equations (14b) and (16b). Curves show the relationships between FR (through the coating), T , and k or L (actually ϕ) for spherical and linear flow geometries when the cesium concentration in the coating nearest the source decreases continuously with time.

can be juggled about to establish final values. Later, these can be checked against the original semilog plots.

To summarize, we need to evaluate three parameters or unknowns, and unless we have three pieces of curve information that are equivalent to three equations, this procedure will degenerate to a bootstrap engineering exercise. The most effective approach is to measure f separately. We now consider cases where release does not depend on f and either ϕ or L values — in other words, cases where the source potential is so high that the coating next to the source becomes saturated and maintains a time-constant concentration.

Fig. 5. Shapes of the Linear Depletion Curves of Figure 4 When Plotted on Rectangular Coordinates. Each constant L curve has a different T_0 intercept, which means that a different constant must be used to evaluate D in terms of breakthrough time, t_0 .

3.2 Constant Potential at the Source Boundary

3.2.1 The Complete Solution

A rather general approach will be employed here in that the equations will be developed using the assumption that an external mass transfer film, or an evaporation coefficient, is operating at the outer boundary at $r = b$. The possible influence of film effects cannot be ignored. We have collected limited data which suggest that films are of importance in strontium transport, and we have no evidence that they are absent in CRNL cesium release experiments.* It develops that the effects of film resistances, actually admittances, cannot be detected in the results from a typical release experiment, even in the initial transient regime.

*Note added in proof: Actually, we are not concerned here with films or evaporation coefficients associated with high-pressure laminar flow or low-pressure Knudsen flow, *per se*. Rather, we anticipate that contributions of sacrificial layers or partition coefficients at $r = b$ might be treated in terms of a film analog.

Fig. 6. Depletion of the Source Region When Equation (16b) Describes Overall Particle Release.

Again we shall adopt equations, as described by Jaeger and Clarke,¹⁴ in linear flow coordinates. These will be adequate for present purposes. It should be noted that the solutions for the limiting case where $L' = \ell h'/D \rightarrow \infty$, h' being the film coefficient, are identical for both spherical and linear systems. The only difference is that one must employ $A = 4\pi ab$ in the spherical case.

Two assumptions are made: (1) that the potential at $r = a$ will remain constant long enough to establish a reasonable period of steady-state release, and (2) that the coating did not take up cesium during irradiation. Thus, we have the initial condition

$$C_2(x,0) = 0, \quad a < x \leq b, \quad (18)$$

with the following boundary conditions:

$$C_2(a,t) = C_0, \quad t > 0; \quad c_2(a,s) = C_0/s, \quad (19)$$

and

$$DA \frac{\partial C_2(b,t)}{\partial x} = h'A [C_2(b,t) - 0] . \quad (20a)$$

which can also be written in transformed x - s space as

$$\frac{dc_2(x,s)}{dx} = -Hc_2(b,s) . \quad (20b)$$

and

$$H = \frac{h'}{D} . \quad (21)$$

These conditions apply to:

$$D \frac{\partial^2 C_2(x,t)}{\partial x^2} = \frac{\partial C_2(x,t)}{\partial t} . \quad (22a)$$

or

$$sc_2(x,s) - C_2(x,0) = D \frac{d^2 c_2(x,s)}{dx^2} . \quad (22b)$$

We now move the origin to position $r = a$, let $b = \ell$, and eliminate the subscript 2. A solution to Eq. (21) that satisfies all conditions is:

$$c(x,s) = \frac{C_0}{s} - \frac{C_0 H \sinh x(s/D)^{1/2}}{s[(s/D)^{1/2} \cosh \ell(s/D)^{1/2} + H \sinh \ell(s/D)^{1/2}]} . \quad (23a)$$

There are three parts to the solution: the inverse of the first term, $C_0/s \rightarrow C_0$; the residue of the simple pole at $s = 0$ from the second term, which we call $\zeta(x,s)$; and a series of residues from $\zeta(x,s)$ for nonzero singularities. The $s = 0$ residue is:

$$\lim_{s \rightarrow 0} s \zeta(x,s) = - \frac{C_0 H x}{1 + H \ell} .$$

The first two parts give:

$$C_0 \left[1 - \frac{Hx}{1 + H\ell} \right] = C_0 \left[\frac{1 + L'(1 - x/\ell)}{1 + L'} \right] ;$$

this is the steady-state solution with $L' = \ell H$. Only $s = 0$ contributions of $\zeta(x,s)$ have been accounted for; the remainder of the problem is to take the inverse of $\zeta(x,s)$ (with the $1/s$ still in). If we let

$$\ell(D)^{1/2} = \beta.$$

one eventually finds that

$$C(x,t) = C_0 \left[\frac{1 + L'(1 - x/\ell)}{1 + L'} \right] \sum_n \frac{2(\beta_n^2 + L'^2) e^{-\beta_n^2 T} \sin(\beta_n x/\ell)}{\beta_n [L' + L'^2 + \beta_n^2]}. \quad (23b)$$

with an auxiliary equation that gives the β_n positive roots, $n = 1, 2, 3, \dots$, as follows:

$$\beta_n \cot \beta_n + L' = 0. \quad (24)$$

with

$$L' = \ell H = \ell h'/D.$$

3.2.2 General Release Equation

The result obtained by Jaeger and Clarke,¹⁴ when the above is manipulated to form the flux at $x = \ell$ and integrated to obtain the cumulative release, was:

$$\frac{N_1(b,t)}{C_0 A \ell} = \frac{L' T}{1 + L'} \cdot \frac{L'(L' + 3)}{6(L' + 1)^2} \cdot \left[1 + \sum_n \frac{(12)L'(L' + 1)^2 e^{-\beta_n^2 T} \sec \beta_n}{(L' + 3)[L'(L' + 1) + \beta_n^2]} \right]. \quad (23c)$$

Everything inside the bracket was defined simply as $\varphi_4(L', T)$. The latter approaches unity within a reasonable fraction of experimental diffusion t , or theoretical reduced time, T (see Fig. 7). Thus the difference of the second term in Eq. (23c) vanishes, and one obtains:

$$\Delta[N_1(b,t)] = A \ell \left[\frac{L' \Delta T}{1 + L'} \right] C_0 = \frac{(A \ell)(\ell h'/D)(D \Delta t/\ell^2) C_0}{(1 + \ell h'/D)},$$

and

$$\frac{\Delta N_1(b,t)}{\Delta t} = A C_0 \left[\frac{1}{h'} + \frac{\ell}{D} \right]^{-1}.$$

This is the steady-state flow equation with both film and diffusion coefficients contributing. If everything but C_0 is known, and

$$\frac{\Delta N_1(b,t)}{\Delta t} = M_1^0 \frac{\Delta(FR)}{\Delta t} = M_1^0 m,$$

where m is the slope of the fractional release curve, then

$$C_0 = \frac{M_1^0 m}{A} \left[\frac{1}{h'} + \frac{\ell}{D} \right] = \frac{M_1^0 m}{A \ell} \left[\frac{1 + L'}{L'} \right] \frac{\ell^2}{D}. \quad (25)$$

Fig. 7. Functions That Govern Approach to Steady-State Constant-Potential Release. These transient curves show release as a function of reduced time for various reduced ratios of the film coefficient to diffusion coefficient.

We shall now temporarily depart from this discussion to consider extrapolation of the $y = N_1(b,t)/C_0 A \ell$ function, at T values corresponding to steady-state operation, back to $y = 0$ with $\phi_4(L',T) = 1$. Thus

$$\frac{L'T_0}{1+L'} = \frac{L'(L'+3)}{6(L'+L')^2}; \quad T_0 = \frac{1}{6} \left(\frac{L'+3}{L'+1} \right) = \frac{Dt_0}{\ell^2}. \quad (26)$$

and

$$\frac{N_1(b,t)}{C_0 A \ell} = \left(\frac{L'}{1+L'} \right) T - \left(\frac{L'}{1+L'} \right) T_0 \phi_4(L',T). \quad (23d)$$

Substitution of Eq. (25), Eq. (26), and the definition $T = Dt/\ell^2$ into Eq. (23d):

$$FR(t) = mt - mt_0 |\varphi_4(L', T)|, \quad (27a)$$

which states an interesting result. So long as C_0 is independent of time, all experimental release curves obtained with a time constant C_0 have the same general shape with or without film effects. They consist of a straight line originating at a maximum lag time, t_0 , with dispersion effects characterized by premature breakthrough in degrees determined by $\varphi_4(L', T)$.

3.2.3 Diffusion Control – No Film

At this limit, h' (and thus L') approaches infinity. Then, using Eqs. (25) and (26), one can show that

$$T_0 \rightarrow \frac{1}{6}$$

and

$$C_0 \rightarrow \frac{M_1^0 m \ell}{AD} = \frac{M_1^0 m b t_0}{A \ell^2}.$$

Equations (23d) and (27a) become:

$$\frac{N_1(b, t)}{C_0 A \ell} = T - \frac{1}{6} \varphi_4(\infty, T). \quad (23e)$$

and

$$FR(t) = mt - mt_0 [\varphi_4(\infty, T)]. \quad (27b)$$

The transient parameter φ_4 approaches the well-known series form obtained from the specialized D controlling derivation outlined by Crank.¹⁶ One finds that

$$\varphi_4(\infty, T) = 1 + \frac{12}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp(-n^2 \pi^2 T),$$

as specified in Fig. 7.

We have found that the normalized relationship, Eq. (23e), is very convenient for presenting results of several related experiments on a single plot. Figure 8 illustrates the shape of this curve, along with that of a "typical" experimental curve that would result if $t_0 = 500$ hr and $m = 1.5 \times 10^{-5}$ /hr. From the intercept, one obtains the diffusion coefficient using

$$D = \frac{1}{6} \frac{\ell^2}{t_0}.$$

Fig. 8. Normalized and Experimental Release Curves During Approach to Steady State. These curves show transient effects as they appear on rectangular coordinates for a constant-potential system with no film effects.

From the slope, one obtains the driving potential using

$$C_0 = \frac{M_1^0 m \ell t_0}{A \ell}$$

where $A = 4\pi r^2$ in spherical coordinates. A knowledge of r is not required to use these relationships. If it were known and applied in the C_0 expression in the proper fashion, it would simply cancel out.

3.2.4 Diffusion with Film Effects

It is of interest to consider (1) how film effects might influence the shape of an experimental release curve, and (2) the degrees of uncertainties in C_0 and D introduced by ignoring their possible presence. We shall assume that film measurements are available, but not to the investigator correlating release data. For discussion, we consider three cases: (1) a total concentration decrease occurs across the medium (no film); (2) $\frac{2}{3} C_0$ across the medium; $\frac{1}{3} C_0$ across a film; and (3) $\frac{1}{3} C_0$ across the medium, $\frac{2}{3} C_0$ across a film. Respective L' values would be ∞ , 2, and $\frac{1}{2}$. Plots of the normalized release prepared on the basis of Eq. (23d) and the interpolated φ_4 values from Fig. 7 are shown at the top of Fig. 9. Each L' case has a separate and distinct normalized plot, ultimate slope, and T_0 intercept value.

Next, a predicted experimental curve for each case was computed using the same information and Eq. (27a). One may see the results at the bottom of Fig. 9. Computed release-vs-time values for all cases fell precisely on the same curve. (Only at very low L' values would some effects be seen.) The unwary experimenter would have no knowledge that a film was influencing his results; he would simply proceed under the assumption that $L' \rightarrow \infty$ and would compute $(C_0)_{app}$ and D^* values accordingly. Errors in D would be gross, as indicated by Eq. (26). For $L' = 2$ and $\frac{1}{2}$, the true D should have been $5D^*/3$ and $7D^*/3$. However, even with the wrong value for D , estimates of C_0 would be quite acceptable since with an approximate $D^* = (\ell^2/6t_0)$,

$$C_0 = \frac{M_1^0 m \ell (L' + 1)^2}{A D^* L' (L' + 3)} = \frac{(C_0)_{app} (L' + 1)^2}{L' (L' + 3)}$$

Thus, at $L' = 2$ and $\frac{1}{2}$, C_0 would be $9C_0^*/10$ and $9C_0^*/7$. In fact, if $L' = 1$, $C_0 = C_0^*$. We conclude that film effects must be determined by direct measurement of concentration profiles, however, even in the absence of such information, good estimates of C_0 can be obtained assuming $L' \rightarrow \infty$.

3.2.5 Approximation of Depletion Curves

In many cases, the diffusion-controlled constant-potential correlation is applied to experimental curves that evidence depletion effects at terminal regions of the time scale investigated. Some question arises as to the interpretations of D and C_0 thus obtained. That is, if depletion were indeed occurring throughout the experiment, would these parameters have physical significance? Now, a theoretical slope m' and diffusion coefficient D' may be acquired from Fig. 5 at a given L . A relationship between the theoretical and approximate slopes, m' and m respectively, is:

$$m = (f T_0'/t_0) m'$$

Fig. 9. Effect of Films on Normalized and Experimental Release Curves. Although normalized curves are drastically different, the experimental curves would be nearly identical.

The constant-potential correlation gives:

$$C_0 = \frac{fM_1^0 m'}{A\ell} \frac{T_0'}{T_0}$$

where

$$T_0 = 1/6, \text{ and } T_0' \text{ is taken from Fig. 5.}$$

The true nonconstant potential is obtained from Fig. 6:

$$C_2(a,t) = \left[\frac{C_1^*(t)}{C_1^*(0)} \right] \frac{fM_1^0}{V_1\phi} = \left[\frac{C_1^*(t)}{C_1^*(0)} \right] \frac{fM_1^0 L}{A\ell}$$

since

$$\phi = A\ell/V_1 L.$$

The ratio between the approximate C_0 and $C_2(a,t)$ is:

$$\frac{C_0}{C_2(a,t)} = \frac{T_0' m'}{T_0 L} \left[\frac{C_1^*(0)}{C_1^*(t)} \right]$$

All parameters here are "theoretical." With this formula, it can be shown that the C_0 estimate is, in fact, a good approximation of the true $C_2(a,t)$ prevailing at the time m was evaluated. The true coefficients range from $(0.6)D^*$ to D^* , where the latter is derived from the $1/6$ approximation.

3.3 Depletion After Constant-Potential Operation

3.3.1 Linear Flow Solution

The approach and techniques used here are quite similar to those used for the depletion relationships derived in Sect. 3.1 – except that the initial conditions are modified. Here we take t' as the new time scale. The new zero time is selected at the point at which the release data show a distinct departure from "straight-line behavior."

The initial conditions are:

$$C_1(0) = C_1^*(\tau), \quad C_2(a,0) = C_2(\tau), \quad (28)$$

and

$$C_2(x,0) = C_2(\tau) [(b-x)/\ell] \quad (29)$$

The symbol τ is a point in old time corresponding to $t'_0 = 0$. If the total release up to τ has been measured, the active amount in the source zone can be computed with a knowledge of f and the steady-state coating content.

The boundary conditions, in transformed coordinates, are:

$$c_2(b,s) = 0, \quad (30)$$

$$c_1^*(s) = \phi c_2(a,s), \quad (31)$$

and

$$sc_1^*(a,s) - C_1(+0) = (DA/V_1) \frac{dc_2(a,s)}{dx}. \quad (32)$$

Application of all the above to

$$sc_2(x,s) - C_2(x,+0) = D \frac{d^2 c_2(x,s)}{dx^2}$$

yields:

$$c_2(x,s) = \frac{C_2(\tau)[b-x]}{s\ell} - \frac{hDC_2(\tau) \sinh[(b-x)(s/D)^{1/2}]}{s\ell \{s \sinh[\ell(s/D)^{1/2}] + h(sD)^{1/2} \cosh[\ell(s/D)^{1/2}]\}},$$

where

$$h = A/V_1\phi = l/a'\phi.$$

The inverse of the first term is canceled out by the inverse of the $s = 0$ pole of the second term. The answer comes from setting

$$i\alpha/\ell = (s/D)^{1/2}$$

and evaluating the complete second term, as dictated by Eq. (11). The result is:

$$C_2(x,t) = C_2(\tau) \sum_{n=1}^{\infty} \frac{2L^2 e^{-\alpha_n^2 \tau} \sin[\alpha_n(b-x)/\ell]}{\alpha_n^2 [L(L+1) + \alpha_n^2] \sin \alpha_n}, \quad (33a)$$

where α_n , $n = 1, 2, 3, \dots$ are the positive roots of

$$\alpha_n \tan \alpha_n = L$$

and

$$L = \ell h = \frac{\ell A}{V_1 \phi}.$$

when $x = b$, $C_2(x,t) = 0$, as it should. When $x = a$,

$$\frac{C_2(a,t)}{C_2(\tau)} = \frac{C_1^*(t)}{C_1^*(\tau)} = \sum_n \frac{2L^2 e^{-\alpha_n^2 T}}{\alpha_n^2 [L(L+1) + \alpha_n^2]} = f_3(L,T). \quad (33b)$$

Formation of the flux at b, followed by integration, gives:

$$N(b,t) = \sum_n A \frac{q^2}{D\alpha_n^2} \frac{2hDC_2(\tau)(1 - e^{-\alpha_n^2 T})}{[(h\ell)^2 + (h\ell) + \alpha_n^2] \cos \alpha_n}. \quad (34)$$

Development of the proper fractional release expression for times greater than τ requires a special base value that includes both source and coating contents. We recall that $h = 1/a'\phi$. Then,

$$\begin{aligned} \text{Total active content} &= [\text{content (kernel + buffer)}] + [\text{content (coating)}], \\ &= C [\text{area of a box} + \text{area of a triangle}], \\ &= aAC_1^*(\tau) + \frac{A}{2} \ell C_2(\tau), \\ &= AC_1^*(\tau) \left[a' + \frac{\ell}{2\phi} \right] = \frac{AC_1^*(\tau)}{\phi} \left[\frac{2 + \ell h}{2h} \right], \\ &= \frac{AC_2(\tau)}{h} \left[\frac{2 + \ell h}{2} \right]. \end{aligned}$$

The ratio of $N(b,t)$ to the above is:

$$FR|_{\tau} = 1 - \sum_n \frac{4L^2(1 - e^{-\alpha_n^2 T}) \sec \alpha_n}{(L+2)\alpha_n^2 [L(L+1) + \alpha_n^2]}, \quad (35a)$$

or

$$FR|_{\tau} = f_4(L,T). \quad (35b)$$

Again, we encounter functions covered by Carslaw,¹⁵ Jaeger,^{14,15} and Clarke.¹⁴ It should be understood that the fraction-remaining function here in terms of measured $FR(t)$ is:

$$FR|_{\tau} = \frac{FR(t') - FR(t'_0)}{FR(\infty) - FR(t'_0)}.$$

3.3.2 Discussion

Generalized curves for this function are shown in Fig. 10, where T is plotted on an exponential basis. Figure 11 shows the results of transposing these curves to rectangular coordinates. In many ways, the curves reflect the same characteristics of those in Figs. 4 and 5. However, there is one important exception. All curves in Fig. 11 proceed directly toward the origin. There is no "delay time" because the coating has been "preconditioned" with a steady profile at time $t'_0 = \tau$.

Fig. 10. Depletion Curves Associated with Equation (35b). The release function represents behavior anticipated for Region C, Figure 1, when the coating concentration starts to decrease after a period of constant-potential operation.

In an effort to evaluate these results, we have fitted Eq. (35b) to the most controversial data at hand, namely, those of Curve I, Fig. 1. The results are presented in Fig. 12. As seen, there is a "right" intercept at about 17 hr which agrees with the bulk of our data in that a coefficient derived in this manner is acceptably high. On the other hand, some event occurring at about 75 hr caused the curve to rise in an inexplicable fashion at a very high rate. Present speculations attribute this strange behavior to an internal failure of the kernel; for example, an appreciable portion of the trapped fraction may have broken free at 75 hr, impinging a new, higher driving force on the system. The coating did not fail because noble gas retention was maintained.

Fig. 11. Shapes of Release Functions of Figure 10 When Plotted on Rectangular Coordinates. All curves pass through the origin.

Clearly, the system was not at constant potential, but it was subject to an initial profile when depletion took over. We arbitrarily set this time at 195 hr, then fitted Eq. (35b) to the remainder of the curve. To obtain the fit, it was necessary to assume that D corresponded to 45 hr and $L \rightarrow \infty$. The decay in this case seems to follow a special "thin-layer" depletion characterized by a zero-source concentration. Rough back-calculations suggest that the source zone became depleted of cesium somewhere between 100 and 200 hr. In any event, Eq. (35b) does give a description of an ultimate decay mode.

4. AUXILIARY DETERMINATIONS

4.1 Experiments with Separated Particle Components

We have mentioned the importance of performing anneals with bare kernels in order to obtain rapid measurements of f for correlation of release data from intact coated particles in depletion modes. Use of this approach presumes that all trapping effects occur in the oxide; it also implies that kernels can be removed intact from cracked particles. There may be considerable merit in proposing attempts to separate all three components — kernel, buffer, and coating — for rough determination of overall fission product distributions. One might also perform individual anneals to assay relative retention characteristics. At least, these anneals would pinpoint the region where permanent trapping occurs.

Fig. 12. Application of Equation (35b) to Region C, Curve 1, Figure 1.

Information sought here would not be of the nature of "fine structure" but would consist of good average values to clarify major experimental features such as the controlling modes of release at the time the particles were cracked. For example, if coatings of particles sampled at different times during an anneal experiment had the same fission product contents, a constant-potential mode would be verified.

Unfortunately, component separation is a very tedious procedure, its success depending on the relative hardness of the components and the degree to which they are bonded together at room temperature. Kernels are the most easily extracted. If buffer material adheres to the kernel, it can be removed with mild abrasive action. Separation of buffer and coating is the most difficult operation of all. In addition, there is the problem of recovering all debris to obtain suitable aliquots. In most cases, the only recourse is to attempt layer-by-layer removal of the coating until the buffer-coating interface is approached. For this and other reasons, we must concede the necessity of grinding coatings.

4.2 Concentration Profiles by Grinding

Nearly all the classical "solid-state" diffusion experiments are arranged such that one or two species (in compatible substrates) will mix in a predictable fashion as reflected by the shape of concentration profiles in the substrates. All volatile species represent special cases requiring special techniques. However, most solid-state studies are concerned with slow-moving nonvolatile species. If, for example, one desires to make

self-diffusion measurements of radioactive silver in polycrystalline silver, an experiment can be devised as follows: A very thin layer of tracer is placed on the substrate (as a Dirac delta function); the substrate is then annealed at various temperatures to form decay patterns [given by $C(x, \bar{t})$, $\bar{t}$ fixed]; and, finally, the patterns are fitted to the function

$$\frac{C(x, \bar{t})}{C(0, \bar{t})} = \exp \left(-\frac{x^2}{4D\bar{t}} \right).$$

The log of activity (proportional to the concentration ratio) is plotted vs x^2 to evaluate D , which is proportional to the slope of the curve. The ultimate objective is to obtain D 's at several temperatures, plot these as a function of $(T^\circ K)^{-1}$, and make some observations concerning the slope of this curve – since it represents an activation energy. While this is an acceptable goal, our overall problem is quite different and much more complicated. We cannot arrange cesium experiments to fit the silver pattern if we have high cesium concentrations in the source and measure vapor evolution at $r = b$. But solid-state theoreticians feel comforted if such data are available. Let us evaluate the utility of grinding data as it will apply to our experiments. It should be noted here that results of an exhaustive study based on profile shapes have been reported by Baumann.¹⁷

We consider any particles that are removed from an anneal to be in a depleting mode. Unless they are obtained during the very initial stages of the anneal, corresponding profiles will show only rather indifferent variations in curvature as influenced by "smeared-out" contributions of several variables. They will not display the clear-cut (maximum) transient behavior characteristic of the silver experiments. To assure ourselves that this would be the case, concentration functions for the depletion cases were manipulated to form integrated grinding equations which give the cumulative amount removed after grinding from b to r . The analytical results are too complex to present here; however, a glance at the results reveals that the shape of release curves – not the shapes of grinding curves – would provide the best means for estimating D and ϕ . Aside from rough verification by profile shapes, ϕ might best be determined by performing a straightforward extrapolation of profiles to $r = a$ in order to estimate $C(a)$, and then combining this information with concentration measurements in the source to determine ϕ directly.

Of course, profile information might be employed in an auxiliary role, particularly when the effects are hidden in the release data. One example is determination or verification of initial conditions; another is detection of elusive boundary conditions as epitomized by film effects. We consider the latter. The most suitable specimens for a study of this type would be found in a release experiment operating in the constant-potential mode with demonstrated steady-state release. Under these conditions, a fair estimate of C_0 can be made even if D (from lag time) is in error. Regardless of D , the general steady-state implies that:

$$JA = N'(t, \text{all } r) = (A) C_a \left(\frac{h'}{L' + 1} \right).$$

The prime on N denotes dN/dt , which is constant in this case.

There are two decreases in concentration: one between $r = a$ and b , and a second (to zero) between $r = b$ and $b + \delta$, where δ is quite small. If we can evaluate the extent of the first decrease, we can calculate the second and determine h' . Over the region of the first decrease, one may express the rate in differential form as:

$$N'(t) = -4\pi r^2 D \frac{dC}{dr}.$$

Integration gives:

$$C(r) = C_a - \left(\frac{1}{a} - \frac{1}{r} \right) \frac{N'(t)}{4\pi D},$$

or

$$N'(t) = \frac{D(4\pi ab)(C_b - C_a)}{(b - a)} = \frac{D(A)\Delta C}{\ell}.$$

Thus,

$$C(r) = \left[C_a - \frac{b\Delta C}{\ell} \right] + \left[\frac{ab\Delta C}{\ell} \right] \frac{1}{r}.$$

This is the profile expression that we have alluded to all through this discussion, as if we had at our disposal some undisclosed means for measuring point concentrations directly. Of course, such means are actually available (e.g., microprobes). Yet, these frequently give too much detail (see jagged line in Fig. 2), and the problem of tying in absolute values to scans is left to the investigator as an expensive calibration exercise. Another profile expression in spherical coordinates may be derived from Eq. (13).

If grinding information is available, one can "estimate" profiles by dividing the count data of an increment by the average increment volume; unfortunately, however, the "tying in" problem remains. It becomes necessary to accept the fact that integrated quantities must eventually be used, although estimated profiles are obviously useful in a general sense.

We write an equation for the amount removed after grinding volumes ΔV away from $r = b$ back to any r between b and a , as follows:

$$\int_{V_r}^{V_b} C(r) dV = \left[C_a - \frac{b\Delta C}{\ell} \right] (V_b - V_r) + \frac{(A)\Delta C}{2\ell} (b^2 - r^2),$$

where $(A) = 4\pi ab$. Now if we let $V_r = V_a$, the integral represents the correct (VC) area under the entire profile. This corresponds to the cumulative count of the coating. Finally, we form the fraction of total removed, let $\Delta C = \gamma C_a$, and draw up a set of these curves as a function of γ . Comparisons of the experimental fractional curves with computed values should give γ if C_a is known. Thus C_b and, in turn, the value of h' , can be determined.

Some predicted experimental curves involving profile information, as discussed above, are shown in Fig. 13. Both linear flow in slab geometry and radial flow in spherical coordinates have been covered. There are significant differences in the two sets of curves due to the difference in the geometry of the flow pattern. The concentration profiles are shown at the top of Fig. 13. Those for slab geometry are straight, while those for spherical geometry are concave (except where $\gamma = 0$) and fall below the linear curves. The curves for the fraction removed are shown at the bottom of Fig. 13. The curves for the linear system are concave (except where $\gamma = 0$), while curves in the spherical system are both concave and convex. Neither set of fraction-remaining curves provide much detail since the lines fall close together in the range $\gamma = 0$ to 1.

Since experimental grinding data may be somewhat scattered, it would seem most practical to smooth the data by plotting the fraction removed vs coating thickness and then to differentiate and obtain the concentration ratios for comparison with theoretical curves to determine γ .

Fig. 13. Concentration and Fraction Removed as a Function of Fractional Coating Thickness During Constant-Potential Release. Curves for both linear and radial (spherical) systems are shown to illustrate effects of films [see Fig. 9].

4.3 Summary

Separation of components of coated particles with subsequent analyses will provide cesium inventories which will aid in the interpretation of release data and grinding results. The separated components may then be annealed as a rapid method of determining f , the available fraction of cesium. Kernels recovered from grinding operations may also be annealed to determine f .

The auxiliary grinding experiments are considered useful to obtain gross internal detail to complement the release experiments, particularly to explore the effects of films. Grinding is the only method by which information on films may be obtained. In the event that grinding techniques can be refined to provide sufficient detail to give meaningful results, they should be presented in terms of concentration profiles obtained by graphically differentiating the integral curves. Correlations must be carried out with equations developed in terms of spherical geometry. Only the release data may be compared with solutions obtained from slab geometry.

5. CLOSURE

Diffusion equations applicable to the release of cesium from pyrocarbon-coated fuel particles were reviewed and/or derived relative to possible initial and boundary conditions which might exist in postirradiation annealing experiments. Limited evidence is presented to show that buffer and kernel regions may be grouped together as one source region for the purpose of simplifying the calculations. Equations for diffusion governed by constant potential, by depleting potential, and by a hybrid situation involving both conditions were considered.

Since diffusion equations for a depleting potential in spherical geometry are exceedingly complex, solutions were compared with similar, simpler equations for slab geometry with dimensional parameters adjusted to correlate with spherical dimensions. Results were shown to be sufficiently equivalent so that linear equations may be used in calculations of release, but significant differences were noted in calculations of concentration profiles for linear and spherical systems, applicable to grinding experiments.

Experimental evidence was presented to show that some cesium is permanently trapped in the kernel. The trapped fraction has no effect on the release when a constant potential is maintained but must be considered when the driving potential is changing (e.g., depleting potential).

The breakthrough time (for cesium to penetrate the coating) determined from the intercept of the linear part of a release-vs-time plot of a constant-potential experiment is used to calculate the diffusion coefficient, D . It was shown that breakthrough times determined from intercepts of near-linear portions of curves in depleting potential experiments, if used in the constant-potential relation, $D = l^2/6t$, would provide close approximate values of D .

It was found that film effects are not apparent in release experiments; the film coefficient and the diffusion coefficient may be combined in an apparent L^* . Separate values can be obtained only from concentration profile experiments. Release data may be used to calculate the apparent diffusion coefficient, D^* ; the trapped fraction, $(1 - f)$; the driving potential, $C_2(a)$; and the partition coefficient, ϕ . Accurate values of D^* and $C_2(a)$ are obtained only from constant-potential experiments. Depleting-potential curves are required to obtain ϕ , and will also furnish approximate D^* values and an average $C_2(a, t)$. The available fraction, f , must also be known in order to calculate ϕ . When the time required to exhaust the source is excessive, f and ϕ may be obtained from depleting potential experiments by manipulating the values of f and ϕ to obtain a fit with calculated curves; however, the experimental curve of release vs time must include at least the beginning of the second break of the S-shaped curve. A better approach would be to obtain f by annealing bare kernels and then use this information, along with the release curve, to compute ϕ .

Finally, we note that the depleting potential implies a limited source and, therefore, would be most applicable to coated particles with low burnup. The constant potential dictates that the source be unlimited with respect to the concentration in the outer coating. This requirement may be met if the source concentration is kept above a certain value for the duration of the constant potential regime, and would be most likely to occur in high-burnup coated particles.

A constant potential may be sustained under two conditions:

- (1) A constant vapor pressure above excess fission products or fission product compounds in the source zone.
- (2) A limiting concentration or "apparent" solubility in the coating such as might be attained when all temporary trapping sites (defects) are occupied in the coating next to the buffer-coating interface.

The first condition will produce a change in potential with temperature, while the second is temperature independent. Annealing and grinding experiments to obtain information on actinide diffusion have produced the temperature-independent limiting concentrations indicated in (2). Average solubilities in

columnar pyrocarbon determined from 13 experiments with uranium and from 8 experiments with thorium were found to be essentially constant at 1.26 and 1.38 mg/cm³, respectively, over the temperature range 1553 to 2065°C. Barium and strontium are known^{1,8} to segregate as oxides in UO₂. If constant-potential release of barium and strontium occurs, it would probably be of the type indicated in (1). Cesium compounds are less stable and highly volatile at high temperatures; therefore, limiting solubilities are more likely to control in this case.

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7. NOMENCLATURE

a'	Volume-to-area ratio, V/A , at the source zone-coating radius, cm
z	Position of source zone-coating interface, cm
A	Area normal to diffusive flow, cm ²
$A(s)$	Constant of integration in "s" space, atom-sec/cm ² or atom-sec/cm ³
b	Outer boundary of coated particle, cm As a subscript denotes buffer region, no units.
$B(s)$	Another constant of integration in "s" space, atom-sec/cm ² or atom-sec/cm ³
$c_2(r,s)$	Transformed fission product concentration in coating, atom-sec/cm ³
$C_2(r,t)$	Fission product concentration in coating as a function of position and time, atoms/cm ³
$C_1(t)$	Total fission product concentration in source zone, atoms/cm ³
$C_1^*(t)$	Mobile fission product concentration in source zone, atoms/cm ³
C_1^0	Initial fission product concentration $C_1^*(0)$ in source zone, atoms/cm ³
D	Diffusion coefficient for fission product migration in coating, cm ² /sec
D^*	Approximate diffusion coefficient when $T'_0 = 1/6$, cm ² /sec
e	The transcendental number, 2.7182... , no units
f	Fraction of mobile fission product in the coated particle, $(1 - f)$ is the trapped fraction, no units
$f_j(L,T)$	Functions of L and T , $j = 1, 2, 3$, and 4, with characteristic roots α_n , no units
$f(s)$	Laplace transform of $F(t)$, $[F(t) \text{ units}] \times [\text{sec}]$
$F(t)$	A general function of time, arbitrary units
FR	Fraction of total fission product released, no units
h	Geometric-partition parameter, $(a'\phi)^{-1}$, for depleting systems, (cm) ⁻¹
h'	Film coefficient for mass transfer, cm/sec
H	Film- or evaporation-diffusion coefficient ratio, h'/D , (cm) ⁻¹

i	The imaginary number $(-1)^{1/2}$, no units
j	An index, no units
$J(r,t)$	Diffusive flux as a function of r and t , atoms/cm ² ·sec
k	Spherical coordinate partition parameter, $3/\phi$, no units
k	As a subscript, denotes kernel region, no units
K_c	Henry's law constant in terms of concentration, no units
K_p	Henry's law constant in terms of pressure, atm·cm ³ /atom
ℓ	Coating thickness, $b - a$, cm
L	Correlation parameter, $h\ell$, for depleting systems, no units
L'	Correlation parameter, $H\ell$, for film systems, no units
m	Slope of experimental FR-vs-plot, (sec) ⁻¹
m'	Slope of theoretical FR/f-vs-T plot, no units
$M_i(t)$	Amount of fission product in source region at any time, t , atoms
$M_i^*(t)$	Amount of mobile fission product in source region, atoms
M_i^0	Initial amount of fission product in source region, atoms
$M_i(\infty)$	Ultimate amount of fission product released, ϕM_i^0 , atoms
n	Index, $n = 1, 2, 3, \dots$, no units
$n'_i(t)$	Partial density of mobile fission product in source region as a function of time, atoms/cm ³ ·pore volume
$N_j(r,t)$	Time-integrated release from position r in zone j as a function of time, atoms
o	Subscript or superscript denoting initial time or starting position, no units
$p'_i(t)$	Partial pressure, $n'_i(t)/RT'$ (see above), atm
$p(s)$	Numerator of Heavyside's form of the Inversion Integral atoms/cm ² or atoms/cm ³
$q(s)$	Denominator of Heavyside's form, (sec) ⁻¹
$Q(a, k, \alpha'_r, \ell)$	Modulus, or common denominator of transport functions in spherical coordinates, no units
r	General radial position in spherical coordinates, cm
R	Ratio of dimensions, a/ℓ , no units
s	The Laplace transform variable, (sec) ⁻¹
RT'	Gas constant—absolute temperature ratio, atm·cm ³ /atom
t	Laboratory anneal time, hr or sec
$\bar{t}$	A particular time t , hr or sec
t_0	Experimental breakthrough time, hr or sec
t'	Displaced anneal time, hr or sec
t'_0	Displaced initial time, hr or sec
T	Reduced time, Dt/ℓ^2 , no units
T_0	Reduced breakthrough time, Dt_0/ℓ^2 , no units
T'_0	Special reduced breakthrough time on depletion curve, no units
$u_2(x,s)$	Transformed concentration function in "s-space," atom-sec/cm ²
$U_2(x,t)$	Transformed concentration function, $rC_2(r,t)$, in "t-space," atoms/cm ²
V_j	Volume decorated with various subscripts j , cm ³

x	General position in linear flow coordinates, cm
y	Ordinates of curves, arbitrary units
α	Complex argument in "s" space, $\ell(s/D)^{1/2}$, radians
α_n	Values of α that satisfy auxiliary equations of the form, $\alpha_n \tan \alpha_n = L$ and $\cot \alpha_n = R\alpha_n/k - 1/P\alpha_n$, $n = 1, 2, 3, \dots$, radians
$\alpha'_n \ell$	An alternate form of α_n , $\alpha'_n = \alpha_n/\ell$, radians/cm
β	Same argument as α , radians
β_n	Values of β that satisfy auxiliary equation of the form, $\beta_n \cot \beta_n + L'$, radians
γ	Concentration ratio, $\Delta C/C_a$, no units
δ	A very small thickness $\rightarrow 0$, cm
Δ	Symbol denoting difference, no units
ϵ	Porosity, a volume ratio, $V_{\text{pores}}/V_{\text{bulk}}$, no units
$\langle \epsilon \rangle$	An average porosity, no units
λ	Dummy of integration for s in complex space, $(\text{sec})^{-1}$
π	The transcendental number, 3.1415... , no units
$\rho_n(t)$	Residues of poles in complex "s-space," arbitrary units
Σ	Symbol denoting sum, no units
ΣV_p	Sum of pore volumes, cm^3
$\zeta(x,s)$	A concentration function in "s-space," $\text{atom}\cdot\text{sec}/\text{cm}^3$
τ	Time t corresponding to $t'_0 = 0$, sec
ϕ	Partition coefficient, $C_1^*(t)/C_2(a,t)$, no units
$\varphi_j(L', T)$	Functions of L' and T , $j = 1, 2, 3$, and 4 , with characteristic roots β_n , no units

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