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Compilation of Fuel Performance and Fission Product Transport Models and Database for MHTGR Design

R. C. Martin

APPLIED TECHNOLOGY

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Metals and Ceramics Division

COMPILATION OF FUEL PERFORMANCE AND FISSION PRODUCT
TRANSPORT MODELS AND DATABASE FOR MHTGR DESIGN

R. C. Martin

Date Published: October 1993

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SUMMARY

A compilation is presented of the current analytical models used to predict the performance of coated particles and fuel compacts and the transport of fission products in MHTGRs. Both normal operating condition and accident condition models are documented and discussed, and the database used in development of these models is documented. The models and data documented herein for fissile fuels are based largely on LEU UO_2 and UC_2 and, to a lesser extent, UCO and HEU fuel particles. This compilation provides:

- (1) a readily available source of models and equations used to predict MHTGR fuel performance and fission product transport for use in MHTGR design and scoping studies, and
- (2) a working document for evaluation of experimental results from reference MHTGR fuels and for future revision of the models to reduce their predictive uncertainty.

Limited critical assessment of the basis of and assumptions behind the models is also provided for perspective on the reliability of the model and insight into potential directions for model revision.

The author of this compilation did not have unlimited access to all relevant documents for background material, source data, and model derivations. This author largely relied on those documents readily available. This compilation does not therefore represent an independent and thorough assessment of the models and database.

This document was issued as a draft in July 1991, and new information available since then has not been incorporated into this revision. Based on this general review and documentation of the models, one can conclude that many models are adequate as presented for MHTGR design, but that other important models are based on questionable assumptions and limited data. Since July 1991, the performance of the irradiation capsules HRB-21, NPR-1, NPR-1A, and NPR-2 seriously undermines the validity of the fundamental models of in-reactor fuel performance presented in §2, and limited heating test data suggest that reference accident condition models based on German data are not valid for application to reference U.S. fuel.

Because it is not possible for all involved in the MHTGR effort to thoroughly review a document of this size within a finite time, one should not expect all program participants to necessarily concur with the evaluations or conclusions presented herein.

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ABBREVIATIONS AND ACRONYMS

AC	accident condition(s)
AERE	Atomic Energy Research Establishment, Harwell, United Kingdom
AVR	Arbeitsgemeinschaft Versuchs-Reaktor
BISO	buffer isotropic coating (buffer and PyC layers)
BNL	Brookhaven National Laboratory
CCCTF	Core Conduction Cooldown Test Facility
CEGA	Combustion Engineering/General Atomics NPR design company
CHST	core heatup simulation test
cm ² -geom	cm ² of geometric surface area (including surface roughness)
CO	carbon monoxide
CP	coated particle
CTE	coefficient of thermal expansion
CVD	chemical vapor deposition
dps	disintegrations per second
DAN	Design Analysis Need
DDN	Design Data Need
EFPD	effective full-power days
EOL	end-of-life
FDDM/C	Fuel Design Data Manual, Issue C (Scheffel, 1979)
FDDM/D	Fuel Design Data Manual, Issue D (Kovacs, 1982)
FDDM/E	Fuel Design Data Manual, Issue E (Myers, 1984a), GA Technologies proprietary document
FDDM/F	Fuel Design Data Manual, Issue F (Myers, 1987), nonproprietary document
FE	fuel element
FG	fission gas(es)
FIMA	fissions per initial metal atom
FP	fission product(s)
FRG	Federal Republic of Germany

FSV	Fort St. Vrain
GA	General Atomics
GN	Goodin-Nabielek
HEU	high-enriched uranium (93% ^{235}U)
HM	heavy metal (thorium and/or uranium)
HRB	Hochtemperatur-Reaktorbau GmbH
HTGR	high-temperature gas-cooled reactor
HTI	high-temperature isotropic
HTR	High-Temperature Reactor
IMGA	Irradiated Microsphere Gamma Analyzer
IPyC	inner pyrocarbon
KFA	Kernforschungsanlage Jülich GmbH
KMC	kernel migration coefficient
LEU	low-enriched uranium ($\leq 20\%$ ^{235}U)
LHTGR	Large HTGR (2240 MW _{th})
LTI	low-temperature isotropic
LWR	light-water reactor
MEU	moderate-enriched uranium
MHTGR	Modular HTGR
n	neutron(s) (e.g., n/m ²)
N.A.	not applicable
NOC	normal operating condition(s)
NE-MHTGR	Nuclear Engineering (civilian) MHTGR design
NP	New Production Reactor
NP-MHTGR	New Production Reactor, MHTGR design
OPyC	outer pyrocarbon
ORNL	Oak Ridge National Laboratory
O/U	oxygen to uranium atom ratio
PC	primary circuit
PIE	postirradiation examination

ppbv	parts per billion, by volume
PPyC	protective pyrocarbon layer
PV	pressure vessel
PyC	pyrolytic carbon (pyrocarbon)
QC	quality control
R	ideal gas constant (8.314 J mol ⁻¹ K ⁻¹ , 1.987 cal mol ⁻¹ K ⁻¹ , 82.06 × 10 ⁻⁶ m ³ atm mol ⁻¹ K ⁻¹ , 8.313 × 10 ⁻⁶ m ³ MPa mol ⁻¹ K ⁻¹)
SG	steam generator
SiC	silicon carbide
SiO ₂	silicon dioxide
SR	shear stress ratio
SS	stainless steel
STP	standard temperature and pressure conditions (273 K and 1 atm)
ThC ₂	thorium carbide
(Th,U)O ₂	mixed thorium-uranium oxide
TRIGA	Training, Research, Isotope-production, GA
TRISO	tristructural (buffer, SiC, PyC) isotropic coating design
UC ₂	uranium carbide
UCNI	Unclassified Controlled Nuclear Information
UCO	mixture of UO ₂ and UC ₂
UO ₂	uranium oxide
UO ₂ *	UO ₂ kernel with a ZrC coating
USAEC	United States Atomic Energy Commission
USDOE	United States Department of Energy
UTS	ultimate tensile strength
v/o	volume percent
w/o	weight percent
ZrC	zirconium carbide

1. INTRODUCTION

1.1 BACKGROUND

Models for fuel performance and fission product transport have been used in the design of high-temperature gas-cooled reactors (HTGRs) in Europe and the United States. The models are often simple bounding assumptions or empirical approximations which were not always well documented. The most comprehensive documentation of U. S. models was carried out by General Atomics in a series of Design Manuals (Scheffel, 1979; Kovacs, 1982; Myers, 1984a; Myers, 1987). The models used in the German program were documented by Moormann et al. (1987). An update of the German models was issued by Verfondern et al. (1993) which also summarized the reference models from other national HTGR programs (U.S., Japan, Russia, etc.).

Significant uncertainty is associated with some current fuel performance and fission product (FP) transport models. For example, models with improved accuracy are needed so that predictions of fission gas release can be made with uncertainties $\leq 4x$ and predictions of metallic FP release with uncertainties $\leq 10x$.¹ Many current models were developed on the basis of data from earlier TRISO particle designs and nonreference fuel and core materials, and may require revision as data from reference MHTGR fuel and core materials become available.

Existing compilations of the model equations do not provide a review of the database and assumptions used in development of these models. A prerequisite to comprehensive model evaluation and revision is a technical document which collects the models, information on their development, and information on the database used in their development into a single source.

¹Although an order-of-magnitude uncertainty implies that significant phenomena or mechanisms are not well understood, the planning of single- and multiple-effect experiments to reduce the uncertainty can be an expensive proposition and is not always guaranteed of success when predicting phenomena which are influenced by many in-reactor variables. A more cost-effective approach is to determine model uncertainty levels which are acceptable in predicting fission product release for safety analyses, and to concentrate on reducing the uncertainty of those models which can have a significant impact on reactor safety design margins.

In the present design philosophy of the U.S. MHTGR program, much weight is given to a predicted result that is "conservative," i.e., overpredicts what one observes in experiment. Often more weight is given to whether a model is conservative than to whether it reliably reflects the physical phenomena involved.

1.2 OBJECTIVES

This effort represents the initial portion of what was planned as a multiyear project, with the goal of improving models to provide better agreement between model predictions and experimental performance of proof-test fuel. This portion of the project incorporates two primary objectives:

- (1) compilation of the set of analytical models for fuel performance and FP transport to be used in MHTGR design until new experimental data from the MHTGR program can be analyzed and incorporated into model revisions, and
- (2) documentation of the database used in support of development of these models to permit critical assessment and/or validation of model accuracy and relevance to MHTGR-specific conditions and as a reference for further model improvement.

One application of this compilation was envisioned to be the documentation of interim models for NP-MHTGR design until further analysis could compare the models to data developed from the NP-MHTGR fuel development program and could compare the models to the specifics of the NP-MHTGR fuel and core design.¹ However, this compilation discusses the database for both LEU and HEU fissile fuels and for fertile fuels, therefore it can be used in support of both NE- and NP-MHTGR programs.

This compilation is in some ways analogous to the recent revision of General Atomics' Fuel Design Data Manual (FDDM) but is more comprehensive in its scope. The FDDM presents the analytical equations for models for use by engineers with little discussion of the background, data, or assumptions on which the models are based. Thus, the FDDM is not constructed in a format amenable to model evaluation and model development. This compilation will fulfill the need for such a working document and will provide the basis for a technical support document for future issues of model compilations to be used in MHTGR core analysis.

¹Subsequent to the drafting of this document, CEGA issued two UCNI documents which are intended to address these issues of NPR-specific models and associated background to the models: "NP-MHTGR Fuel Design Data Manual," (CEGA-002100, Rev. 0, September 1992, and "NP-MHTGR Fuel Design Manual Basis Report," CEGA-002322, Rev. 0, September 1992. These documents have not been reviewed by this author, therefore the degree to which the above Basis Report duplicates the effort represented by this document, ORNL/NPR-91/6, if any, cannot be commented on.

Only limited data on HEU UCO was available at the time of writing of this document, therefore the models documented herein are primarily based on data for LEU UO_2 , UC_2 , and, to a limited extent, UCO. Whatever HEU-UCO-specific models have since become available should be documented in the two above-mentioned UCNI reports.

1.3 ORGANIZATION

The first section discusses the fuel particle performance models, i.e., fuel coating integrity and failure and its general relation to FP release. Performance models of the fuel compact are discussed next, including fuel thermal properties. The following sections on gaseous and metallic FP transport present the models in a sequence which approximates the transport of the FP: transport starting at the kernel, through the particle coating layers, from the particle to the coolant via the fuel compact matrix and graphite, and finally throughout the primary circuit. Models for tritium transport and heavy metal transport are presented in subsequent chapters. The models for oxidation and hydrolysis of core materials are then presented, followed by a chapter which briefly presents background on some nonreference materials of current interest to gas-cooled reactor programs.

The format for presentation of each model is as follows:

- (1) a brief introduction to the model including assessment of its present status and uncertainty, and a list of references in approximate order of importance;
- (2) the models for normal operating condition (NOC) and accident condition (AC) regimes are presented separately, where appropriate, and include the model equations, range of experimental and model validity, list of assumptions used in the development of each model, and quantification of the model uncertainty; and
- (3) sections on the model chronology, discussion of the model including theoretical background, associated experimental database, implications of the assumptions used and related model shortcomings, general considerations for further model development, and finally some presentation of the experimental database not included in the other sections.

This format is organized so that users of the model can obtain concise model equations and highlight information from the beginning of the model section, while detailed information on model derivation, analysis, and supporting database are provided in the subsequent expanded sections.

Preliminary analysis of the current validity of these models and suggestions for further analysis are provided as appropriate. The section on "Additional Considerations for Model Development" suggests possible avenues for fruitful study related to model improvement. The presentation of assumptions used in development of the model tends to be rigorous to provide a sound basis for thorough evaluation and subsequent comparison with alternate models. Although listing of some assumptions may appear pedantic, presentation of such detailed assumptions does not imply criticism of the model or of the efforts or thoroughness of the model developers.

1.4 GENERAL COMMENTS

It should be emphasized that other MHTGR program participants do not necessarily concur with model interpretation and evaluation as presented here. Thorough review of a document of this size by all involved was not possible within the finite time available.

The comments and analysis provided on each model should not be construed as a comprehensive and independent review of the model. The author did not have unlimited access to all background material, documents, and source data and thus relied on that information at hand. A thorough independent review of the models would require greater access to this background information.

Quantities are generally specified in SI units. Non-SI units are sometimes presented when used by the source references. The list of references for each model is presented in a sequence which approximates their relative significance to the model. The model uncertainties are presented in terms of the standard deviation of the experimental values or of the propagation of errors formulation. As stated in FDDM/F, the upper and lower bounds of a quantity can be calculated from its mean value and standard deviation:

$$(\chi)_b = \chi_i e^{\pm c\sigma} \quad , \quad (1.4.1)$$

- χ_i = mean value of the quantity χ ,
- b = upper bound ($b = u$) or lower bound ($b = l$),
- c = multiplicative factor for the confidence level desired (often taken to be the 95% confidence level),
- σ = standard deviation of the quantity χ or of the natural logarithm of χ .

It should be noted that uncritical use of these models outside the specified range of validity may provide unreasonable predictions.

A general objective of this compilation is its presentation in a format amenable to future revision, to incorporate current data analyses and model revisions, and to expand the discussion of related topics. A more systematic presentation of the contents of this compilation would include explicit discussion of the reactor event cases related to the use of these models, more emphasis on the range of operating conditions expected for the MHTGR design, detailed discussion of the existing computer codes used to simulate the reactor events, and discussion of the implementation of these models into the codes and their relation to the specifics of MHTGR design. The time available for completion of this document did not permit comprehensive expansion beyond the original objectives of providing detailed compilation and analysis of the models. If a future revision of this compilation is mandated, then the contents can be modified to incorporate these improvements and additional suggestions. Time restrictions may have also limited some inclusions such as the explicit mention of the original sources of data or figures which were taken from other documents; future revision should correct any such oversight.

1.5 PROGRAM UPDATE, 1993

This document was drafted before irradiation results became available from the NPR irradiation capsules NPR-1, NPR-1A, and NPR-2, and the NE capsule HRB-21. This document was not updated to incorporate the information obtained from those capsules, although final "update" sections were added to each chapter to mention recent and upcoming work relevant to the models discussed in that chapter. In reality, the disappointing performance of the fuel is not consistent with some of the fundamental models presented herein. In particular, the reservations expressed in the analysis of the pressure-vessel model (§2.3) were more than vindicated, with the preirradiation predictive capability in error by nearly two orders of magnitude in relation to the experiments. Limited heating data at 1600°C on U.S. UCO fuel from HRB-17/18 piggyback samples indicated cesium release one to two orders of magnitude higher than German fuel under comparable conditions. As such, the validity of reference AC models derived from the German database is cast in serious doubt.

This irradiation experience demonstrates the difficulty in deriving models from a database representative of earlier vintage and lower-quality fuel than that required by current design requirements, or of high-quality fuel based on a different design and manufacturing process. By reducing the initial heavy-metal contamination and exposed kernel fractions to new lows, one can observe failure phenomena which may not be characteristic of fuel of poorer initial quality or earlier design. This fact highlights the weakness of models designed more for consistency of prediction with previous observations than for accurate reflection of underlying physical phenomena, and the questionable relevance of such models for modified fuel designs.

2. COATED FUEL PARTICLE PERFORMANCE MODELS

2.1 INTRODUCTION

This chapter discusses the fuel particle performance models (i.e., those related to the structural integrity of the particle and coating layers which affect the retention of FP). A combinatorial model is first discussed which algebraically combines the various fractions of particles having manufacturing and irradiation-induced defects into generalized equations describing the fractions of particles with exposed kernels or with defective SiC layers and intact OPyC layers. The pressure-vessel model for particle integrity is then presented, first the models described by analytical equations for failure and then the general phenomenological model which serves as the basis for the pressure-vessel analysis. Finally the models are presented which describe the structural failure of the SiC and OPyC layers, including the well-known SiC failure mechanisms of kernel migration, FP corrosion, thermal decomposition, and heavy metal dispersion.

2.2 COMBINATORICS OF COATED PARTICLE FAILURE MODELS

function	Given the various fractions of particles with manufacturing and irradiation-induced defects, these equations provide the fractions of particles with exposed kernels and with defective SiC - intact OPyC layers.
present status	This model is useful provided the coating failure mechanisms and manufacturing defect fractions are well defined. With present-day uncertainties in both, use of this model is limited to approximations of failure probabilities. Actual use of this model appears to be limited.
model uncertainty	No discussion of the uncertainty of this approach has been presented. Considering the present uncertainties in quantifying the coating failure mechanisms and the manufacturing defect fractions, use of this model would propagate significant uncertainties in any estimate of failure and FP release probabilities.
references	Nabielek (1984); Goodin (1984a); Kovacs (1981)

INTRODUCTION

If the particle failure mechanisms which enhance FP release are understood, and quantification of manufacturing defect fractions is possible, then numerical combination of the probabilities of failure are possible using combinatorial methods. This approach emphasizes two classes of failure probabilities and modes of FP release from the particle:

(1) those that contribute to exposed kernels (i.e., failure of all coating layers and the direct release of fission products from the kernel), and (2) those that contribute to failure of the SiC layer while the OPyC layer remains intact, leading to diffusive release through the OPyC. The mechanisms which lead to these particle failures are grouped into two categories: failure mechanisms occurring in standard, initially intact particles, and failure mechanisms resulting from initial manufacturing defects. Although elegant in its analytical approach, literature references to the combinatorial method are not common, probably because of the difficulty in defining failure and release mechanisms quantitatively and unambiguously.

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The following equations are taken from the source references (Nabielek, 1984; Goodin, 1984a). The analogous equations presented in FDDM/F use different symbolism and vary slightly but are not fundamentally different than those presented below. FDDM/F references two internal GA memoranda (in addition to Nabielek, 1984) which have not been reviewed by this writer. The formalism and symbolism of the open-literature references is retained below.

2.2.1 PERFORMANCE OF STANDARD PARTICLES

Standard particles refer to reference fuel particles with initially intact coating layers and no manufacturing defects. Defective particles refer to fuel particles with initial manufacturing defects. The fraction of standard particles with failed SiC layers (during irradiation) and intact OPyC layers, D_I , is given by (Nabielek, 1984; Goodin, 1984a):

$$D_I = (1 - X_M) (1 - F_{OP}) F_{SC} \quad , \quad (2.2.1)$$

and the fraction of nondefective particles with failed SiC and failed OPyC layers, P_F , is given by:

$$P_F = (1 - X_M) F_{OP} (F_f + F_{SC}) + (1 - X_M) (1 - F_{OP}) F_I \quad , \quad (2.2.2)$$

- X_M = fraction of particles with manufacturing defects,
- F_{OP} = probability of OPyC failure in intact particles (i.e., intact SiC layer),
- F_{SC} = probability of chemical failure of the SiC layer (via corrosion, kernel migration, or decomposition),
- F_f = probability of SiC failure in particles with failed OPyC layers,
- F_I = probability of SiC failure in particles with intact OPyC layers.

2.2.2 PERFORMANCE OF PARTICLES WITH MANUFACTURING DEFECTS

The fraction of all particles with manufacturing defects, X_M , is given by:

$$X_M = X_{HM} + X_{MI} + X_{MS} + X_{MB} + X_{MO} , \quad (2.2.3)$$

- X_{HM} = fraction of particles with excessive heavy metal dispersion,
- X_{MI} = fraction of particles with missing IPyC layers,
- X_{MS} = fraction of particles with initially defective SiC layers,
- X_{MB} = fraction of particles with missing buffer layers,
- X_{MO} = fraction of particles with missing or initially defective OPyC layers.

The fraction of particles with manufacturing defects which result in SiC failure and diffusive FP release through intact OPyC layers, D_M , is given by:

$$D_M = [(X_{HM} + X_{MI}) F_{HM} + X_{MS}] (1 - F_o) , \quad (2.2.4)$$

and the fraction of particles with manufacturing defects which result in both SiC and OPyC failure (exposed kernels), P_M , is given by:

$$P_M = [(X_{HM} + X_{MI}) F_{HM} + X_{MS}] F_o + X_{MB} F_{MB} + X_{MO} (F_f + F_{SC}) , \quad (2.2.5)$$

- F_{HM} = probability of SiC failure due to excessive heavy metal dispersion,
- F_o = probability of OPyC failure on particles with failed SiC layers,
- F_{MB} = probability of SiC and OPyC failure on particles with missing buffer layers,
- F_f and F_{SC} as defined in §2.2.1 above.

2.2.3 COMBINED FUEL PERFORMANCE

The total failure fractions for exposed kernels and for defective SiC/intact OPyC is simply given by summing the appropriate terms as given above in §2.2.1 and §2.2.2. The total fraction of particles with defective SiC and intact OPyC layers, D_T , is given by:

$$D_T = D_I + D_M , \quad (2.2.6)$$

and the total fraction of particles with exposed kernels, P_T , is given by:

$$P_T = P_F + P_M , \quad (2.2.7)$$

with all terms previously defined.

Range of validity (§2.2.1, §2.2.2, and §2.2.3)

The combinatorial formulation gives increasing error for failure probabilities of the individual mechanisms above 0.01 (Nabielek, 1984); small failure probabilities are required in order to accurately neglect higher-order terms (cross products). The range of validity for each individual failure probability is specified elsewhere in this compilation, where the model for the failure mechanism is discussed.

Assumptions

1. The mechanisms for coating failure are well defined.
2. The possible existence of intermediate failure states (i.e., gradual loss of coating integrity) is not significant with respect to total FP release. In other words, a coating is either failed or unfailed, with no significant transition in between.
3. No synergistic effects are significant for the different failure mechanisms. The defect mechanisms must be mutually exclusive.
4. The assumptions relevant for each failure model as specified elsewhere in this compilation are valid.

Uncertainty

The uncertainty of the model includes the uncertainties of quantification of the manufacturing defect fractions and of the models for coating layer failure. These uncertainties are significant (e.g., see "Discussion" below).

FDDM/F provides some quantification of the uncertainties in the fuel performance models for the general quantities F_D and F_E "which represent, respectively, (1) the fraction of particles with intact OPyC layers, failed SiC layers and implicitly, failed IPyC and buffer layers from which fission products are released after diffusion through the intact OPyC layer and (2) the fraction of particles with exposed kernels from which fission products are directly released to the exterior of the particle." The standard deviation in $\ln F_i$, for $i = D$ or E , is given by:

$$\sigma(\ln F_i) = 1.4 \quad (2.2.8)$$

MODEL CHRONOLOGY

The first apparent reference to this combinatorial model was by Kovacs (1981), who categorized the pressure-vessel (PV) failure model based on either metallic FP release or on gaseous plus metallic release. In 1984 Goodin (1984a) duplicated the model of Kovacs (1981) as a part of the PV model, but emphasized the categories of exposed kernels and of diffusive release through OPyC.

Nabielek (1984) refined the combinatorial model by adding an explicit term for the chemical failure of the SiC layer (corrosion, amoeba, decomposition) and providing a more

precise formulation of failure probabilities. The formulation of FDDM/F is similar to but not identical with that of Nabielek (1984).

DISCUSSION

Predicted FP release using PV coating failure models is usually insignificant compared to release attributed to heavy metal contamination or other manufacturing defects. It seems likely that this combinatorial approach was pursued as a means of synthesizing the PV and manufacturing defect models. However, no detailed discussion of the evolution of or background to this model has been located.

One difficulty of applying this model for reference fuels is that manufacturing defect and PV failure fractions are often so low, usually limited by experimental uncertainty, that accurate modeling based on this approach is difficult.

The combinatorial model as presented is only as good as the models of failure fractions which provide the numerical input. For example, the fraction of particles with initially defective SiC layers, X_{MS} , will strongly impact FP release predictions under normal operating conditions. If uncertainty exists in the analytical methods used for quality control (QC) determinations of manufacturing defect fractions, that uncertainty is directly transferred to the combinatorial model. A discussion by Kovacs et al. (1980) on the dependence of SiC manufacturing defect fraction values on the experimental technique used is presented below, as an example of the weakness of the combinatorial model.

Examination of the particle batches used in irradiation capsules GF-1, GF-2, and GF-3 showed evidence of localized microfissures, which were equated with defective SiC layers and "... further evaluation of the level of defective SiC layers ... showed that all defective SiC layers were not detected by the current QC burn-leach technique. Specifically, the level of defective SiC layers determined by radiographic evaluation after mercury intrusion at 69 MPa ranged from 2.3% to 11.8% ... A large fraction of these defects were SiC layers with localized microfissures ... This type of defect would not be readily discernable by the burn-leach technique since this method depends on complete burning of the IPyC and leaching of the kernel substrate. Microfissures of the type shown ... would restrict oxidation of the IPyC layer and fuel kernel leaching. Consequently, the burn-leach technique would tend to underestimate the true fraction of defective SiC layers. This result is supported further by Cs-137 diffusive release studies, which show that defective SiC layers in GF-1,2,3 fissile particles ranged between 0.1% and 3.5% ... The fraction defective SiC layers determined radiographically was greater than that determined by Cs-137 release ..."

Thus, depending on the method used for detection of defective SiC from manufacturing processes, the combinatorial method might give significantly different results for the same phenomenon. The combinatorial method is only as good as its input parameters.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

As discussed above, too much ambiguity exists in some of the variables used as input into the combinatorial model to justify much further effort in refinement of this model. Effort is better spent in attempting to reduce the uncertainties in the input parameters. For

example, the possibility of diffusive release of metallic fission products through an intact or slowly decomposing SiC layer is not considered by this model, although such a phenomenon may be important for the low levels of fractional release expected under accident conditions. Such fundamental phenomena need to be better understood.

DATABASE USED IN MODEL DEVELOPMENT

From the available literature, it appears this analytical model is based on logic and assumptions of failure mechanisms rather than specific data. Therefore, the only database relevant to this model would appear to be the data on which the individual failure mechanisms are based, and reference should be made to those specific models within this compilation as appropriate.

2.3 PRESSURE-INDUCED STRUCTURAL FAILURE OF PARTICLE COATINGS

2.3.1 INTRODUCTION

The pressure-induced structural failure of particle coatings is commonly referred to as PV failure, because of the model upon which the equations are based. Model equations have been developed for the failure of standard coated particles, and for coated particles with missing buffer layers and failed OPyC layers. Model equations for pressure-induced failure of these several particle coating configurations are based on a single equation, with the model constants derived for each failure mode. However, derivation of these constants is not directly based on experimental results, but rather on the results of a computer code designed for PV-model calculations. Pressure-vessel failure of particle coatings has been treated as insignificant in AC modeling in the United States (Goodin et al., 1985), although it is extended to AC modeling in Germany by incorporating decomposition and thinning of the SiC layer (Verfondern et al., 1990).

All evidence suggests that the model equations in §2.3.2 were designed specifically for reference LEU particle designs with maximum burnup of 26% FIMA. A phenomenological model for PV failure that was suggested for use in NP-MHTGR design is presented in §2.3.3. As used below, fissile particles refer to UCO kernels, and fertile particles refer to ThO₂ kernels.

Goodin et al. (1985) provide a concise summary of the present state of the PV model. "This classic fuel failure mechanism has been studied extensively in the past and offered as the explanation for fuel failure during normal reactor service and during accidents ... However, it has never been particularly successful in predicting fuel particle performance or even reproducing the shape of observed performance curves. After careful consideration, this failure mechanism is omitted from the present work as being of negligible impact [in accident condition modelling]. This is not to say that the pressure vessel failure calculations and codes are not useful as guidelines in fuel particle design or for making changes in that design. However, modern day fuels have been designed not to fail by pressure vessel failure and appear from their performance measurements to have achieved this goal."

2.3.2 PRESSURE-VESSEL FAILURE OF PARTICLE COATINGS

function	This model determines the pressure-induced failure of the coating layers (SiC and OPyC) based on the magnitude of the buildup of internal fission gas pressure relative to the strength of the SiC and OPyC layers.
present status	The U.S. model considers this contribution to FP release to be insignificant for standard particles and only significant for defective particles under NOC, and to be insignificant for AC modeling in general. In contrast, PV failure has been retained as a dominant feature of German AC models by incorporating decomposition and thinning of the SiC layer.
model uncertainty	For standard particles, the uncertainties are "large but insignificant" for modern fuels and present fuel production techniques (Myers, 1988) (i.e., pressure-induced failure of reference-quality modern fuels is not expected to be a concern). The uncertainties for the failure of defective particles are of greater significance. The uncertainty inherent in the calculations on which the model equations are based has been reported to be $\pm 10x$ (Kovacs et al., 1983). Because the model equations are derived from computational results rather than experimental results, the inherent uncertainty is at least $\pm 10x$. The somewhat arbitrary choice of a reference value for SiC fracture strength compounds the uncertainty. In practice (i.e., recent irradiation tests) the uncertainty is closer to $\pm 100x$.
references	Myers et al. (1985d); FDDM/F; Kovacs et al. (1983); Goodin et al. (1985)

NORMAL OPERATING CONDITIONS

Model equations

By combining the concepts of a Weibull failure distribution with the circumferential stress in the spherical SiC shell, an approximation for the failure function can be formulated as (FDDM/F):

$$\phi = 1 - \exp \left\{ - \left[(a + bT) T f_b^n \right]^5 \right\} \quad (2.3.2.1)$$

- ϕ = probability of pressure vessel failure,
- T = temperature (K),
- a = constant (K^{-1}),
- b = constant (K^{-2}),
- n = constant (dimensionless),
- f_b = fractional burnup of the kernel, that is,

$$f_b = \frac{F}{F_{\max}} , \quad (2.3.2.2)$$

F = burnup (% FIMA),

$F_{\max}$ = maximum burnup (26% FIMA for fissile particles, 7% FIMA for fertile particles).

Myers et al. (1985d) suggest a slightly different model equation:

$$\phi = \left[(a + bT) T f_b^n \right]^{\frac{1}{n}} , \quad (2.3.2.3)$$

which can be obtained from Eq. (2.3.2.1) by Taylor series expansion and which is accurate for small values of the exponential term.

In the NP-MHTGR HEU UCO TRISO particle, the SiC tensile stress at the maximum burnup of 75% FIMA is similar to that of LEU UCO particles at their maximum burnup of 26% FIMA. As a result, Eq. (2.3.2.1) might be expected to approximate the behavior of NP-MHTGR particles if the correct $F_{\max}$ of 75% FIMA is used in Eq. (2.3.2.2). For confirmation, this assumption must be checked using the CON*STA code. Alternatively, the phenomenological pressure-vessel model of §2.3.3 can be applied to model the performance of NP-MHTGR HEU particles.

2.3.2.1 STANDARD PARTICLES

The PV failure model has been incorporated into the GA code CON*STA (Kovacs et al., 1983). Model Eq. (2.3.2.1) was applied to the CON*STA computational results for simulation of standard particle performance (i.e., particles with intact coating layers), and the following parameters for Eq. (2.3.2.1) were obtained [parameter values from FDDM/F; uncertainties from Myers et al. (1985d)]:

fissile particles: $a = 4.0 \times 10^{-5}$, $b = 0.0$, $n = 1.5$, rms deviation = 27%
 fertile particles: $a = 1.2 \times 10^{-5}$, $b = 0.0$, $n = 2.0$, rms deviation = N.A.¹

These parameters are listed in Table 2.3.1 for all particle configurations. The reported rms deviation represents the ability of Eq. (2.3.2.3) to duplicate the computational results from CON*STA, and is not a comparison of prediction with experimental data. Figures 2.3.1 and 2.3.2 compare the results using Eq. (2.3.2.3) with the computational data points obtained from the CON*STA code. The data points in Figure 2.3.2 represent upper limits.

The values for a and b reported in FDDM/F and reproduced in Table 2.3.1 are exactly 40% of those reported by Myers et al. (1985d) for fissile particles and 20% of those reported by Myers et al. for fertile particles. The reduction for fissile particles is consistent with the

¹N.A., not available

Table 2.3.1. Values of constants in pressure-vessel failure equation, Eq. (2.3.2.1) [parameter values from FDDM/F; uncertainties from Myers et al. (1985d)]

Particle configuration	a	b	n	rms deviation
Fissile, intact	4.0×10^{-5}	0.0	1.5	27%
Fertile, intact	1.2×10^{-5}	0.0	2.0	N.A. ^(a)
Fissile, failed OPyC	3.2×10^{-5}	2.0×10^{-8}	1.5	24%
Fertile, failed OPyC	-1.0×10^{-5}	2.1×10^{-8}	2.0	18%
Fissile, missing buffer	-2.07×10^{-3}	4.22×10^{-6}	2.0	N.A.
Fertile, missing buffer	-1.04×10^{-3}	2.11×10^{-6}	2.0	N.A.

(a) N.A. = not available.

assumption of 40% release of fission gas from the kernel (Bramblett, 1990) rather than 100% release assumed by Myers et al. (1985d). An analogous reduction to 20% gas release from the fertile kernels was apparently also implemented into the model.

2.3.2.2 PARTICLES WITH FAILED OPyC LAYERS

Model equation parameters were obtained using the same approach as for intact particles, and the resulting parameters for particles with failed OPyC layers are [parameter values from FDDM/F; uncertainties from Myers et al. (1985d)]:

fissile particles: $a = 3.2 \times 10^{-5}$, $b = 2.0 \times 10^{-8}$, $n = 1.5$, rms deviation = 24%
 fertile particles: $a = -1.0 \times 10^{-5}$, $b = 2.1 \times 10^{-8}$, $n = 2.0$, rms deviation = 18%

Figures 2.3.3 and 2.3.4 compare the results from these model equations with computational data points.

Range of validity (§2.3.2.1 and §2.3.2.2)

1. Model equations were calculated in the range from 1000 to 1600°C. They are explicitly not valid above 1600°C, where other failure mechanisms come into play.

Fig. 2.3.1. Pressure-vessel failure for fissile particles with intact OPyC layers (from Myers et al., 1985d).

Fig. 2.3.2. Pressure-vessel failure for fertile particles with intact OPyC layers (from Myers et al., 1985d).

Fig. 2.3.3. Pressure-vessel failure for fissile particles without OPyC layers (from Myers et al., 1985d).

Fig. 2.3.4. Pressure-vessel failure for fertile particles without OPyC layers (from Myers et al., 1985d).

2. Model equations were derived for reference-design LEU UCO particles, that is,
 - (a) burnup $\leq 26\%$ FIMA
 - (b) kernel diameter $\approx 350 \mu\text{m}$
 - (c) buffer thickness $\approx 100\text{-}115 \mu\text{m}$
 - (d) IPyC thickness $\approx 35\text{-}50 \mu\text{m}$
 - (e) SiC thickness $\approx 35 \mu\text{m}$
 - (f) OPyC thickness $\approx 40 \mu\text{m}$
 - (g) buffer porosity $\approx 50\%$
 - (h) kernel porosity $\leq 5\%$

The above particle parameters are estimates of those which were used to derive the (1985) model equations. Myers et al. (1985d) does not explicitly state the particle design parameters used, thus these dimensions are obtained from comparisons of H. Nabielek's statements in Myers et al. (1985d) with several period references. It seems reasonable to assume that the calculations based on this particle design and reported in Myers et al. (1985d) also form the basis of the values reported in FDDM/F, with the only change resulting from a new less-conservative assumption of the fractional release of fission gas from the kernel. Of particular importance to the NP-MHTGR design, FDDM/F explicitly confirms that the range of validity of this model is limited to 26% FIMA and is thus not directly applicable to NP-MHTGR particle design at high burnup. The same can be said of the kernel size.

Assumptions: specific (§2.3.2.1 and §2.3.2.2)

1. For the Weibull failure distribution, a Weibull parameter of $m = 5$ and a SiC fracture strength of 350 MPa are assumed for all calculations and all particle batches.
2. These two values for the failure distribution constants do not change over time and thus are not affected by the irradiation conditions or by subsequent heating.
3. Specifically, PV failure is independent of the neutron fast fluence.
4. Apparently, 40% gas release from fissile particle kernels is assumed and 20% gas release from fertile kernels.¹
5. The ideal gas law, or some variation thereof [i.e., Redlich-Kwong equation of state (Kovacs et al., 1983)], is applicable and valid in determining the behavior of these pressure-related phenomena.

Assumptions: general

1. The specific kernel fuel (UO_2 vs UC_2 vs UCO) is related to PV failure only by the amount of gas it generates during irradiation.
2. The PV-failure model accurately represents pressure-induced particle failure and the resulting FP release.

¹These values for fractional release of long-lived fission gases should not be confused with those of short-lived gases from exposed kernels, which are usually closer to 1%.

3. The assumptions used in developing the CON*STA code are valid for describing the pressure-related phenomena and PV-failure mechanisms within particles.
4. The CON*STA code is not flawed in its design or implementation.

Uncertainty

The uncertainty reported in Table 2.3.1 only represents the difference between the results predicted by Eq. (2.3.2.3) and those from the CON*STA code and thus does not represent a true model uncertainty. The actual model uncertainty is reported to be $\pm 10\%$ (Myers et al., 1985d; Kovacs et al., 1983). The uncertainty statement from FDDM/F in §2.2, Eq. (2.2.8) is also applicable here.

2.3.2.3 PARTICLES WITH MISSING BUFFER LAYERS

Model equation parameters are provided by FDDM/F for use in Eq. (2.3.2.1) to describe the PV failure of particles with missing buffer layers:

fissile particles: $a = -2.07 \times 10^{-3}$, $b = 4.22 \times 10^{-6}$, $n = 2.0$, rms deviation = N.A.
 fertile particles: $a = -1.04 \times 10^{-3}$, $b = 2.11 \times 10^{-6}$, $n = 2.0$, rms deviation = N.A.

These constants were not reported by Myers et al. (1985d). Source documents which discuss the calculation of these parameters have not been reviewed by this writer, therefore any discussion of range of validity, assumptions, etc. is not possible beyond suggesting that the statements given in §2.3.2.1 and §2.3.2.2 are probably also applicable here. One might note that the failure probability for fertile particles with missing buffers is 100 times that of fertile particles with failed OPyC layers. Such a direct comparison for fissile particles is not possible because of different values of n for failed OPyC layers vs missing buffer layers.

ACCIDENT CONDITIONS

Model equations

Pressure-vessel modeling is truncated at 1600°C; therefore, PV-induced particle failure above 1600°C would be described by:

$$\phi(T > 1600^\circ\text{C}) = \phi(T = 1600^\circ\text{C}), \quad (2.3.2.4)$$

as defined by the previous equations.

Range of validity

The model is stated to apply to all temperatures above 1600°C. The formulation of the PV model used in the German program would dispute this range of validity.

Assumptions

1. Pressure-vessel failure is insignificant at temperatures above 1600°C relative to other failure mechanisms.
2. High-temperature weakening of the SiC and OPyC layers is not significant with respect to PV failure mechanisms.

The first assumption was concluded from an analysis of high-temperature FP release data (Goodin, 1984a), while the second assumption is made tenable by the use of a conservative, but constant, value for SiC fracture strength.

Uncertainty

The uncertainty of the model has not been quantified but could be debated. The German model simulates PV failure above 1600°C but incorporates SiC decomposition mechanisms. The U.S. modeling program considers SiC decomposition separately from the PV model.

MODEL CHRONOLOGY (§2.3.2.1, §2.3.2.2, §2.3.2.3)

The model equations presented in §2.3.2.1 and §2.3.2.2 were based on the work of Myers et al. (1985d) but assumed 100% fission gas release from the kernel. Values for the model parameters given in Table 2.3.1 were apparently obtained using the assumption of 40% gas release from fissile kernels and 20% release from fertile kernels (see Bramblett, 1990 for supporting evidence). Model parameters for particles with missing buffer layers were added sometime after 1985. An earlier model for the failure of particles with missing buffer layers can be obtained from Goodin (1984a); the probability of particle failure increased linearly from 0% at zero fractional burnup to 100 at 20% fractional burnup.

Pressure-vessel modeling has a long history of development from early BISO particle designs (ca. 1966) through design and modeling of TRISO particles. A brief chronology of the development of the PV model is presented by Martin (1990) and the references therein.

DISCUSSION

Pressure-vessel modeling has been useful historically for particle design, for qualitative understanding of the expected integrity of a pressurized particle with coating layers of varying thicknesses. As discussed below, the quantitative predictions of failure are often too low to permit either validation of the model or confirmation that the expected failure mechanisms are operative in practice.

Beginning with the governing equation for a Weibull failure distribution,

$$\phi = 1 - \exp \left[- \ln 2 \left(\frac{\sigma}{UTS} \right)^m \right], \quad (2.3.2.5)$$

and incorporating the equation for the circumferential (hoop) stress in a spherical shell,

$$\sigma = \frac{rp}{2t}, \quad (2.3.2.6)$$

one can obtain an approximation for the failure function in the form of Eq. (2.3.2.1), with

- σ = circumferential stress on the SiC layer (MPa),
- UTS = ultimate tensile stress of the SiC layer (MPa),
- m = the Weibull parameter,
- r = radius of the spherical SiC shell (m),
- p = pressure inside the SiC shell (MPa),
- t = thickness of SiC shell (m).

The ultimate tensile strength (UTS) of the SiC layer is represented by the median SiC fracture strength (at 50% failure). The recommended values of 350 MPa for the SiC strength and 5 for the Weibull parameter are based on KFA measurements of GA UCO particles, which determined UTS to be approximately 600 MPa and m to be 5 (Myers et al., 1985d; Kovacs et al., 1983; KFA, 1982), thus the exponent of 5 in Eq. (2.3.2.1). A more conservative value of SiC strength was apparently chosen for calculations, to accommodate radiation-induced strength reduction as reported from the German program. General Atomics (1989) recommends instead a value of 7 for m , but does not discuss the origin of this value. Kovacs et al. (1983) also mentioned a value of 7 for m in calculations.

Although PV failure is considered insignificant for modern standard particles (General Atomics, 1989), any phenomenon which weakens the SiC layer would be expected to enhance the potential for PV failure at AC temperatures. For example, the significant thinning of and development of porosity in the SiC layer observed at high temperatures would logically be expected to impact the strength of the SiC layer. The FRG approach of combining these effects with PV-failure calculations would appear to be more consistent than the U.S. approach of terminating all PV model calculations at 1600°C. The U.S. approach is based on the observation that the OPyC layer does not fail when the SiC layer undergoes mechanical failure at high temperatures. Thermal creep reduces the potential for PV failure of the OPyC layer at high temperatures, despite the mechanical failure of the SiC layer.

Some of the "general assumptions" listed for §2.3.2.1 and §2.3.2.2 may appear pedantic, but Goodin in Myers et al. (1985d) discusses some CON*STA calculations which appear to raise some concerns about the accuracy of the calculations. Goodin reported variation in the computational results up to an order of magnitude when the number of Monte Carlo simulations was increased ten-fold and more, although the conditions simulated were apparently the same in both cases. An order of magnitude variation in the results with variation in the number of simulations would normally not be expected with Monte Carlo

simulations and would suggest the need for analysis to resolve this apparent computational contradiction. Any error in calculations would impact the reliability and uncertainty of this PV model.¹

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

A determination of whether the apparent calculational discrepancies in the CON*STA code results are a concern, as mentioned above, or whether revision of CON*STA has eliminated these uncertainties, would be reassuring. The general belief that PV failure was not significant for today's standard particles (General Atomics, 1989; Goodin et al., 1985) would have suggested that reanalysis of the PV model and supporting data would not be a high priority. However, the recent irradiation performance of NPR and NE capsules indicated fuel failures as much as two orders of magnitude higher than preirradiation predictions based on the PV model. Although larger-than-expected OPyC failure fractions may contribute to some enhanced failure, the general validity and reliability of the PV model as presently formulated must be seriously questioned.

DATABASE USED IN MODEL DEVELOPMENT

The database used in development of the PV model is too extensive for discussion here, as this model was used throughout the development of TRISO fuel particles to evaluate the irradiation results, but with varying degrees of success. The only database which will be presented here is that discussed by Kovacs et al. (1983) in comparing CON*STA code calculations with experimental release in several capsule tests. The experimental tests are summarized in Table 2.3.2. In the discussion below, Category I failure refers to failure of a standard intact particle and Category II failure refers to failure of particles with defective SiC layers which are incapable of supporting a tensile load.

For irradiation capsule F-30, Kovacs et al. (1983) comment: "The measurements show a random variation in fuel failure between 0 and 2.1% with no systematic dependence on burnup. If a classical pressure vessel failure mechanism were operating, failure levels would increase exponentially with burnup ... This type of expected behavior is defined by a dashed line in Fig. [2.3.5] and shows that the observations in capsule F-30 are inconsistent with a pressure vessel failure mechanism. The results imply that fuel failure must be attributed to some other cause, namely, manufacturing defects in either the OPyC and/or SiC layer causing premature coating failure. This position is further supported by out-of-reactor temperature ramp tests on irradiated F-30 fuel".

For irradiation capsule GF-4, Kovacs et al. comment: "The predicted gaseous release values are based exclusively on exposed uranium and thorium contamination and assume no contribution from pressure vessel failure during irradiation. This is supported by predicted

¹A conversation with L. H. Menke of EG&G Idaho (1992) suggests the random number generator used in the original CON*STA code may have in fact generated nonrandom numbers, adversely affecting the reliability of the results.

Table 2.3.2. Summary of GA irradiation tests supporting TRISO-coated particle pressure-vessel performance models
(from Kovacs et al., 1983)

Category	Irradiation Test	TRISO-Coated Fuel Types Tested	Irradiation Conditions			Relevance to Pressure Vessel Performance
			Temperature (°C)	Fluence (10^{25} n/m ² (E > 29 eV) _{HTGR})	Burnup (% FIMA)	
Qualification test	HT-34	ThO ₂	1210 to 1440	6.1 to 11.7	6.0 to 13.2	Test thin buffer layers and high burnup
	HRB-16	(8Th,U)O ₂	1140 to 1250	3.4 to 6.0	3.2 to 7.2	Test performance margin in TRISO particles with OPyC layer removed
		UO ₂	1220	5.4	24.5	
		UCO	1275	5.0 to 6.3	24 to 27.6	
Proof test	P13L	UC ₂	1225 to 1275	7.8	73 to 74	Test pressure vessel failure under peak SiC tensile stresses
		UO ₂				
	HRB-15A	ThO ₂	1160	6.5	6.3	Test improvements in performance due to smooth inner SiC layer surface
	F-30	(4Th,U)C ₂	800 to 1250	3.7 to 9.4	12 to 20	Verify that in-pile pressure vessel failure is consistent with performance model predictions
		ThC ₂			1 to 5.7	
	GF-4, Cell II	UC ₂ (HEU)	1020	9.5	77	
		ThO ₂			4.8

Fig. 2.3.5. Estimated fuel failure in F-30 fuel rods vs relative fuel burnup (from Kovacs et al., 1983).

... pressure vessel failure fractions at end of life of $<6 \times 10^{-7}$... Consequently, pressure vessel performance model predictions in cell II of GF-4 are consistent with observed failure levels based on Kr-85m R/B." These results are summarized in Table 2.3.3.

The PV-failure predictions for capsule HT-34 are summarized in Table 2.3.4. The large FP releases were attributed to chemical attack of the SiC layer rather than PV failure. Kovacs et al. conclude "the [Category II pressure vessel failure] predictions are reasonably consistent with the observations with the exception of [one] batch".

The PV failure predictions for capsule HRB-16 are summarized in Table 2.3.5. Kovacs et al. state: "Observed failure fractions exhibited a random fluctuation between 0 and 0.046. No systematic increase in failure with burnup was noted for any of the fuel types ... These observations imply that fuel failure in HRB-16 loose particle trays must be attributed to causes other than pressure vessel failure, possibly manufacturing defects or failure of a small fraction of fuel characterized by low SiC fracture strengths ... Capsule HRB-16 demonstrated that considerable pressure vessel failure performance margin exists for fuel containing one or more of the following defects: no OPyC layers, defective SiC layers, or faceted particles."

The PV failure predictions for capsule P13L are summarized in Table 2.3.6. Kovacs et al. comment: "Observed failure in this batch was 0.6% versus a predicted value of 14.6%. In addition, predicted failure levels for UC_2 fuel in Table [2.3.6] are systematically greater (~20 to 40 times) than observed levels. These disparities may be rationalized on the basis of particle size differences (namely, P13L fuel that was produced at the inception of the HTGR TRISO-coated fuel program had a nominal particle diameter of $\sim 350 \mu m$) ... This is less than half the current reference TRISO-coated particle size ($800 \mu m$). The smaller P13L fuel size could have a higher median SiC fracture strength due to the reduced SiC volume. This would result in lower pressure vessel failure than currently predicted."

The PV failure predictions for particles from capsule HRB-15A are summarized in Table 2.3.7. Kovacs et al. comment: "These observations are reasonably consistent with predictions based on the median fracture strength of 350 MPa ... recommended here."

Several additional analyses were performed on out-of-reactor heating tests. Some of the conclusions were that "the functional form of the failure predictions is not consistent with the observed failure ... regardless of the median SiC fracture strength ... This experiment cannot be explained on the basis of the pressure vessel performance model utilizing a Weibull fracture strength criterion. In order to rationalize this behavior, a bimodal SiC fracture strength distribution would need to be assumed ..." In another test: "Failures at such low temperatures [$\sim 1450^\circ C$] are difficult to rationalize on the basis of an SiC thermal decomposition mechanism, even in fuels heated without the OPyC layer. Consequently, pressure vessel failure appears to be responsible for this premature failure ... The agreement of the model prediction with the data is quite good" provided a SiC fracture strength of 55 MPa is arbitrarily chosen.

Kovacs et al. (1983) summarize the previous discussion in Fig. 2.3.6 and state: "Insufficient irradiation data exist to provide high precision in model predictions; however, the available data plotted in Fig. [2.3.6] tend to indicate a general correlation between predictions and observations."

Table 2.3.3. Summary of irradiation test results for capsule GF-4 (cell 2) containing TRISO-coated UC₂/ThO₂ fuel
(from Kovacs et al., 1983)

Particle Type (Batch Designation)	Number of Particles Tested	Nominal Particle Dimensions (μm)					Irradiation Conditions			Category I Predicted Pressure Vessel Failure Fraction
		Kernel	Buffer	IPyC	SiC	OPyC	Temperature (°C)	Fluence [10^{25} n/m ² (E > 29 fJ) _{HTGR}]	Burnup (% FIMA)	
UC ₂ (6151-17-020) (HEU)	7,500	204	100	35	30	33	1020	9.5	77.2	4×10^{-9}
ThO ₂ (6252-03-010)	16,900	529	63	30	33	37	1020	9.5	4.8	6×10^{-7}
(6252-04-010)		528	63	30	33	39				
(6252-05-010)		519	63	30	33	49				

Table 2.3.4. Summary of irradiation test results for capsule HT-34 containing TRISO-coated ThO₂
(from Kovacs et al., 1983)

Batch Designation 6252-	Nominal Particle Dimensions (μm)					Irradiation Conditions			Failure Fractions(10 ⁻²) Determined By		Predicted Pressure Vessel Failure Fractions	
						Temperature (°C)	Fluence [10 ²⁵ n/m ² (E > 29 fJ) _{HTGR}]	Burnup (% FIMA)	Kr-85m R/B(a)	Cs-137 Release(b)	Category I	Category II(c)
	Kernel	Buffer	IPyC	SiC	OPyC							
14-0261-001	455	27	35	35	40	1210	6.1	6.0	0	5.3	2 x 10 ⁻³	7 x 10 ⁻³
14-0171-001	455	35	32	35	41	1230	6.7	6.7	0(d)	5.3	5 x 10 ⁻⁵	5 x 10 ⁻³
13-0161-001	447	57	32	43	48	1220	7.0	7.0	1.8	21.0	<10 ⁻¹¹	2 x 10 ⁻²
15-0161-001	450	56	36	38	45	1250	7.7	7.9	1.8	7.0	<10 ⁻¹¹	<10 ⁻³
20-0161-002	452	82	40	35	45	1430	9.2	10.5	6.2(d)	97.5	<10 ⁻¹¹	11 x 10 ⁻²
07-0262-002	449	57	39	37	41	1430	9.4	10.9	36(d)	95.0	<10 ⁻⁹	30 x 10 ⁻²
14-0271-001	443	86	35	38	45	1440	9.7	11.6	71(d)	100	<10 ⁻⁹	1.6 x 10 ⁻²
13-0171-001	443	79	32	43	49	1440	10.2	12.7	19(d)	94	<10 ⁻⁹	15 x 10 ⁻²

(a) Based on (R/B)_f for failed fuel of (R/B)_f = 0.0013 + 0.0018 (% FIMA)^{0.9}.

(b) Based on low Cs-137/Zr-95 ratios determined by gamma spectroscopy.

(c) SiC defect fraction equivalent to fraction Cs-137 release.

(d) Determined by visual examination.

Table 2.3.5. Summary of irradiation results for loose particle tests in capsule HRB-16
(from Kovacs et al., 1983)

Loose Particle Tray No.	TRISO-Coated Kernel	Batch Designation	Fuel Description	Irradiation Conditions			Visually Determined Particle Failure Fraction	Category I Predicted Pressure Vessel Failure Fraction
				Temp (°C)	Burnup (% FIMA)	Fluence [10^{25} n/m ² (E > 29 eV) _{HTGR}]		
2	(8Th,U)O ₂	6155-01-030	No OPyC ^(a) ; no SiC defects	1140	3.2	3.4	0.046	4×10^{-13}
3	(8Th,U)O ₂	6155-01-030	No OPyC with SiC defects ^(b)	1140	3.2	3.4	0.037	4×10^{-13}
9	UO ₂	6152-04-010	No OPyC	1223	24.5	5.4	0.000	6×10^{-6}
10	(8Th,U)O ₂	6155-01-030	Parent batch material	1235	6.7	5.7	0.010	1×10^{-8}
11	(8Th,U)O ₂	6155-01-030	No OPyC; no SiC defects	1251	7.2	6.0	0.038	1×10^{-5}
12	(8Th,U)O ₂	6155-01-030	No OPyC with SiC defects	1251	7.2	6.0	0.037	1×10^{-5}
15	UC _{0.5} O _{1.5}	6157-11-010	Parent batch material	1283	27.6	6.3	0.010	5×10^{-5}
16	UC _{0.5} O _{1.5}	6157-11-010	No OPyC; most faceted ^(c)	1284	27.4	6.2	0.010	7×10^{-4}
17	UC _{0.5} O _{1.5}	6157-11-010	No OPyC; nonfaceted	1284	27.4	6.2	0.036	7×10^{-4}
22	UC _{0.5} O _{1.5}	6157-11-010	No OPyC; most faceted	1274	24.1	5.0	0.019	1×10^{-4}
23	UC _{0.5} O _{1.5}	6157-11-010	No OPyC; nonfaceted	1274	24.1	5.0	0.010	1×10^{-4}

(a) OPyC layer burned off of parent batch prior to irradiation.

(b) Detected by mercury intrusion at 69 MPa (10 ksi)

(c) Characterized by particle aspect ratio (maximum/minimum particle diameter) ≥ 1.20 .

Table 2.3.6. Summary description of TRISO-coated fissile particles tested in capsule P13L (from Kovacs et al., 1983)

Batch Designation	Particle Dimensions ^(a)					Irradiation Conditions			SiC Failure Due to Pressure Vessel Effects ^(c) (%)	Category I Predicted Pressure Vessel Failure (%)	
	Fuel Kernel		Buffer Thickness (μm)	Inner Isotropic Thickness ^(b) (μm)	SiC Thickness (μm)	Outer Isotropic Thickness ^(b) (μm)	Temp (°C)	Fast Fluence [10 ²⁵ n/m ² (E > 29 fJ) _{HTGR}]			Burnup (% FIMA)
	Type	Diam (μm)									
4403-143	UC ₂	112	48	24	23	28	1250	7.8	73	0.1	3.76
4413-5	UC ₂	111	49	24	23	24	1250	7.8	74	0.1	3.19
4413-21	UC ₂	109	48	21	21	20	1250	7.8	73	0.2	4.06
4413-7	UC ₂	106	43	14	19	22	1200	7.8	73	3.7	4.20
3516-39	UC ₂	113	56	16	23	20	1225	7.8	73	4.0 ^(d)	1.30 ^(d)
4413-67	UO ₂	117	43	22	23	23	1275	7.8	74	0.6	14.60

(a) Batch mean dimensions.

(b) All carbon layers were low-temperature isotropic (LTI) except as noted in (d).

(c) Measured percent failure was obtained from examination of 2000 to 4000 particles per batch.

(d) 88% of the high-temperature isotropic (HTI) outer PyC layers had failed at end of life.

Table 2.3.7. Summary description of TRISO-coated ThO₂ fuel produced with smooth IPyC layers and tested in capsule HRB-15A (from Kovacs et al., 1983)

Batch Designation 6252-	Nominal Particle Properties (μm)					Irradiation Conditions			Observed Failure Fraction ^(a)	Category I Predicted Failure Fraction ^(b)
	Kernel Diameter	Buffer Thickness	IPyC Thickness	SiC Thickness	OPyC Thickness	Temp (°C)	Fluence [10 ²⁵ n/m ² (E > 29 fJ) _{HTGR}]	Burnup (% FIMA)		
24-010	593	56	19	38	39	1160	6.5	6.2	1.9 x 10 ⁻²	1 x 10 ⁻³
25-010	591	52	31	36	40	1160	6.5	6.3	0	1.5 x 10 ⁻²

(a) Visually determined from loose particle bed of approximately 50 particles.

(b) Based on a median SiC fracture of 350 MPa (51 ksi).

Fig. 2.3.6. Category I predicted vs observed pressure vessel failure fractions (from Kovacs et al., 1983).

In analyzing the results of Kovacs et al. (1983), the following statements appear valid.

1. PV failure is predicted to be insignificant in modern reference fuel particles relative to other modes of FP release.
2. PV failure models are useful for qualitative scoping studies, but do not appear to be reliable for quantitative predictions of FP release.

2.3.3 ALTERNATIVE PHENOMENOLOGICAL MODEL

function	This simplified PV model permits quick semiquantitative analytical predictions of particle performance without the need of computer codes or detailed analysis.
present status	This simple model incorporates the same governing phenomena that the computer code CON*STA employs in the calculations of §2.3.2, but average values are used for layer thicknesses, SiC strength, etc. rather than the variable distributions used by CON*STA. Simple analytical equations are obtained which should approximate the more refined calculations, especially at significant failure levels.
model uncertainty	In general, the model uncertainties should be analogous to those mentioned in §2.3.2, but somewhat larger due to the simplified model used with no consideration of coating and strength distributions.
references	General Atomics (1989); Bramblett (1990); Myers et al. (1985d)

INTRODUCTION

This phenomenological model for pressure-vessel failure of standard (nondefective) particles is very useful for providing quick approximations of internal particle pressures and the likelihood of particle failure under given irradiation conditions. The model would not be as detailed as CON*STA for calculating very small failure probabilities. For estimations of standard particle integrity under a variety of conditions and for comparisons between different particle designs and kernel materials, the model provides useful approximations of particle behavior.

This model has recently been recommended for general particle design and analysis, including the NP-MHTGR design (General Atomics, 1989). As stated by T. E. Serafin in Bramblett (1990), the Monte Carlo calculations of the CON*STA code can be time consuming and costly, thus the use of these simple approximations is often useful.

An additional consideration for the NP-MHTGR design may be the inapplicability of the analytical equations as presented in §2.3.2 above. The model equations as derived from CON*STA results are specific to the NE-MHTGR program particle design. The different kernel and coating dimensions might affect the pressure-vessel behavior of NP-MHTGR

particles. CON*STA calculations for the NP-MHTGR particle design have apparently not appeared in the open literature, thus this simple phenomenological model may be used in its place.¹

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The gas pressure inside the intact SiC layer is first calculated, which gives the resulting hoop stress on the SiC layer and finally the failure fraction as based on a Weibull strength distribution. The gas pressure, P , is given by the ideal gas equation:

$$P = \frac{nRT}{V_v} , \quad (23.3.1)$$

- n = number of moles of gas produced during fission [Eq. (23.3.4) below],
- T = temperature (K),
- V_v = void volume (m³) [Eq. (23.3.2) below].
- R = ideal gas constant (8.313×10^{-6} m³ MPa mol⁻¹ K⁻¹).

The void volume includes contributions from the kernel, $V_{v,k}$ and the buffer, $V_{v,b}$:

$$V_v = V_{v,k} + V_{v,b} = \frac{4}{3} \pi r_k^3 \varrho_k + \frac{4}{3} \pi [(r_k + r_b)^3 - r_k^3] \varrho_b , \quad (23.22)$$

- r_k = kernel radius (m),
- r_b = buffer layer thickness (m),
- ϱ_i = fractional porosity of zone i ($i = k$ or b for kernel or buffer, respectively).

Values commonly used for fractional porosity are 5% for the kernel and 50% for the buffer layer. In terms of the density, ρ , of the kernel and buffer layer, the fractional porosity can be defined as:

$$\varrho_i = 1 - \frac{\rho_i}{\rho_{th,i}} , \quad i = k, b, \quad (23.33)$$

- ρ_i = density of zone i ,
- $\rho_{th,i}$ = theoretical density of the material in zone i .

¹Subsequent to this writing, effort at EG&G Idaho was devoted to providing an improved computer code for PV modeling of NP-MHTGR particles to replace CON*STA. See, e.g., Bennett (1991).

The number of moles of gas produced is given by:

$$n = f_r F \frac{V_k}{V_m} , \quad (2.3.3.4)$$

- f_r = fractional release of gas atoms per fission of kernel material [Eq. (2.3.3.5) below],
 F = fractional burnup (FIMA),
 V_k = kernel volume (m^3),
 V_m = molar volume of heavy metal in the kernel ($\text{m}^3 \text{mol}^{-1}$) [Eq. (2.3.3.6) below].

The fractional release of gas atoms can be represented as:

$$f_r = f_{r,g} f_g + f_{r,o} f_o , \quad (2.3.3.5)$$

- $f_{r,j}$ = fractional release of atoms of species j per fission of kernel material, where $j = g$ for noble gas atoms (Kr, Xe) and $j = o$ for oxygenated gases (CO),
 f_j = fractional yield per fission of species j .

The value of f_g is typically on the order of 0.29 (General Atomics, 1989), while f_o is assumed to be zero for UCO fuels or approximately 0.13 for oxide fuels (Homan et al., 1978). The exact value of f_o may be as high as 0.4 depending on the thermodynamic calculations. For more information on the variation in value of f_o , one can refer to Homan et al. (1977) or, for more experimental detail, to the work of Proksch and Strigl (1982). The values of $f_{r,g}$ and $f_{r,o}$ are conservatively assumed to be 1 (General Atomics, 1989), although Serafin in Bramblett (1990) recommends a value of 0.40 for $f_{r,g}$.

The molar volume of heavy metal in the kernel can be calculated from:

$$V_m = \frac{M_k}{\rho_k} , \quad (2.3.3.6)$$

M_k = molecular weight of the kernel material (g mol^{-1}).

Equation (2.3.3.6) is accurate for typical MHTGR kernel materials such as UCO and UO_2 , in which one mole of kernel material provides one mole of heavy metal atoms. With the kernel material represented as UC_xO_y , the value of M_k can be calculated from:

$$M_k = M_U + 12x + 16y , \quad (2.3.3.7)$$

in which the molecular weight of the heavy metal, M_U , can be calculated as a function of the ^{235}U enrichment fraction, f_e :

$$M_U = 235 f_c + 238 (1 - f_c) \quad (23.3.8)$$

After calculation of the gas pressure from the above equations, the hoop stress, σ , on the SiC layer is calculated from:

$$\sigma = \frac{r_{SiC} P}{2 t_{SiC}} \quad (23.3.9)$$

- σ = stress on the SiC layer (MPa),
- P = gas pressure inside the SiC layer (MPa) [from Eq. (23.3.1) above],
- r_{SiC} = inner radius of the SiC layer (m),
- t_{SiC} = thickness of the SiC layer (m).

The particle failure fraction, ϕ , can then be calculated assuming a Weibull distribution, as discussed previously:

$$\phi = 1 - \exp \left[-\ln 2 \left(\frac{\sigma}{UTS} \right)^m \right] \quad (23.3.10)$$

- UTS = median ultimate tensile strength of the SiC layer (MPa),
- m = Weibull parameter.

The values recommended for calculations (Bramblett, 1990) are 350 MPa for the SiC strength and 5 for the Weibull parameter.

Range of validity

The range of validity of this phenomenological model has not been analyzed although the model in principle can be applied throughout the expected range of temperatures encountered by the fuel, except when SiC structural deterioration is expected (in the range of 1600°C after hundreds of hours, or at higher temperatures after shorter times).

Assumptions

In general, the same assumptions hold as those presented in §2.3.2 ("Normal Operating Conditions") except for those assumptions specifically related to the CON*STA code.

Uncertainty

The uncertainty has not been evaluated. As the uncertainty in the CON*STA code calculations has been given as $\pm 10\%$, the uncertainty for this model can be considered to be $\geq 10\%$.

MODEL CHRONOLOGY

The basic principles of this model have been around for many years. The more detailed computational format presented by Kovacs et al. (1983) dominated PV modelling until the simpler methodology presented here was reevaluated by Myers et al. (1985d). This model was recently restated in this form and recommended for use in calculations by General Atomics (1989) and Bramblett (1990).

DISCUSSION

The model equations presented above are very similar to, but not identical with, the equations presented in the references, and some related model equations were added here for completeness. A few minor errors in definition of terms were discovered in the references, and the presentation above attempts to avoid any such possible confusion.

No consideration of the effect of the OPyC layer in reducing the stress on the SiC layer is considered by this model, although this effect is discussed in other references.

In theory, this phenomenological model should also be applicable to particles with manufacturing defects, if the resulting effects (change in void volume, layer radii and thicknesses, UTS of SiC, etc.) are included in the governing equations. No discussion of this application of the model to manufacturing defects has been located.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The statements made in §2.3.2 related to "Discussion", "Additional Considerations ...", and "Database ..." are in general applicable to this phenomenological model and are not repeated here.

DATABASE USED IN MODEL DEVELOPMENT

The summary statements in §2.3.2, "Database ..." are also generally applicable to this phenomenological model.

2.4 FUNCTIONAL FAILURE OF THE SiC LAYER

2.4.1 INTRODUCTION

Four mechanisms are known which cause the structural deterioration of the SiC layer and result in enhanced FP release. High-temperature thermal decomposition of the SiC is not postulated to be affected by the nuclear environment, while the other three are nuclear-specific: corrosion by interaction with FP, breaching by contact with a migrating kernel (also called the "amoeba" effect), and degradation by the fissioning of heavy-metal atoms dispersed throughout the interior of the particle. High-quality fuels reduce concerns about the last mechanism, and both corrosion and kernel migration are believed to be of little significance for the temperatures and thermal gradients expected in the MHTGR core. Reduction of these concerns has been accompanied by the increasing relative importance of thermal decomposition for SiC failure. Another mechanism for SiC corrosion in oxide fuels has been sporadically mentioned over the years (e.g., Homan et al., 1978): the reaction of SiC with CO gas produced during fissioning of the kernel. However, this mechanism has not been seriously considered since the 1970s and does not enter into existing fuel performance models. The effects of fast neutron damage on SiC have received limited analysis and as a result such effects are not explicitly considered in SiC failure models.

2.4.2 KERNEL MIGRATION

function	This model calculates the distance the kernel migrates within the particle as a function of kernel material, temperature, and thermal gradient across the particle, and the probability of SiC failure due to contact with the kernel.
present status	This fuel failure mechanism was well studied throughout the 1970s and the model parameters derived for most kernel types at that time. Data for UC ₂ kernels are applied to modeling of UCO. Present MHTGR core designs are expected to reduce this mechanism to negligible levels at the temperatures and temperature gradients involved.
model uncertainty	"The uncertainty for this process is known but the process is insignificant in UCO particles and is therefore of little concern" (Myers, 1988).
references	FDDM/F; Kovacs (1981); Lindemer et al. (1977); C. L. Smith (1977); Smith (1974); Gulden (1972)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations: general theory

The following model equations for probability calculations are taken from FDDM/F. The equations for kernel migration coefficients are available from several references. The probability of SiC failure due to kernel migration is calculated from (FDDM/F):

$$P_{KM}(x) = P(\zeta) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\zeta} e^{-u^2/2} du, \quad (2.4.2.1)$$

$$\zeta = \frac{x - m}{\sigma}, \quad (2.4.2.2)$$

- $P_{KM}(x)$ = probability that the migrating kernel comes into contact with the SiC layer (with instantaneous SiC failure upon contact),
 x = migration distance of the kernel (m),
 m = mean value of the (normally distributed) combined thickness of the buffer and IPyC layers (m),
 σ = standard deviation of the normal distribution of buffer/IPyC thickness around the mean m (m).

FDDM/F provides the following values of m and σ for reference LEU UCO fissile particles:

$$\begin{aligned} m &= 150 \mu\text{m} \\ \sigma &= 20.4 \mu\text{m} \end{aligned}$$

and for reference ThO₂ fertile particles:

$$\begin{aligned} m &= 115 \mu\text{m} \\ \sigma &= 14.8 \mu\text{m}. \end{aligned}$$

FDDM/F then comments that the "function $P(x)$ is normally tabulated in computer library routines and can, therefore, be evaluated. If the tabulation is based only on positive values for the argument of P , then:"

$$P_{KM}(x) = 1 - P(|\zeta|), \quad \text{for } x < m, \quad (2.4.2.3)$$

$$P_{KM}(x) = P(|\zeta|), \quad \text{for } x \geq m. \quad (2.4.2.4)$$

"The kernel migration distance is generally small; to avoid possible numerical difficulties in this case, the following approximate expression can be used:"

$$P_{KM}(\chi) = \frac{e^{-\chi^2/2}}{\sqrt{2\pi}} \sum_{i=1}^3 \frac{a_i}{(1+b\chi)^i}, \quad (2.4.2.5)$$

$$\chi = |\zeta|, \quad (2.4.2.6)$$

$$\begin{aligned} a_1 &= 0.43618, \\ a_2 &= -0.12017, \\ a_3 &= 0.93730, \\ b &= 0.33267. \end{aligned}$$

The model equation for kernel migration distance is given by (FDDM/F; Kovacs, 1981):

$$x(t) = \int_0^t K_{MC}(T) \frac{1}{T(\tau)^2} \frac{dT(\tau)}{dx} d\tau, \quad (2.4.2.7)$$

$$\begin{aligned} x(t) &= \text{total migration distance at time } t \text{ (m)}, \\ K_{MC}(T) &= \text{kernel migration coefficient as a function of temperature (m}^2 \text{ K s}^{-1}\text{)}, \\ dT(\tau)/dx &= \text{temperature gradient across the particle at time } \tau \text{ (K m}^{-1}\text{)}, \\ T(\tau) &= \text{average particle temperature at time } \tau \text{ (K)}, \\ t &= \text{total time for particle irradiation/heating conditions (s)}. \end{aligned}$$

The evaluation of the kernel migration coefficient is specific to the kernel material.

Model equations: fissile particles

The expression for LEU UCO fuel is assumed to be (Kovacs, 1981):

$$K_{MC}(T) = 0.62 \exp\left(-\frac{3.11 \times 10^5}{RT}\right), \quad (2.4.2.8)$$

$$\begin{aligned} K_{MC}(T) &= \text{kernel migration coefficient (m}^2 \text{ K s}^{-1}\text{)}, \\ T &= \text{temperature (K)}, \\ R &= \text{ideal gas constant (8.314 J mol}^{-1} \text{ K}^{-1}\text{)}. \end{aligned}$$

Model equations: fertile particles

ThO₂ kernels in TRISO particles are assumed to migrate in agreement with the data derived for ThO₂ BISO particles. An incubation time, θ , has been observed during which no migration occurs ($K_{MC} = 0$) if (Kovacs, 1981; C. L. Smith, 1977):

(1) kernel burnup is less than 2% FIMA, and

$$(2) \quad \sum_i \frac{t_i(T_i)}{\theta_i(T_i)} < 1, \quad (24.2.9)$$

θ_i = incubation time at temperature T_i (s),

t_i = time interval at temperature T_i (s),

T_i = temperature (K).

The incubation time at temperature T_i is calculated from:

$$\theta_i = 4.7 \times 10^{-4} \exp \left(\frac{3.16 \times 10^5}{RT_i} \right). \quad (24.2.10)$$

all variables defined as above.

After the incubation time the ThO₂ kernel migration coefficient is calculated from (C. L. Smith, 1977):

$$K_{MC}(T) = 0.39 \exp \left(-\frac{2.96 \times 10^5}{RT} \right), \quad (24.2.11)$$

all variables defined as above.

Range of validity

The model is assumed to apply to all reactor operating conditions. Apparently the migration of UCO kernels has not been quantified from experimental data as "migration has not been observed for UCO ..." (FDDM/F). The experimental data used in modelling the migration of UCO kernels was apparently obtained for HEU UC₂ kernels, and the data used in modelling the migration of ThO₂ kernels was apparently obtained for ThO₂ kernels in BISO particles.

Assumptions

1. The SiC fails instantaneously upon contact with the migrating kernel.
2. No failure of the OPyC layer by the migrating kernel is considered.
3. The expression for K_{MC} for LEU UCO kernels is assumed to be the same as that for LEU UC₂ kernels.

4. The expression for K_{MC} for LEU UC_2 kernels is assumed to be the same as that for HEU UC_2 kernels.
5. ThO_2 kernels in TRISO particles are assumed to migrate at rates comparable to the measured rates for ThO_2 kernels in BISO particles.
6. The combined thickness of the buffer and IPyC layers is assumed to be normally distributed around the mean combined thickness.

Uncertainty

FDDM/F states that the uncertainty for the fraction of particles, F_D , "with intact OPyC layers, failed SiC layers and implicitly, failed IPyC and buffer layers" is given by the standard deviation of $\ln F_D$:

$$\sigma(\ln F_D) = 1.4 \quad (2.4.2.12)$$

In practice, if kernel migration is not believed to be significant for the MHTGR then the uncertainty in the model is not of practical significance.

MODEL CHRONOLOGY

Kernel migration has long been recognized to be a serious concern for fuel particles exposed to large thermal gradients. C. L. Smith (1974) reports that kernel migration has been recognized in UC_2 fuel since the early 1960s. The use of UC_2 in the Fort St. Vrain reactor and the large thermal gradients inherent in the LHTGR core designs stimulated the analysis and modeling of kernel migration. By the late 1970s model equations had been developed for kernel migration of the common fuels, based on averaging of the available test data to obtain a temperature- and gradient-normalized gross transport parameter called the kernel migration coefficient. As HTGR designs became smaller and predicted thermal gradients decreased, both experiments and models suggested kernel migration should be insignificant for the current reference designs for the MHTGR.

Equations (2.4.2.7) through (2.4.2.11) are well established in the literature, but Eqs. (2.4.2.1) through (2.4.2.6) apparently originate in an internal GA memorandum referenced by FDDM/F.

DISCUSSION

Heating of BISO and TRISO particles at high temperatures in a thermal gradient stimulates gross transport of the kernel up the temperature gradient, depositing carbon in its wake on the colder side. This kernel migration mechanism (often called the "amoeba" effect) has long been known to limit fuel integrity by kernel penetration through the coating layers, resulting in the loss of FP containment. The mechanism for kernel migration of carbide fuels is known to involve the thermal-gradient-induced solid-state diffusion of carbon down the temperature gradient and through the kernel (Gulden, 1972). The mechanism for kernel migration in oxide fuels is not as certain, although the final result of mass transport

of carbon to the cool side of the kernel is the same. A detailed discussion of the proposed mechanisms for kernel migration in oxide fuels is given by Lindemer et al. (1977) and will not be repeated here. Lowering the oxygen potential of the fuel by adding oxygen getters or buffers is known to reduce the migration of oxide kernels (Homan et al., 1978), but the specific mechanism by which oxygen enhances migration can only be speculated on beyond being a solid-state diffusion process and related to oxygen exchange between CO and CO₂.

A recent summary of fuel performance models relevant to the NP-MHTGR design (General Atomics, 1989) states: "For the time and temperature conditions of the NPR fuel, the kernel migration coefficient (*KMC*) is calculated to be:

$$KMC = 6.0 \times 10^{-11} \text{ m}^2 \text{ K s}^{-1} , \quad (2.4.2.13)$$

for oxide fuel and

$$KMC = 9.17 \times 10^{-13} \text{ m}^2 \text{ K s}^{-1} , \quad (2.4.2.14)$$

for carbide fuel [referring to UO₂ and UC₂ respectively]. The UCO particle exhibits migration at least as slow as UC₂ fuel. In fact, the UCO kernels have shown no measurable migration in tests comparable to MHTGR service conditions ...The calculations indicate that particle failure by kernel migration is negligible ($< 10^{-6}$) and is not a factor for the in-reactor or accident condition performance of the NPR driver fuel." No further details are provided for these calculations. Although no equation for the kernel migration coefficient of UO₂ is given by FDDM/F, an equation is given by Kovacs (1981) which may have been used to calculate Eq. (2.4.2.13).

Figure 2.4.2.1 (from Stansfield et al., 1983) indicates the relative insignificance of kernel migration for present MHTGR designs.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

If all analyses suggest that kernel migration is insignificant for modern fuels under MHTGR-like conditions and that "UCO kernels have shown no measurable migration in tests comparable to MHTGR service conditions," then further analysis of this model is not warranted without evidence to the contrary.

DATABASE USED IN MODEL DEVELOPMENT

Gulden (1972) derived the theoretical model for kernel migration and presented experimental data for the migration of UC₂ disks coated with PyC. C. L. Smith (1974) summarized the in-pile and out-of-pile data on the migration of UC₂ kernels (Fig. 2.4.2.2), and C. L. Smith (1977) reported analogous experiments for the migration of ThO₂ kernels (Figs. 2.4.2.3 through 2.4.2.5). Lindemer et al. (1977) summarized similar work on fissile oxide kernels through 1977 (mostly mixed thorium-uranium oxides and some carbide data). Figure 2.4.2.6 shows data for the migration of UO₂ kernels (Kovacs, 1981).

Fig. 2.4.2.1. Thermal design basis for kernel migration (from Stansfield et al., 1983).

Fig. 2.4.2.2. Kernel migration coefficient vs inverse temperature determined from out-of-pile thermal gradient testing of irradiated and unirradiated UC₂ fuel particles (from Smith, 1974).

Fig. 2.4.2.3. Variation in kernel migration coefficient with $1/T$ for ThO_2 kernels having burnups in the range 0.9 to 5.8% FIMA (from C. L. Smith, 1977).

Fig. 2.4.2.4. Comparison of in-pile and out-of-pile ThO_2 data (from C. L. Smith, 1977).

Fig. 2.4.2.5. Variation in incubation time with inverse temperature for ThO_2 kernels having burnups of 0.9 and 1.5% FIMA (from C. L. Smith, 1977).

Fig. 2.4.2.6. Kernel migration coefficient data from testing of UO_2 fuels (from Kovacs, 1981).

2.4.3 FISSION PRODUCT CORROSION

function	This model calculates the probability of SiC layer failure due to corrosion by fission products as a function of thermal and irradiation conditions.
present status	This model is ambiguous in its relevance for MHTGR modeling, as most corrosion data are not relevant to MHTGR conditions (i.e., obtained under large thermal gradients). The model presented here was derived for an AC model in 1985, but a 1989 revision of this AC model dropped consideration of corrosion as a SiC failure mechanism at AC temperatures. The 1985 model parameters have been retained by FDDM/F and are presented below. Despite the ambiguity of the model, the reduced significance of the model should make further model revision a low priority.
model uncertainty	"The uncertainties associated with these processes are large and the mechanisms of them are poorly known for the structural environment and imposed conditions of interest" (Myers, 1988).
references	FDDM/F; Goodin et al. (1985); Montgomery et al. (1982b)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The model for calculating the probability of SiC failure, P_{SR} , resulting from FP-induced corrosion incorporates the Weibull parameter and a kinetic term for the frequency of SiC/FP reaction [FDDM/F; T. E. Serafin in Bramblett (1990)]:

$$P_{SR} = 1 - 2^X, \quad (243.1)$$

$$X = (-\Delta_{SR})^{m_{SR}}, \quad (243.2)$$

$$\Delta_{SR} = \int_0^t k_{SR}[T(\tau), t] d\tau, \quad (243.3)$$

- m_{SR} = Weibull parameter (dimensionless),
 k_{SR} = frequency factor of SiC/FP reactions (h^{-1}),
 T = temperature (K),
 t = time interval for irradiation or heating (h),
 τ = time variable (h).

The frequency factor is given by:

$$k_{SR}[T(\tau), t] = G[T(\tau), t] \exp\left(-\frac{Q}{RT(\tau)}\right), \quad (2.4.3.4)$$

$$G[T(\tau), t] = G_o[T(\tau), t] + |G_{\max} - G_o[T(\tau), t]| g(\Omega), \quad (2.4.3.5)$$

$$g(\Omega) = \frac{\exp\left[-\frac{b}{1 + (0.01 \Omega)^n}\right]}{1 + \exp[-a(\Omega - \Omega_{init})]}, \quad (2.4.3.6)$$

$$G_o[T(\tau), t] = A_{SR} T_{irr}^a f_{SiC}^b, \quad (2.4.3.7)$$

Ω	= thermal gradient across the coated fuel particle ($K m^{-1}$),
Ω_{init}	= thermal gradient at $(G_o + G_{\max})/2$ ($K m^{-1}$); i.e., an approximation for the average gradient across the particle during the irradiation,
T_{irr}	= irradiation temperature (K),
f_{SiC}	= fission density within the volume enclosed by the SiC layer (fissions m^{-3}),
Q	= activation energy ($J mol^{-1}$),
R	= ideal gas constant ($8.314 J mol^{-1} K^{-1}$),
$T(\tau)$	= temperature (K),
a	= constant ($m K^{-1}$),
A_{SR}	= constant [$(K^{-a} (fissions m^{-3})^{-b})$],
$G_{\max}, n, b, \alpha, \delta$	= constants (dimensionless).

FDDM/F presents Eq. (2.4.3.6) incorrectly due to a transcription error; see Martin (1993) for discussion.

FDDM/F goes on to state: "During a sequence in which an accident is preceded by a period of normal operation, the total probability is calculated, using Eqs. [2.4.3.1] through [2.4.3.7], as the sum of (1) P_{SR} for the period of normal operation and (2) P_{SR} for the period during which an accident has been in progress. For the period of normal operation, set $T(\tau) = T_{irr}$ and choose the appropriate value of Ω and for the accident period, choose the appropriate value of $T(\tau)$ and set $\Omega = 0$. When $\Omega = 0$, the second term of Eq. [2.4.3.5] is negligible in comparison with the first term, $G_o[T(\tau), t]$."

The values of the model parameters are as follows:

m_{SR}	= 1.6
A_{SR}	= $7.24 \times 10^{-34} K^{-3} (fissions m^{-3})^{-1}$ for UCO and UC_2
	= $1.07 \times 10^{-33} K^{-3} (fissions m^{-3})^{-1}$ for ThO_2

α	=	3.0
δ	=	1.0
Q	=	$2.52 \times 10^5 \text{ J mol}^{-1}$
a	=	$2.2 \times 10^{-4} \text{ m K}^{-1}$
b	=	10.0
G_{max}	=	1.49×10^4
n	=	1.3
Ω_{init}	=	$1.0 \times 10^4 \text{ K m}^{-1}$

Range of validity

Although the model is stated to apply to both normal and accident conditions (FDDM/F), the model parameters were specifically derived for an AC model (Goodin et al., 1985). Refer to Tables 2.4.3.1 through 2.4.3.2 from Goodin et al. (1985) for the experimental range of the source data used in the derivation of the model. Goodin et al. (1985) indicate that only isothermal heating data were used in the model derivation rather than the more abundant data for thermal gradient tests. The data were separated into categories based on oxide vs carbide fuels and the fission density was used as a variable for normalization of the different particle dimensions. The use of these model equations is recommended for the range of f_{SiC} between 0.1×10^{27} and 2.0×10^{27} fissions m^{-3} and for the irradiation temperature range of 700 to 1500°C.

Goodin (1989) concludes that this model may not be applicable at temperatures above 1600°C, a regime in which thermal decomposition of the SiC is now believed to be the dominant SiC failure mechanism.

Assumptions

1. The measured cesium release is assumed to be identical to the SiC failure fraction.
2. The above statement implies an assumption that cesium does not diffuse in significant amounts through intact SiC, even at AC temperatures.
3. As no separate model is presented for FP corrosion in fertile particles, one might tentatively assume the model is valid for both fissile and fertile particles.

Uncertainty

FDDM/F states that the uncertainty for the fraction of particles, F_D , "with intact OPyC layers, failed SiC layers and implicitly, failed IPyC and buffer layers" is given by the standard deviation of $\ln F_D$:

$$\sigma(\ln F_D) = 1.4 \quad (2.4.3.8)$$

Table 2.4.3.1. Description of oxide TRISO fuel samples used for SiC corrosion study (from Goodin et al., 1985)

Irradiation Conditions										
Sample Identification No.	Type	Kernel Diameter (μm)	Location	Average Temperature (°C)	Time EPPD	Exposure (10 ²⁵ n/m ²) (E > 29 fJ)	Burnup (X FIMA)	f _{SIC} Fission Density (10 ²⁷ m ⁻³)	log k (h ⁻¹) (From Experiment)	Fitted log k _o (h ⁻¹)
EO 1674	(Th,U)O ₂	496	R2-K13/1	1170	517	8.3	10.3	0.68	3.68 ^(a)	2.34
AVR 70/26	(Th,U)O ₂	500	AVR 15	700	590	1.2	8.2	0.52	<3.16 ^(a)	2.71
AVR 70/7	(Th,U)O ₂	500	AVR 15	700	520	1.0	7.3	0.46	<4.25 ^(b)	2.66
AVR 70/15	(Th,U)O ₂	500	AVR 15	700	505	1.0	7.1	0.45	<4.41 ^(a)	2.65
AVR 69/13	(Th,U)O ₂	500	AVR 15	700	610	1.2	8.6	0.54	<3.87 ^(a)	2.73
Bullock data	UO ₂	300	HRB-15B	915	169	4.5	22	0.80	3.27	3.16
EUO 2308	UO ₂	497	IFR-K3/1	1175	359	3.9	7.9	0.52	3.00	3.23
Fitted expression	log k _o (h ⁻¹) = -32.97 + 3.0 log T _{irr} (K) + log f _{SIC} n = 3.3									

^(a) Upper limits not used in fitting.

Table 2.4.3.2. Description of carbide TRISO fuel samples used for SiC corrosion study (from Goodin et al., 1985)

Sample Identification No.	Type	Kernel Diameter (μm)	Location	Irradiation Conditions					log k (h ⁻¹) (From Experiment)	Fitted log k _o (h ⁻¹)
				Average Temperature (°C)	Time EFPD	Exposure (10 ²⁵ n/m ²) (E > 29 fJ)	Burnup (% FIHA)	f _{SiC} Fission Density (10 ²⁷ m ⁻³)		
1600°C heating										
4161-01-032-02	UC ₂	233	PI3P	1350	201	6.1	61	1.9	3.91	3.77
4161-01-034-2	UC ₂	176	PI3P	1420	201	6.0	60	1.2	3.62 ^(a)	3.63
4161-01-030	UC ₂	203	FTE-14	1000	377	1.2	23	0.6	<3.54 ^(a)	2.95
1800°C heating										
4161-01-030	UC ₂	203	FTE-14	1000	377	1.2	23	0.6	<2.92 ^(a)	2.95
4161-01-032-02	UC ₂	233	PI3P	1350	201	6.1	61	1.9	3.45	3.77
2000°C heating										
4161-01-030	UC ₂	203	FTE-14	1000	377	1.2	23	0.6	2.95	2.95
4161-01-034-2	UC ₂	176	PI3P	1420	201	6.0	60	1.2	3.88	3.62
Fitted expression	log k _o (h ⁻¹) = -33.14 + 3.0 log T _{irr} (K) + log f _{SiC} n = 3.3									

(a) Upper limits not used in fitting.

MODEL CHRONOLOGY

The most recent model incorporating a SiC corrosion mechanism is provided by the 1985 US/FRG model (Goodin et al., 1985), and this model is presented above. An earlier model derived reaction rates for the thinning of the SiC layer by palladium and assumed SiC failure when reaction had progressed through one-half the thickness of the SiC layer. These models will not be discussed, but can be pursued using the summary provided by Stansfield et al. (1983b).

Although this model was specifically developed as an AC model in 1985, the 1989 US/FRG model revision dropped corrosion as a significant SiC failure mechanism at AC temperatures, leaving the model in an ambiguous state. FDDM/F also references a document by B. F. Myers ("Update of Accident Condition Models," General Atomic Document No. 908776/1, 1986) which may be the source of Eqs. (2.4.3.5) and (2.4.3.6).

DISCUSSION

Background

Fissioning of uranium and plutonium produces FP which can attack and corrode the SiC layer, with loss of integrity under appropriate conditions of temperature, thermal gradient, and burnup. Of greatest concern are lanthanide and palladium FP. Carbide fuels readily release lanthanides, enhancing SiC corrosion. The oxide fuels retain the lanthanides in the kernel in the form of oxides, thus reducing SiC corrosion. Palladium is readily released from these fuels, resulting in SiC corrosion in all types of fuels (General Atomics, 1989). Corrosion by Pd is a greater concern in LEU fuel than in HEU fuel because the larger fraction of Pu fissions in LEU fuel generates more Pd atoms per fission, which can then concentrate into nodules and attack the SiC. The thermal gradient affects corrosion by preferential directional transport and concentration of FP species at the SiC surface, rather than random transport to the SiC.

Myers (1988) comments on the mechanisms of the FP-SiC interaction. "This consists of the reaction of fission products with the SiC and of the decomposition of SiC. The uncertainties associated with these processes are large and the mechanisms of them are poorly known for the structural environment and imposed conditions of interest. In the former case, a rate expression, meant to describe the reaction of the SiC, is based only on measurements, and in a selected plane at that, of the reduction in thickness of the SiC layer."

Model development

Stansfield et al. (1983b) present details of the corrosion process and presented an equation for the rate of corrosion across the SiC layer as obtained by Montgomery et al. (1982b):

$$\dot{X} = 2.613 \times 10^5 \exp \left(- \frac{2.522 \times 10^5}{8.314 T} \right) , \quad (2.4.3.9)$$

$\dot{X}$ = rate of advance of the corrosion zone across the SiC layer ($\mu\text{m/h}$),
 T = temperature (K).

The activation energy for corrosion in Eq. (2.4.3.9) is the same as that recommended for use in Eq. (2.4.3.4).

In the 1985 US/FRG AC fuel performance model (Goodin et al., 1985) the measured cesium release is assumed to be identical to the SiC failure fraction, ϕ . This failure fraction is equated to the compound distribution of SiC layer thickness and SiC degradation rate using the Weibull distribution:

$$\phi = 1 - 2^{-(kt)^m} , \quad (2.4.3.10)$$

k = corrosion frequency factor (h^{-1}),
 t = heating time (h),
 m = Weibull parameter.

The value $m = 3.3$ is used for single test batches of particles, and $m = 1.6$ is recommended when considering corrosion data from all the available test batches. This latter value of m corresponds to that recommended by FDDM/F. The frequency factor is represented by an Arrhenius-type equation:

$$k = k_0 \exp \left(- \frac{Q}{RT} \right) , \quad (2.4.3.11)$$

k_0 = pre-exponential constant (h^{-1}),
 Q = activation energy for corrosion (J mol^{-1}),
 T = temperature (K),
 R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

The detailed equation for the frequency factor is given by (Goodin et al., 1985):

$$k = (10^{-A} \cdot T_{irr}^3 \cdot f_{SiC}) \exp \left(- \frac{30300}{T} \right) , \quad (2.4.3.12)$$

T_{irr} = irradiation temperature (K),
 T = heating temperature (K),
 f_{SiC} = fission density (fissions m^{-3} inside the SiC layer),
 A = 32.97 for oxide fuel, 33.14 for carbide fuel.

The values of the parameters in the equation above are identical with the model parameters presented previously for Eqs. (2.4.3.1) through (2.4.3.7). Significant extrapolation is required to obtain k_p from the available range of Cs release data available. An introduction to the methodology used to derive the model parameters by Goodin et al. (1985) can be obtained from inspection of Fig. 2.4.3.1.

General Atomics (1989) comments on the relevance of FP corrosion as a failure mechanism for the NP-MHTGR design: "SiC corrosion distances may be estimated ... Even if the thermal gradient is assumed to be 200°C/cm, the calculated failure fraction is still quite small ($<1 \times 10^{-5}$)." Additional information on the declining importance of FP corrosion as an AC mechanism for SiC failure can be obtained from §2.4.4.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

With FP corrosion not predicted to be a significant concern for MHTGR conditions, further evaluation of this model does not appear to warrant high priority. The limited understanding of the reaction mechanisms involved would make any effort at model revision more difficult. The lack of attention to the potential effects of oxygen activity on the reactivity of FP and SiC is not reassuring, as several statements on the significance of the effects of oxygen and of oxygen-enhanced corrosion can be found in the literature.

DATABASE USED IN MODEL DEVELOPMENT

Much of the database used in derivation of the model is presented in Tables 2.4.3.1 through 2.4.3.2. The data used to derive the rate of corrosion of Eq. (2.4.3.9) are shown in Fig. 2.4.3.2 (from Montgomery et al., 1982b). Additional corrosion rate data are presented in Fig. 2.4.3.3 (General Atomic, 1979).

2.4.4 SiC THERMAL DECOMPOSITION

function	This model calculates the time-dependent high-temperature failure of the SiC layer as a function of temperature and irradiation conditions.
present status	This mechanism is dominant for SiC failure under high-temperature accident conditions, and was recently postulated to dominate at temperatures down to 1600°C. The model is based on an activation energy for vaporization of the silicon, with kinetic factors introduced empirically. The state of experimental knowledge and level of uncertainty for this important AC mechanism is wanting.
model uncertainty	"[T]he loss of SiC from exposed surfaces has been measured but the conditions of interest have not been addressed. Within a particle, the decomposition of SiC involves not only the process of decomposition but

Fig. 2.4.3.1. Example of simultaneous least squares curve fitting with two GA and two KFA fuel testing results. The fitting is designed to provide a single best value of slope (m) and a best value for k_0 for each test (from Goodin et al., 1985).

Fig. 2.4.3.2. Temperature dependence of fission product - SiC reaction in HTGR fuel using data from out-of-pile tests and real time irradiations (from Montgomery et al., 1982b).

Fig. 2.4.3.3. Variation in SiC - fission product reaction rate with inverse temperature assumed for TRISO MEU UC_2 (from General Atomic, 1979).

also the transport of the decomposition products away from the site; thus carbon and silicon transport in the SiC and surrounding coatings is important. There is little hope that a better understanding of these processes will be obtained" (Myers, 1988). That is, unless additional experimental and modelling effort is made toward this understanding.

references Goodin (1989); Goodin et al. (1985); Benz (1982)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

In particle heating tests, the measured cesium release is assumed to be identical to the SiC failure fraction, ϕ . This failure fraction is equated to the compound distribution of SiC layer thickness and SiC degradation rate using a Weibull distribution (Goodin, 1989):

$$\phi = 1 - 2^{-(kt)^m}, \quad (2.4.4.1)$$

k = decomposition frequency factor (h^{-1}),
 t = heating time (h),
 m = Weibull parameter.

The value $m = 2$ is used for calculations involving heating tests, while $m = 1.7$ is recommended for predicting overall core performance. The frequency factor is represented by the Arrhenius equation:

$$k = k_0 e^{-Q/RT}, \quad (2.4.4.2)$$

k_0 = pre-exponential constant (h^{-1}),
 Q = activation energy for corrosion (J mol^{-1}),
 T = temperature (K),
 R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

The frequency factor is calculated using the expression:

$$k = 5.029 \times 10^{-4} e^{-65540/T} \max(f_{\text{SiC}}^{2.09} \cdot T_{\text{irr}}^{0.041} \cdot T_{\text{irr}}^{4.14}, 2.74 \times 10^{14}), \quad (2.4.4.3)$$

f_{SiC} = fission density (10^{26} fissions m^{-3} inside the SiC layer),
 T_{irr} = irradiation temperature (K),

Γ = fast fluence (10^{25} n m⁻², $E > 0.1$ MeV).¹

The *max* in Eq. (2.4.4.3) specifies the use of the maximum of the two terms within the parentheses. If the heating temperature varies, the product kt in Eq. (2.4.4.1) is replaced by:

$$kt \rightarrow \int_0^t k[T(\tau, t)] \cdot d\tau, \quad (2.4.4.4)$$

t = time interval for heating (h),

τ = time variable (h).

Range of validity

Although the model is derived from data obtained only at 1600°C and above, the model could be considered applicable also at NOC temperatures because the temperature dependence will render the model insignificant at lower temperatures. Also, FDDM/F does not explicitly limit the range of validity of an earlier model derived using the same methodology.

The above equations are derived using Cs release data from particles with UO₂ kernels. The activation energy for thermal decomposition used in Eq. (2.4.4.2) is derived from the data of Benz (1982) for heating of unirradiated particles with oxide kernels but with the OPyC layer removed.

Assumptions

1. The measured cesium release is assumed to be identical to the SiC failure fraction.
2. The above statement implies an assumption that cesium does not diffuse in significant amounts through intact SiC, even at AC temperatures.
3. SiC corrosion by FP is insignificant relative to thermal decomposition above 1600°C.
4. The activation energy for thermal decomposition of bare SiC (no OPyC layer) is representative of that for sealed SiC in intact particles.
5. The activation energy for thermal decomposition of irradiated SiC should not change from that of unirradiated SiC.
6. The kinetics of SiC decomposition are independent of the kernel type and of the oxygen potential within the particle.
7. Oxygen-enhanced SiC decomposition at temperatures below 1600°C is not significant.

¹This 0.1 MeV cutoff energy for evaluating fast neutron fluence is standard for the German program, but a 0.18 MeV (29 fJ) cutoff is used as a standard by the U.S. program. For a given reactor, the fast fluence based on 0.10 MeV is a factor of approximately 1.15 larger than that based on 0.18 MeV (Myers, 1984e).

Uncertainty

The uncertainty of the model is stated in terms of the standard deviation of the logarithm of the SiC failure, F (Goodin, 1989):

$$\sigma(\log F) = 0.64 \quad (2.4.4.5)$$

However, this uncertainty analysis assumes that the postulated functional dependencies and activation energies are correct, based on the results of a data fit. The methodology used to convert sphere release data to particle release data also introduces a significant level of uncertainty, and the actual irradiation temperatures are often highly variable compared to those assumed in calculations. As a result, the stated value for model uncertainty must be considered to be overly optimistic.

MODEL CHRONOLOGY

FDDM/F presents the same model equations but different model parameter values than those presented above. The values presented here are based on a more recent AC model revision (Goodin, 1989) with a much larger database than that used in the derivation of the model referenced by FDDM/F (Goodin et al., 1985).

It is interesting to note that the thermal decomposition mechanism for SiC failure was rarely mentioned until the early 1980s. For example, C. L. Smith (1977) attributed SiC decomposition at 2000°C to FP corrosion. Stansfield et al. (1983a) did not discuss a thermal decomposition mechanism in 1983 but did in 1985 (Stansfield et al., 1985). References to this decomposition mechanism within the U.S. program prior to Goodin (1983) are not common.

DISCUSSION

The modeling approach to SiC thermal decomposition is similar to that of SiC corrosion as presented in the 1985 US/FRG AC fuel performance model (Goodin et al., 1985) (see §2.4.3). The 1989 US/FRG model revision assumed that SiC corrosion is insignificant relative to thermal decomposition at AC temperatures and rederived the coefficients for the governing equations. The 1985 version of this model (Goodin et al., 1985) considered two mechanisms for SiC failure: (1) corrosion of SiC by FP and (2) high-temperature thermal decomposition of SiC. Above 2000°C thermal decomposition was known to be the dominant mechanism for SiC failure, but at the lower AC temperatures characteristic of the MHTGR (~1600°C) and in the range 1600 to 2000°C SiC corrosion was believed to be the primary limiting mechanism for fuel integrity.

As pointed out in D. T. Goodin's 1987 reevaluation of the model (Goodin, 1987), the assumption of the corrosion model was based on earlier corrosion studies of U.S. TRISO particles which employed large thermal gradients (Montgomery, 1981a). Earlier U.S. designs for the 2240-MW(t) LHTGR included significant thermal gradients across the fuel, and the large thermal gradients chosen for the corrosion tests accelerated the FP attack on SiC and

reduced the times required for corrosion experiments. According to Goodin (1987), during derivation of the 1985 version of the US/FRG model the magnitude of corrosion was decreased to better approximate the reduced maximum temperatures expected in the MHTGR, but the activation energy for corrosion obtained from the earlier thermal gradient tests was retained in the model.

Subsequent to the 1985 version of the US/FRG model, newly-available AC simulation heating data on reference FRG fuels became available. In rederiving the model parameters to approximate these new data, the 1989 version of the US/FRG model determined an activation energy for thermal decomposition very close to that obtained experimentally by Benz (1982) and reported by Nabielek et al. (1989) (see Fig. 2.4.4.1). In addition, recent metallography of reference FRG fuels heated to 1600°C for extended times (Schenk et al., 1988) did not show significant corrosion similar to the earlier U.S. tests (C. L. Smith, 1977), but rather showed development of porosity which is more characteristic of SiC decomposition (Goodin, 1987).

As a result of these considerations, the US/FRG model (1989) concluded that SiC thermal decomposition is the dominant SiC degradation mechanism throughout the temperature range of 1600°C and above and gave no further consideration to FP-induced corrosion of SiC as an important mechanism in AC modeling of the performance of modern TRISO fuels.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The activation energy for SiC thermal decomposition was determined by Benz (1982) using particles without an OPyC layer. A SiC layer which is sealed by surrounding PyC layers is known to decompose more slowly than one which is exposed to the atmosphere. A question naturally arises as to how well the results obtained by Benz actually reflect the reality of an intact particle with unexposed SiC.

Goodin (1989) places great emphasis on the agreement of his derived activation energy with that obtained experimentally by Benz (1982). However, the use of a single activation energy for a complex reaction is not necessarily valid. For example, G. W. Castellan (*Physical Chemistry*, 2d ed., Addison-Wesley, 1971, pp. 758-759) comments that a multi-step process may need to incorporate the activation energies of each step into a net activation energy, with pre-exponential factors similarly combined. In such a situation, the understanding of the mechanisms involved in a reaction then becomes important. An assumption that a single activation energy can be used to represent a reaction over all conditions is not necessarily justified.

Any future experimental examination of the effects of heating and irradiation on the SiC microstructure would be very helpful in formulating a refined kinetic model of SiC decomposition which might consider the applicability of nucleation theory and of the extensive non-HTGR scientific literature on SiC. The potential effects of oxygen on SiC decomposition might be considered as briefly discussed in §11.3 and in more detail by Martin (1990).

A comment by Myers (1986) that a Weibull distribution can also be used to model chemical reactions raises the possibility of coupling the kinetics of SiC decomposition with

Prediction For US Fuel: 16% FIWA, Fluence Of
 $4.0 \times 10^{25} \text{ n/m}^2/\text{s}$, Irradiation Temperature Of 1000C

Fig. 2.4.4.1. Comparison of frequency factors for failure (from Goodin, 1989).

the Weibull formulation already used in this model. Such an approach holds promise for a more mechanistic and phenomenological approach to modelling SiC microstructural evolution than a failure model based only on SiC strength considerations.

DATABASE USED IN MODEL DEVELOPMENT

Table 2.4.4.1 presents the SiC thermal decomposition data of Benz (1982) as reported by Nabielek et al. (1989), and Fig. 2.4.4.2 represents the derivation of the experimental activation energy for SiC decomposition. Tables 2.4.4.2 through 2.4.4.4 represent the database used in the derivation of the model presented here.

2.4.5 HEAVY-METAL DISPERSION

function	This model attempts to quantify in a simplistic way the enhanced particle failure observed for particles with fissionable material dispersed between the kernel and SiC layer, often associated with defective IPyC layers.
present status	The existing model for failure of the SiC layer from excessive heavy-metal dispersion is very approximate, with failure related to nonquantitative radiographic observations of dispersion (i.e., excessive heavy-metal dispersion is either present or it is not present). Present fuel production methods have reduced dispersion to a level of minor concern for the performance of reference fuel particles.
model uncertainty	The magnitudes of heavy-metal dispersion involved have not been quantified. Although the uncertainties are large, the "dispersion of uranium and thorium is not of significance in particles fabricated in present production facilities" (Myers, 1988).
references	Kovacs (1981); Stansfield et al. (1983a); Goodin (1984a)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The probability of SiC failure due to excessive heavy-metal dispersion, P_{HM} , is given by (Kovacs, 1981; Goodin, 1984a):

$$P_{HM} = 0.5 f_b, \quad (2.4.5.1)$$

Table 2.4.4.1. Determination of SiC structure and SiC layer thinning due to thermal decomposition on unirradiated coated particles from a large number of coating batches (OPyC layer removed) (from Nabielek et al., 1989)

Particle Designation	SiC Coating Process Data		SiC Structure		SiC Thinning Rate ($\mu\text{m/h}$)		
	Temperature ($^{\circ}\text{C}$)	Deposition Rate ($\mu\text{m/min}$)	Microstructure ^a	Secondary Phase ^b	66 h, 2000 $^{\circ}\text{C}$	24 h, 2100 $^{\circ}\text{C}$	7 h, 2200 $^{\circ}\text{C}$
HOBEG Particles							
EO 249-51	1450	0.5	C	FTr	0.13 ± 0.04	0.62 ± 0.12	2.0 ± 0.8
EO 403-5	1490	0.62	L	Tr	0.25 ± 0.13	0.67 ± 0.12	1.6 ± 0.5
DO 474 k	1600	1.0	C	---	0.10 ± 0.02	0.43 ± 0.07	1.4 ± 0.6
DO 475 k	1600	1.0	C	W	0.24 ± 0.06	0.77 ± 0.07	3.0 ± 0.6
DO 576-8	1550	---	L	---	0.28 ± 0.04	---	---
EO 740-1	1500	---	C	---	0.14 ± 0.02	0.85 ± 0.14	3.3 ± 0.7
EO 819-20	1500	---	C	---	0.13 ± 0.02	---	---
EC 1338-9	---	---	C	Tr	0.31 ± 0.10	0.72 ± 0.02	3.7 ± 0.7
ECO 1541	---	---	C	---	0.12 ± 0.05	1.3 ± 0.3	2.2 ± 1.0
EUO 1551	---	---	C	---	0.40 ± 0.10	1.7 ± 0.1	4.6 ± 0.3
EO 1607	---	---	C	---	0.15 ± 0.03	0.62 ± 0.11	1.7 ± 0.5
EO 1674	---	---	C	---	0.29 ± 0.08	1.2 ± 0.2	2.7 ± 0.5
KFA Institut für Reaktorwerkstoffe Particles							
SPA ₃ UASiC ₅ O							
2277	1550	0.50	C	W	0.39 ± 0.06	1.7 ± 0.3	4.2 ± 0.3
2278	1505	0.54	C	---	0.30 ± 0.05	1.8 ± 0.2	4.1 ± 0.2
2279	1400	0.42	C	Tr	0.15 ± 0.03	1.5 ± 0.2	3.6 ± 0.8
2280	1400	0.45	C	---	0.23 ± 0.03	1.2 ± 0.3	4.0 ± 0.4
2282	1300	0.46	FG	Tr	0.26 ± 0.05	0.85 ± 0.03	3.3 ± 0.5
2283	1300	0.38	L	Mod	---	1.3 ± 0.2	3.5 ± 0.4
2289	1500	0.50	C	Tr	0.22 ± 0.04	1.8 ± 0.1	3.3 ± 0.4
2290	1580	0.54	C	Tr	0.50 ± 0.04	2.0 ± 0.1	2.4 ± 0.6
GA Particles							
6157-11-010	1650	0.26	C	---	0.24 ± 0.05	---	1.6 ± 0.2
6157-11-020	1650	0.25	C	FTr	0.31 ± 0.04	---	1.8 ± 0.1
6252-12T-04A	1650	0.33	C	FTr	0.22 ± 0.06	---	1.7 ± 0.1
6252-12T-04B	1650	0.33	C	FTr	0.24 ± 0.05	0.74 ± 0.18	1.8 ± 0.4
6252-12T-Comp.	1650	0.32	C	FTr	0.21 ± 0.05	---	1.6 ± 0.2

^aIn this column C = columnar microstructure, L = laminar microstructure, and FG = fine grains too small to identify any grain habit optically.

^bReflections from a disordered component located near the strongest reflections of β -SiC are described as FTr for a faint trace diffuse film darkening, Tr for a greater trace of diffuse darkening, W for a still greater diffuse darkening, and Mod for the identification of additional reflections associated with α -SiC.

Fig. 2.4.4.2. The SiC removal rate from TRISO-coated particles follows an Arrhenius temperature dependence. Experiments at KFA Jülich were performed with unirradiated particles after the OPyC layer had been burned off (from Nabielek et al., 1989).

Table 2.4.4.2. Comparison of observed and calculated k values for spheres irradiated in the AVR (from Goodin, 1989)

AVR Sphere No.	Fission Density (x E26)	Fluence (x 10 ²⁵ n/m ²)	Irradiation Temperature (K)	k-Value Observed	k-Value Calculated
70/33	1.1	0.2	(a)	1.29E+11	1.38E+11
71/7	1.2	0.2	(a)	3.40E+10	1.38E+11
73/12	2.1	0.4	(a)	1.30E+11	1.38E+11
74/10	3.8	0.8	(a)	6.45E+11	1.38E+11
74/11	4.3	0.9	1090	3.98E+10	(b)
76/18	4.9	1.9	1390	1.48E+11	(b)
80/22	6.3	2.4	1400	2.57E+11	(b)
82/20	5.9	2.2	1535	3.31E+11	(b)
82/9	6.1	2.3	1430	2.62E+11	(b)

(a) Irradiation temperature are calculated from the AVR sphere heating results and the fitted model, these calculated temperatures were unreasonably high and indicate either in-reactor failure or temperature exposures outside of the usable range of the fitted model.

(b) The observed k -values are used to determine the irradiation temperature and thus the calculated values fit the observed values exactly, the minimum k -value allowed by the model is 1.38E+11.

Table 2.4.4.3. Comparison of observed and calculated k values for spheres and compacts irradiated in capsules (from Goodin, 1989)

Sphere or Compact No.	Fission Density (x E26)	Fluence (x 10 ²⁵ n/m ²)	Irradiation Temperature (K)	k-Value Observed(a)	k-Value Calculated
HFRP4 1/12	7.3	5.5	1173	1.76E+11	1.74E+11
HFRP4 1/8	9.1	7.2	1173	2.82E+11	2.80E+11
HFRP4 2/8	9.5	7.2	1173	2.73E+11	3.06E+11
HFRP4 3/7	9.2	7.5	1323	4.47E+11	4.72E+11
HFRP4 3/12	7.9	5.5	1323	3.73E+11	3.39E+11
HFRK3/3	6.7	6.0	1273	2.33E+11	2.05E+11
FRJ2K13/4	5.0	0.1	1373	1.08E+11	1.29E+11
R2K13/1	6.8	8.3	1373	2.40E+11	2.94E+11
FRJ2K13/2	5.3	0.1	1473	2.17E+11	1.95E+11

(a) $k = 5.029E-04 e^{-65540/T_K} f_{sic}^{2.09} f_{lue}^{0.041} T_i(K)^{4.14}$.

Table 2.4.4.4. Irradiation and particle parameters for spheres irradiated in capsules and used in model revision
(from Goodin, 1989)

Irradiation Experiment	Particle Type	Particle Batch No.	Kernel		Buffer		IPyC		SiC		OPyC		Irradiation Conditions			Total Cs-137 Integration Over Sphere Volume
			Diameter (μm)	Density (Mg/m^3)	Thick (μm)	Density (Mg/m^3)	Thick (μm)	Density (Mg/m^3)	Thick (μm)	Density (Mg/m^3)	Thick (μm)	Density (Mg/m^3)	Burnup (% FIMA)	Fast Fluence (n/m^2 , $E > 0.1 \text{ MeV}$)	Temperature ($^{\circ}\text{C}$)	
FRJ2-K13/2	UO ₂ TRISO	EUO-2308	497	10.81	94	1.0	41	--	36	3.20	40	1.88	8.0	0.1×10^{25}	1000 to 1200	--
FRJ2-K13/4	UO ₂ TRISO	EUO-2308	497	10.81	94	1.0	41	--	36	3.20	40	1.88	7.6	0.1×10^{25}	1000 to 2000	1.4×10^{-1}
HFR-K3/1	UO ₂ TRISO	EUO-2308	497	10.81	94	1.0	41	--	36	3.20	40	1.88	7.7	3.9×10^{25}	1000 to 1200	6.3×10^{-4}
HFR-K3/3	UO ₂ TRISO	EUO-2308	497	10.81	94	1.0	41	--	36	3.20	40	1.88	10.2	6.0×10^{25}	800 to 1000	4.2×10^{-2}
SL-P1,6	UO ₂ TRISO	EUO-2308	497	10.81	94	1.0	41	--	36	3.20	40	1.88	10.7	6.7×10^{25}	790	--
SL-P1,10	UO ₂ TRISO	EUO-2308	497	10.81	94	1.0	41	--	36	3.20	40	1.88	10.3	6.0×10^{25}	790	--
HFR-P4,1.8	UO ₂ TRISO	EUO-2308	497	10.81	94	1.0	41	--	36	3.20	40	1.88	13.8	7.2×10^{25}	900	--
HFR-P4,1.12	UO ₂ TRISO	EUO-2308	497	10.81	94	1.0	41	--	36	3.20	40	1.88	11.1	5.5×10^{25}	900	--
HFR-P4,3.7	UO ₂ TRISO	EUO-2308	497	10.81	94	1.0	41	--	36	3.20	40	1.88	13.9	7.5×10^{25}	1050	--
HFR-P4,3.12	UO ₂ TRISO	EUO-2308	497	10.81	94	1.0	41	--	36	3.20	40	1.88	12.0	5.5×10^{25}	1050	--
HFR-P4,2.8	UO ₂ TRISO	EUO-2309	497	10.81	93	1.00	37	--	51	3.20	38	1.87	13.8	7.2×10^{25}	900	--
R2-K13/1	UO ₂ TRISO	EUO-1674	496	10.10	89	1.06	37	1.90	33	3.19	39	1.90	10.3	8.3×10^{25}	1200	1.2×10^{-3}

$$f_b = \frac{F}{F_{max}} \quad , \quad (2.4.5.2)$$

f_b = fractional burnup,
 F = burnup (% FIMA),
 F_{max} = maximum burnup.

For fissile particles, $F_{max} = 26\%$ FIMA. For fertile particles, $F_{max} = 7\%$ FIMA.

The probability of SiC failure as given by this model is shown in Figure 2.4.5.1, taken from Stansfield et al. (1983a). This model is reproduced in FDDM/F.

Range of validity

The model as stated is applicable for fissile fuel burnups $\leq 26\%$ FIMA and fertile fuel burnups $\leq 7\%$ FIMA and is therefore applicable only for low-enriched fissile fuels. The model is applicable to those particles with "significant" heavy-metal dispersion, although this criterion has not been quantified. The experimental range of the data relevant to this model is unknown.

Assumptions

1. One is able to specify what constitutes "excessive" HM dispersion (i.e., the threshold for "excessive").
2. Failure due to HM dispersion has no significant dependence on temperature or other irradiation conditions.
3. Failure due to HM dispersion has no significant quantitative dependence on the concentration of chlorine inside the SiC layer.
4. The model was apparently derived for non-UCO fuels; therefore, one must assume the effects of HM dispersion do not significantly vary with type of fuel or kernel behavior under manufacture or irradiation.

Uncertainty

The uncertainty inherent in this model has not been quantified. Quantification of "significant" HM dispersion has not been stated, which introduces significant uncertainty into the model. The general uncertainty statement of FDDM/F is applicable here: the uncertainty for the fraction of particles, F_D , "with intact OPyC layers, failed SiC layers and implicitly, failed IPyC and buffer layers" is given by the standard deviation of $\ln F_D$:

$$\sigma(\ln F_D) = 1.4 \quad . \quad (2.4.5.3)$$

Fig. 2.4.5.1. Defective particle model for failure resulting in only metal release (from Stansfield et al., 1983a).

MODEL CHRONOLOGY

Kovacs (1981) presented Eq. (2.4.5.1) in its present form as valid for LEU fissile fuels up to 26% burnup. Stansfield et al. (1983a) presented missing/defective IPyC layers and excessive HM dispersion as two separate categories, but considered both to lead to identical failure probabilities (i.e., both fail linearly with increasing burnup to a maximum of 50% failure for maximum burnup). Goodin (1984a) extended the model of Eq. (2.4.5.1) to fertile fuels by using a value of 7% FIMA for F_{max} in Eq. (2.4.5.2). FDDM/F restates the model without change. The origin of the model prior to Kovacs (1981) is unknown to this writer.

DISCUSSION

Excessive HM dispersion describes the transport of fissionable HM atoms (uranium and thorium) into the buffer and IPyC layers during particle fabrication. Heavy-metal dispersion is sometimes correlated with missing IPyC layers during the manufacturing process. The IPyC layers prevent the intrusion of chlorine into the kernel and buffer regions during the chemical vapor deposition (CVD) of the SiC layer. The presence of chlorine at the kernel is believed to enhance the chemical reactivity of the kernel material and increase the dispersion of the kernel material outward toward the SiC layer. Heavy-metal dispersion has two deleterious effects on SiC layer integrity: (1) any generated FP are transported rapidly to the inner SiC surface, thus increasing the active FP concentration at the SiC (i.e., enhancing FP corrosion of the SiC), and (2) FP recoil atoms from the fissioning of HM atoms near the SiC can be very damaging to the SiC microstructure. With SiC integrity compromised, further fissioning of the dispersed HM acts to enhance ^{85}Kr release relative to that of a simple exposed kernel.

Heavy-metal dispersion falls under the category of "missing or defective" coatings, and should be distinguished from HM contamination which is considered to occur by damage to the coatings during coating and fuel compact manufacturing which exposes the kernels and disperses HM contaminant over the surfaces of particles and the fuel compact matrix. Heavy-metal dispersion and HM contamination can be distinguished as HM impurities inside vs HM impurities outside the SiC layer of the fuel particles, respectively, or as undamaged vs damaged SiC layers prior to irradiation. Heavy-metal dispersion does not initially degrade fuel performance, but it results in premature failure of the SiC layer during the operating lifetime of the fuel.

Because the projected effect of HM dispersion is so severe for particle failure under NOC (i.e., 50% failure at end-of-life), any additional AC effects would be insignificant by comparison. No discussion of HM dispersion in relation to AC modeling has been located.

General Atomics (1989) does not mention HM dispersion as a failure mechanism for the NP-MHTGR program, but Serafin in Bramblett (1990) does mention this mechanism in relation to the NE-MHTGR program.

This writer does not know where this model actually came from or from what irradiation data or capsule tests it was developed. None of the references mentioned above provide any further reference on the origin of this model, thus any range of validity or estimate of uncertainty is impossible to determine beyond that presented above, and detailed

analysis of the model is impossible. Because of the simple linear relationship on burnup and the maximum failure probability of 50% postulated for both fissile and fertile fuels and the failure to provide any quantification of HM dispersion, it appears likely that a very approximate model was developed to account for greatly enhanced failure in particles lacking an intact IPyC layer or those whose radiographs exhibit poor retention of HM atoms within the kernel before the start of irradiation.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Lacking information on the database used in the derivation of this model, some questions arise. Was the relevant data obtained under conditions of significant thermal gradients representative of LHTGR simulations and if so, would these conditions enhance the SiC failure relative to the smaller thermal gradients representative of MHTGR conditions? Was any data obtained from fertile fuel particles, or was the model assumed to apply to both fissile and fertile particles in lieu of available data?

In general, the database used in the derivation of this HM dispersion model needs to be located and evaluated to better assess the validity of this model and the conditions under which the data were obtained. However, significant effort on evaluation of this model cannot be justified unless there is some evidence that HM dispersion will be a concern for MHTGR fuels.

DATABASE USED IN MODEL DEVELOPMENT

The database used in the development of this model is unknown.

2.5 IRRADIATION-INDUCED STRUCTURAL FAILURE OF THE OPyC LAYER

function	This model attempts to quantify in a simplistic way the observed irradiation-induced failure of the OPyC layers as a function of fast neutron fluence.
present status	Although the model states an upper limit for the PyC failure fraction, the interpolation used to approach that limit appears to be open to question. The accuracy of the model with respect to modern fuels is not known from the available evidence.
model uncertainty	The current model assumes failure occurs with increasing fast fluence only until exposure to a specified value of fast fluence, with no subsequent failure beyond that value. It seems reasonable that "those OPyC layers which do not fail are surely also affected by the irradiation and presumably become more porous ... Clearly a large uncertainty exists here..." (Myers, 1988).

references Kovacs et al. (1985); Goodin (1984a); Kovacs et al. (1980); Harmon et al. (1975)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

For standard TRISO particle designs, the maximum OPyC failure fraction is assumed to be 0.03 (Kovacs et al., 1985; Myers, 1988). The failure is assumed to occur early in the irradiation cycle, with failure complete when the fast fluence reaches $2.0 \times 10^{25} \text{ n m}^{-2}$. Available references indicate some debate over the nature of the failure function up to this maximum, but FDDM/F recommends a model which assumes a linear increase in the failure fraction: "The probability of failure of the OPyC layer in particles with or without SiC layers by irradiation-induced effects, P_{OP} , is given by":

$$P_{OP} = 0.015 \gamma_n, \quad \gamma < 2.0 \times 10^{25} \text{ n m}^{-2} (E > 29 \text{ fJ})_{HTGR}, \quad (25.1)$$

$$P_{OP} = 0.03, \quad \gamma > 2.0 \times 10^{25} \text{ n m}^{-2} (E > 29 \text{ fJ})_{HTGR}, \quad (25.2)$$

γ = fast neutron fluence [n m^{-2} , $(E > 29 \text{ fJ})_{HTGR}$],

γ_n = normalized fast neutron fluence ($\gamma/10^{25}$, dimensionless).

Range of validity

The model is assumed to apply over the entire range of reactor operating conditions. The experimental range of some of the associated data is mentioned in "Discussion" below.

Assumptions

1. The maximum failure fraction for the OPyC layer under all irradiation conditions is 0.03.
2. The failure fraction increases linearly from 0% failure at the beginning of irradiation to 3% failure at a fast neutron fluence of $2.0 \times 10^{25} \text{ n m}^{-2} (E > 29 \text{ fJ})_{HTGR}$.
3. The accumulation of fast neutron fluence above $2.0 \times 10^{25} \text{ n m}^{-2} (E > 29 \text{ fJ})_{HTGR}$ has no effect on OPyC failure.
4. The irradiation temperature has no significant effect on the rate or magnitude of OPyC failure.

Uncertainty

FDDM/F makes no statement of uncertainty applicable to this model. Myers (1988) suggests a large uncertainty exists for this model.

MODEL CHRONOLOGY

This model has been stated in several forms with different values of maximum failure and different postulated dependencies of failure on fast neutron fluence, but the maximum failure is never postulated to exceed a few percent.

DISCUSSION

Irradiation-induced failure of the OPyC layer has been observed during normal irradiation and is believed to be due to the effects of the fast fluence. Because of the high-temperature stability of the PyC layers, no additional contribution to OPyC failure from this mechanism is postulated under AC, thus no separate AC model is presented.

Harmon et al. (1975) and Kovacs et al. (1985) provide some detailed discussion of the effects of microporosity, particle size, and increasing anisotropy during irradiation which induces greater strain within the OPyC structure. These references can be reviewed for the theory relevant to this model.

The maximum failure fraction is typically stated to be 3%, although others (Goodin, 1984a; Stansfield et al., 1983b) have stated the maximum failure fraction to be on the order of 1%. Different formulations of the failure function have been advocated. Goodin (1984a) gives an analytical expression exponentially dependent on temperature and linearly dependent on burnup and also makes reference to a previous analysis which assumed OPyC failure to be independent of temperature. Goodin (1984a) states: "the present data base is insufficient to determine the functional relationship [of failure to burnup]. Since most of the data has been acquired at high burnups, the linear assumption is more conservative than an exponential assumption in the intermediate burnup range."

Kovacs et al. (1980) comment on some of the relevant data: "[Capsule] GF-2 results imply that OPyC failures occur early in life at fluences $< 2.8 \times 10^{25} \text{ m}^{-2}$ ($E > 29 \text{ fJ}$)_{HTGR}. This observation is consistent with a much larger base of empirical data ... The impact of temperature on OPyC failures has been documented for other capsules ... and the general trend appears to be a marked increase in OPyC failure between 1000 and 1350 C for a given fast fluence exposure ... One batch exhibited a correlation between OPyC failure and fluence. This correlation, which is summarized in Fig. 2.5.1, shows OPyC failure increasing linearly with fluence ... OPyC failures occur early in life ... This is attributed to peak irradiation-induced stresses that develop in the pyrocarbon layer due to rapid densification and strain anisotropy." Kovacs et al. (1980) describe the OPyC failure in each of the capsules GF-1, GF-2, and GF-3, with OPyC failure as high as 40% in one of the capsules.

Kovacs (1981) comments: "The fraction of fuel with irradiation induced failed OPyC layers is independent of fluence above $2.0 \times 10^{25} \text{ m}^{-2}$ ($E > 20 \text{ fJ}$)_{HTGR} [sic] and increases linearly from zero to the maximum X_f value of 0.01 ... with fluences between 0 and $2.0 \times 10^{25} \text{ m}^{-2}$."

For capsule HRB-14, Young (1980) commented that the fissile particles exhibited good OPyC performance (0 to 4.6% failure) but that the fertile particles exhibited 1.5 to 29.1% failure, and that "failure was generally higher for the samples exposed to the higher

Fig. 2.5.1. Correlation between OPyC failure (determined visually) and fluence for TRISO-coated loose particle batch 6155-00-010 (from Kovacs et al., 1980).

temperatures and fluences." Inert particles used in the capsule experiments exhibited very high failures, from 28 to 100%.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

This writer has not evaluated the data in sufficient detail to suggest possible refinement of the model. As the OPyC failure fractions sometimes vary significantly between different experiments, the maximum failure fraction postulated by this model should be confirmed using MHTGR-specific data. Temperature-dependent data could also be considered for the effects of irradiation temperature on OPyC failure, as mentioned above.

DATABASE USED IN MODEL DEVELOPMENT

Some of the relevant database was discussed above, such as that presented in Fig. 2.5.1. The references mentioned above should be reviewed for more detailed information on the relevant database.

2.6 UPDATE

Several references have been suggested whose contents would be relevant to this chapter, in particular with regard to the Japanese approach to and models of fuel performance. These references have not been reviewed by this writer and are mentioned for informational purposes and as relevant to future document revision.

Benz, R., R. Förthmann, H. Grübmeier, and A. Naoumidis, "Fission-Product Behavior in Irradiated HTR Fissile Particles at High Temperature," IAEA-SM-236/19, IAEA Symposium on Thermodynamics of Nuclear Materials, Jülich, FRG, Jan. 29 - Feb. 2, 1979, pp. 565-585.

Goodin, D. T., "Accident Condition Performance of Fuels for High-Temperature Gas-Cooled Reactors," *J. Am. Ceram. Soc.*, 65 (1982) 238-242.

Kovacs, W. J., "Gaseous Fission Product Release Predictions in TRISO HTGR Fuel Particles," *J. Am. Ceram. Soc.*, 65 (1982) 154-157.

Fukuda, K., and K. Iwamoto, "Diffusion and Evaporation of Fission Products in Coated Fuel Particles," *J. Nucl. Sci. Technol.*, 12 (1975) 181-189.

Kikuchi, T., T. Tobita, and I. Katsuichi, "Uranium Contamination in Coating and in Matrix Material of Unirradiated Coated Particle Fuel," *J. Nucl. Sci. Technol.*, 21 (1984) 233-242.

Fukuda, K., K. Minato, and K. Ikawa, "Coating Failure of VHTR Reference Fuel by Irradiation," *J. Nucl. Sci. Technol.*, 20 (1983) 584-592.

Ogawa, T., and K. Fukuda, "Performance of the Model Fuel Pin of the Very High-Temperature Gas-Cooled Reactor at Temperature Above 2000°C," *Nucl. Eng. Design*, 92 (1986) 15-26.

Minato, K., and K. Fukuda, "Structure of chemically vapour deposited silicon carbide for coated fuel particles," *J. Mater. Sci.*, 23 (1988) 699-706.

Minato, K., and K. Fukuda, "Chemical Vapor Deposition of Silicon Carbide for Coated Fuel Particles," *J. Nucl. Mater.*, 149 (1987) 233-246.

A summary of models used by Japan and other members of the international HTGR community can be obtained from Verfondern et al. (1993).

The fractional OPyC failure observed in NPR and HRB-21 irradiation capsules was unexpectedly large (typically >50%) and bore no resemblance to the reference model of 3%. The explanation suggested is that cracks from the PPyC and seal coat layers propagated into the OPyC layer, although this is contrary to the assumptions initially used to justify the deposition of a seal coat between the OPyC and PPyC layers.

The stoichiometry of NPR UCO kernels has been observed to vary from all UO_2 to all UC_2 . Kernels with UO_2 ratios above the nominal value will generate CO gas at some point during capsule irradiation, in contradiction to the assumptions of the PV model for fuel with nominal UCO stoichiometry.

"Gold spots" have been observed at the percent level in SiC layers which are attributed to free silicon "soot" deposited during coating. The reference SiC decomposition model should not be valid for these particles because of enhanced vaporization of silicon at high temperatures.

Although refined PV codes were developed at EG&G Idaho as part of the NP-MHTGR program (Bennett, 1991), the four recent irradiation capsule results, with fuel failure fractions orders of magnitude larger than predicted, brings serious doubt on the reliable use of the reference fuel performance models. The final data and analysis of the PIE results for NPR and HRB-21 capsules will be relevant for further analysis.

Another effort at refined PV failure approximations was undertaken at EG&G Idaho as part of the code/model validation effort. This effort by C. Lee and W. D. Wagner included some analysis related to the assumption of a rigid SiC layer. Whether this analysis was completed or documented is unknown to this writer.

The derivation of models for SiC corrosion and thermal decomposition from, primarily, German fuel data raises questions as to the appropriateness of the use of these models for U.S. fuel, considering the significant differences observed in Cs retention at 1600° for the two fuels (Martin, 1993a).

3. FUEL COMPACT DESIGN AND PERFORMANCE MODELS

3.1 INTRODUCTION

No accident-condition-specific models have been developed to describe the performance of the fuel compacts, thus one model describes compact performance under both NOC and AC.¹ Most compact performance models were originally developed by the mid-1970s on the basis of UC₂-fueled particles. Many of the recent model equation revisions presented here are discussed in internal GA memoranda which have not been reviewed; therefore, comment on some of these model derivations is limited. Most of these revisions appear to be based on numerical approximations of the data using polynomial series; therefore, the writer assumes that many of these recent model revisions are based on the original 1970s-era data and that comments on the original model derivations are generally applicable to the recent model revisions.

The volumetric and dimensional changes of the fuel compact are a concern in relation to their interaction with the surrounding graphite block, both mechanically and thermally. If the graphite block shrinks more than the fuel compacts, compression of the compacts could result in the possibility of crumbling of the compacts and loss of structural integrity. The relative shrinkage of the compacts and the graphite block can also vary the size of the gap between them, thus affecting the thermal transport properties across the fuel hole gap. Previous discussion (Scott et al., 1977) of relative shrinkage of compact vs. core graphite suggests that compact dimensional changes should not be a mechanical concern, with compact shrinkage greater than the core graphite shrinkage, although the change in the initial gap dimensions may be a thermal concern.

As an historical note, the HTGR literature used the terminology of fuel rod in reference to what is now called the fuel compact. For example, the 1985 report on irradiation capsule R2-K13 (Myers et al., 1985c) discussed the irradiation performance of fuel rods. The terminology of fuel compact was introduced within the last decade to differentiate the MHTGR fuel element design from that of the light-water reactors.

¹No information on the effect of moisture ingress on fuel compact mechanical and thermal properties has been located except the limited information presented in §11 on hydrolysis and oxidation of the bulk material.

3.2 FUEL COMPACT VOLUMETRIC AND DIMENSIONAL CHANGES

3.2.1 FUEL COMPACT VOLUMETRIC CHANGE

function	This model calculates the compact's volumetric change as a function of temperature, fast neutron fluence, and graphite shim content. The result is used to determine the compact's dimensional changes (§3.2.2).
present status	A recent model revision appears to apply linear interpolation and extrapolation to 1970s-era data at two temperatures and two shim contents, obtaining analytical equations covering temperature and shim content ranges not included in the original data sets.
model uncertainty	Quantification of the uncertainty is not presented in the open-literature discussions of this model, and apparently has not been determined at this time. An unknown degree of uncertainty arises from the smaller diameters of the NP-MHTGR fuel particles relative to those in the compacts from which the data was obtained, and from the limited experimental temperature range (950 to 1250°C) relative to NP-MHTGR conditions.
references	FDDM/F; Kovacs (1981); General Atomic (1977a)

Model equations

The volumetric change of the fuel compact during irradiation, $\hat{V}$, is defined as the relative change in volume:

$$\hat{V}(\%) = \frac{\Delta V}{V} . \quad (3.2.1.1)$$

ΔV = change in compact volume (arbitrary units),

V = original compact volume (units consistent with ΔV).

The model equation for percent volumetric change as a function of fast neutron fluence, graphite shim content, and temperature is given in FDDM/F as:

$$\hat{V}(S_v, T) = \sum_{i=1}^4 (\alpha_i + \beta_i S_v + \delta_i S_v T) \gamma^{i-1} , \quad (3.2.1.2)$$

S_v = volume fraction of graphite shim in the compact,

T = temperature (K),

γ = fast neutron fluence [10^{25} n m⁻², (E > 29 fJ)_{HTGR}],

$\alpha_i, \beta_i, \delta_i = \text{constants, for } i = 1, 2, 3, 4.$

The values for the coefficients are given in Table 3.2.1.1, taken from FDDM/F. The source reference given in FDDM/F for this model is an internal GA memorandum which has not been reviewed by this writer.

Range of validity

FDDM/F does not mention any limitation on the use of this model, but only states that the model equation "represents a linear interpolation and extrapolation based on volumetric changes corresponding to the three sets of S_v and T values" (i.e., 30% shim at 950 and 1250°C, and 0% shim at 950°C). An earlier model presented by Kovacs (1981) is based on data representing the same experimental parameters, therefore likely the same data as that used in the model revision. Kovacs also states that the 1981 model equations can be used to extrapolate over the full range of core conditions, based on the assumptions given below. Of particular relevance to the NP-MHTGR design is Kovacs' statement that the "fuel [compact] dimensional change in an HTGR core containing TRISO coated fissile and fertile fuel nominally 800 μm in diameter with a 40 μm thick OPyC layer is presented." According to General Atomics (1989), the NPR driver particle will have a nominal diameter of 635 μm (725 μm if the low-density outer protective layer is included). As stated, the model equation given above is therefore not directly applicable to NP-MHTGR compacts without further analysis. FDDM/F, in discussing dimensional changes in fuel particles, refers to a 635 μm particle, but such particles would induce volumetric changes in a compact different from that by particles with low-density PPyc coatings.

Assumptions

Assumptions 1 through 3 are explicitly stated by Kovacs (1981) and are probably applicable to the recent model revision which also "represents a linear interpolation and extrapolation based on volumetric changes corresponding to the three sets of S_v and T values," which are identical to the values presented by Kovacs.

Table 3.2.1.1. Coefficients for use in the model equation for the volumetric change in fuel compacts under irradiation, Eq. (3.2.1.2) (from FDDM/F)

Coefficient	$i = 1$	$i = 2$	$i = 3$	$i = 4$
α_i	-0.3930	-1.769	0.3334	-0.01500
β_i	1.351	11.09	-2.263	0.1221
δ_i	-5.556×10^{-5}	-8.678×10^{-3}	1.678×10^{-3}	-8.889×10^{-5}

1. The volumetric change for fuel compacts without graphite shim particles has no dependence on temperature.
2. The temperature dependence of volumetric swelling for compacts with 30 v/o shim is obtained by interpolation between the curves for ≤ 950 and 1250°C .
3. The dependence of volumetric swelling on shim content between 0 and 30 v/o (volume %) is obtained by interpolation between the respective curves for $\leq 950^\circ\text{C}$.

Application of the model equation to NP-MHTGR fuel compacts introduces another important assumption: use of different-sized particles in NP-MHTGR compacts (and NP-MHTGR-specific particle loadings) will not quantitatively affect the dimensional change of the compacts.

Uncertainty

Apparently no determination of the uncertainty has been made for the fuel compact dimensional change model, as none is mentioned in FDDM/F.

MODEL CHRONOLOGY

As stated, the recent model revision explicitly extends the ranges of temperature and graphite shim content beyond those of the experimental data. The earlier model presented by Kovacs (1981) only provides analytical equations for the three data sets, without interpolation and extrapolation. This earlier model is presented below.

DISCUSSION

The existing model for the volumetric change of the fuel compacts during irradiation is an extension of the previous model (Kovacs, 1981) of three polynomial equations given for different fuel to shim volumetric ratios and different temperatures. The volumetric change for compacts with 28 v/o fuel and 30 v/o shim, at temperatures $\leq 950^\circ\text{C}$, was given as (Kovacs, 1981):

$$\hat{V} = -0.008 - 1.626 \gamma + 0.27 \gamma^2 - 0.011 \gamma^3, \quad (3.2.1.3)$$

for compacts with 28 v/o fuel and 30 v/o shim at 1250°C :

$$\hat{V} = -0.013 - 2.407 \gamma + 0.421 \gamma^2 - 0.019 \gamma^3, \quad (3.2.1.4)$$

and for compacts with 58 v/o fuel and no shim, at temperatures $\leq 950^\circ\text{C}$:

$$\hat{V} = -0.02 - 2.09 \gamma + 0.41 \gamma^2 - 0.022 \gamma^3, \quad (3.2.1.5)$$

$\hat{V}$ = relative volumetric change of the fuel compact during irradiation,
 γ = fast neutron fluence [10^{25} n m^{-2} , $E > 29 \text{ fJ}$]_{HTGR}].

The parametric curves for this older model, as given by Eqs. (3.2.1.3), (3.2.1.4), and (3.2.1.5), are shown in Figure 3.2.1.1, taken from Kovacs (1981). Note the representation of the fast neutron fluence by the symbol ϕ in this older figure.

More recent data on dimensional changes of fuel compacts were obtained from Capsule R2-K13 (Myers et al., 1985c). These data were compared to predictions based on the model presented in Kovacs (1981), Eqs. (3.2.1.3) through (3.2.1.5), and the results presented in Fig. 3.2.1.2. Better agreement was obtained for the radial dimensional change for cell 3 than for cell 2. The poorer agreement for the axial dimensional change was attributed to the failure to measure the compact lengths after curing and before irradiation, thus requiring estimation of their initial lengths.

The concern was mentioned in "Range of validity" that the diameters of NP-MHTGR particles are expected to vary from those on which the model equations were based. General Atomic (1977a) discusses the dimensional changes of fuel particles during irradiation, and comments that the "diameter change of TRISO coated fissile fuel as a function of fast neutron exposure is dependent exclusively on the dimensional change of the OPyC layer; i.e., the SiC layer is assumed to be dimensionally stable during irradiation ... Density changes in the OPyC layer are assumed to be independent of temperature"

Another area of uncertainty is the relatively limited temperature range over which the experimental data was obtained (approximately 950 to 1250°C) compared to that over which the NP-MHTGR compacts will be exposed.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

From the preceding statement, one might compare the total volume fraction occupied by the OPyC layers within the NP-MHTGR fuel compact (and the respective volumetric change during irradiation) to that upon which the model equation is based, to determine whether any revision of the above model equation may be justified to reflect the size of NP-MHTGR particles. If the only change in particle size is that due to the OPyC layer dimensional/volumetric change, one might normalize the above model equation with respect to relative OPyC volumetric change within NP-MHTGR compacts vs that in the non-NP compacts. Equations are available for prediction of OPyC dimensional changes during irradiation (General Atomic, 1977a; FDDM/F) to expedite these calculations. The fuel particle fraction in NP-MHTGR compacts vs that in the standard commercial compact design needs to be considered. The effect of the low-density PPyC layer on the overall fuel compact volumetric change must be considered.

Compact manufacturing techniques have probably not changed so much since the model equations were developed as to cast doubt on the accuracy of the results, although this should be verified.

DATABASE USED IN MODEL DEVELOPMENT

The compact dimensional change data from several capsule tests was tabulated by General Atomic (1977a) along with predictions of dimensional change using a computer code called SHRINK. This tabulation is reproduced in Table 3.2.1.2. Data for the

Fig. 3.2.1.1. Volumetric change of fuel compacts versus fluence, temperature, and shim content (from Kovacs, 1981).

Fig. 3.2.1.2. Fuel compact dimensional change results compared to the FDDM/E predicted dimensional change (from Myers et al., 1985c).

Table 3.2.1.2. Comparison between measured and predicted HTGR fuel compact dimensional change (from General Atomic, 1977a)

Capsule	Sample Position	Particle Packing Fraction	Irradiation Conditions		Dimensional Change			Macro (%)	Filler wt %
			Fast Fluence (10 ²⁵ n/m ²) (E > 29 fJ) HTGR	Temp. (°C)	Measured D/D ₀ (a) (%)	Calculated D/D ₀ (b) (%)	Percent (c) Difference		
P13M	3A	0.629	7.5	1140	-2.42	-3.04	-25.6		
	3B	0.598	7.5	1130	-2.25	-2.78	-23.6		
	3C	0.604	7.4	1180	-3.01	-3.32	-10.3		
	3D	0.609	7.3	1140	-2.52	-2.75	-9.1		
	3E	0.611	7.3	1170	-2.87	-3.36	-13.6		
	5A	0.626	4.0	1430	-5.71	-5.67	0.7		
	5B	0.612	3.7	1400	-4.99	-5.17	-3.6		
	5C	0.600	3.4	1450	-6.14	-6.11	0.2		
	5D	0.608	3.1	1365	-4.41	-4.76	-7.9		
	5E	0.624	2.8	1375	-4.62	-4.85	-5.0		
P13N	1D	0.429	4.1	1750	-2.4	-3.0	-20.0		
	1E	0.605	4.2	1720	-1.8	-3.2	-43.8		
	2B	0.583	4.7	1645	-2.1	-2.8	-25.0		
	2D	0.601	4.8	1695	-1.9	-2.9	-34.5		
	3A	0.427	4.5	1355	-2.5	-3.1	-19.4	50	
	4A	0.628	3.5	1270	-3.0	-3.9	-23.1	28.7	
	4C	0.621	3.2	1205	-2.4	-3.5	-31.4	30.5	
	5X	0.600	2.1	1210	-2.4	-2.5	-4.0	28.7	
	5A	0.599	2.0	1235	-2.6	-2.8	-7.1	31	
	5B	0.594	1.8	1220	-2.4	-2.6	-7.7	25.6	
	5C	0.622	1.6	1165	-2.6	-2.5	-4.0	25.9	
P13P	1C	0.601	5.5	1093	-1.98	-4.46	-55.6		
	1D	0.598	5.7	1084	-2.37	-4.30	-44.9		
	3C	0.601	6.7	1314	-2.64	-3.68	-28.3		
	4A	0.600	5.5	1053	-1.73	-3.27	-47.1		
	4B	0.592	5.4	1068	-2.04	-3.78	-46.0		
	4C	0.604	5.0	1041	-1.36	-3.12	-56.4		
	4D	0.593	4.7	1003	-1.64	-3.68	-55.4		
	5A	0.573	3.5	1390	-1.84	-3.25	-43.4		
	5B	0.597	3.2	1300	-0.48	-3.46	-86.1		
	5C	0.592	3.0	1211	-1.62	-3.39	-52.2		
	5D	0.588	2.9	1123	-1.50	-3.60	-58.3		
	5E	0.570	2.7	1036	-0.56	-2.78	-79.9		
P13R	1A		7.3	1050	-0.87	-2.53	-65.6	31	37
	1B		8.1	1000	-1.54	-2.65	-41.9	40	34
	1C		8.7	1015	-1.52	-2.28	-33.3	42	33
	1D		9.3	1045	-0.33	-1.83	-82.0	35	34
	1E		9.9	1070	-0.60	-1.92	-68.8	32	34
	2A		11.8	975	-0.27 (d)	(e)	--		
	2B		12.0	985	+1.13 (d)	(e)	--		
	2C		12.2	980	-0.48	(e)	--		
	2D		12.3	965	+1.61 (d)	(e)	--		
	2E		12.4	915	-0.12 (d)	(e)	--		
	5A		9.4	1230	-1.19	-2.73	-56.4	37	35
	5B		9.0	1175	-1.33	-2.62	-49.2	35	34
	5C		8.5	1180	-1.53	-2.79	-45.2	35	30
	5D		8.2	1170	-1.33	-2.90	-54.1	42	33
	5E		7.7	1215	-1.35	-3.87	-65.1	27	32
	6A		5.4	1035	-2.01	-2.85	-29.5	34	33
	6B		5.0	1020	-1.63	-2.40	-32.1	41	32
	6C		4.5	975	-1.77	-2.71	-34.7	43	30
	6D		4.1	985	-1.44	-2.25	-36.0	40	31
	6E		3.6	970	-1.63	-2.47	-34.0	36	33

Table 3.2.1.2 (continued)

Capsule	Sample Position	Particle Packing Fraction	Irradiation Conditions		Dimensional Change			Macro (%)	Filler wt %
			Fast Fluence ₂ (10 ²⁵ n/m ²) (E > 29 fJ) HTCR	Temp. (°C)	Measured D/D ₀ (a) (%)	Calculated D/D ₀ (b) (%)	Percent(c) Difference		
P135	1A		7.0	965	-1.18	-2.58	-54.3	31	37
	1B		7.7	925	-1.26	-2.50	-49.6	40	34
	1C		8.5	950	-1.04	-2.31	-55.0	42	33
	1D		9.1	965	-0.20	-2.00	-90.0	35	34
	1E		9.6	980	-0.25	-1.89	-86.8	32	34
	2A		11.5	970	-0.27(d)	(e)	—		
	2B		11.7	945	+0.48(d)	(e)	—		
	2C		11.9	915	+0.09(d)	(e)	—		
	2D		12.0	920	+0.28(d)	(e)	—		
	2E		12.1	910	+0.13(d)	(e)	—		
	5A		9.2	1330	-1.64	-2.73	-39.9	37	35
	5B		8.7	1290	-1.17	-2.86	-59.1	35	34
	5C		8.4	1285	-1.58	-2.77	-43.0	35	
	5D		7.9	1280	-1.36	-2.98	-54.4	42	
	5E		7.5	1295	-1.63	-2.95	-44.7	27	32
	6A		5.3	1050	-2.03	-2.84	-28.5	40	33
	6B		4.8	1010	-1.52	-2.33	-34.8	29	
	6C		4.4	1020	-2.34	-2.72	-14.0	38	29
	6D		3.9	985	-2.05	-2.63	-22.1	32	44
	6E		3.5	965	-1.55	-2.44	-36.5	30	ND
HRB4	2A	0.569	8.9	1250	-2.22	-4.31	-48.5	32.6	40.21
	2A	0.565	8.9	1250	-1.49	-4.29	-65.3	24.1	50.45
	2C	0.589	8.7	1250	-2.07	-4.30	-51.9	25.0	40.29
	4A	0.574	5.4	1250	-2.59	-4.08	-36.5	32.6	40.21
	4B	0.561	4.5	1250	-2.40	-3.97	-39.5	24.1	50.45
	4C	0.576	3.6	1250	-2.63	-3.65	-27.9	25.0	40.29
HRB5	2A	0.575	4.0	1250	-2.24	-3.80	-41.0	32.6	40.21
	2B	0.566	3.9	1250	-1.69	-3.76	-55.0	24.1	50.45
	2C	0.576	3.8	1250	-2.48	-3.73	-33.5	25.0	40.29
	4A	0.574	2.4	1250	-2.21	-3.00	-26.3	32.6	40.21
	4B	0.567	2.0	1250	-1.74	-2.75	-36.7	24.1	50.45
	4C	0.579	1.5	1250	-2.07	-2.40	-13.8	25.0	40.29
HRB6	2A	0.550	6.7	1250	-3.10	-4.37	-29.1	27.7	39.15
	2B	0.566	6.7	1250	-3.08	-4.42	-30.3	17.7	36.77
	2C	0.554	6.5	1250	-3.00	-4.37	-31.4	36.9	39.38
	4A	0.558	4.0	1250	-2.88	-3.94	-26.9	25.1	38.85
	4B	0.562	3.3	1250	-2.77	-3.82	-27.5	22.8	38.05
	4C	0.604	2.6	1250	-2.61	-3.69	-29.3	31.2	37.35

(a) Measurements made with dial gauge micrometer.

(b) Dimensional changes calculated using SHRINK computer code.

(c) Percent difference between calculated and measured dimensional change:

$$\frac{\Delta x/x_{\text{meas}} - \Delta x/x_{\text{calc}}}{\Delta x/x_{\text{calc}}} \times 100 = \text{difference.}$$

(d) Fuel rods were constrained by graphite crucibles at end of irradiation; therefore, dimensional change of rods may not be representative.

(e) Fast neutron exposure received by these rods exceeds limits of pyrocarbon and graphite shim dimensional change data; therefore, fuel rod dimensional changes cannot be predicted using SHRINK code.

dimensional changes in the fuel compacts irradiated in capsule R2-K13 are presented in Tables 3.2.1.3 and 3.2.1.4 (Myers et al., 1985c).

3.2.2 FUEL COMPACT DIMENSIONAL CHANGE

function	This model calculates the axial and radial dimensional change of the fuel compact during irradiation as a function of the volumetric change (§3.2.1) and the fast neutron fluence.
present status	The irradiation-induced compact dimensional changes appear to be based on a standard formulation. The origin for the model equation of strain anisotropy as a function of fluence is unknown.
model uncertainty	The model uncertainty is quantified below. Uncertainties resulting from the dependency on the compact volumetric change (§3.2.1) also apply here.
references	FDDM/F; Kovacs (1981)

Model equations

The irradiation-induced relative dimensional changes of the fuel compact in the axial and radial directions can be calculated as a function of the relative compact volumetric change, $\hat{V}$, and the strain anisotropy, $\Delta\epsilon$:

$$\left(\frac{\Delta\ell}{\ell}\right) = \frac{1}{3} (\hat{V} + 2 \Delta\epsilon) , \quad (3.2.2.1)$$

$$\left(\frac{\Delta r}{r}\right) = \frac{1}{3} (\hat{V} - \Delta\epsilon) , \quad (3.2.2.2)$$

$$\Delta\epsilon = 0.115 \gamma , \quad (3.2.2.3)$$

- $(\Delta\ell/\ell)$ = axial dimensional change of the compact of length ℓ (%),
 $(\Delta r/r)$ = radial dimensional change of the compact of radius r (%),
 $\hat{V}$ = volumetric change of the compact (%),
 $\Delta\epsilon$ = strain anisotropy (%),
 γ = fast neutron fluence [10^{25} n m^{-2} , ($E > 29 \text{ fJ}$)_{HTGR}].

The compact volumetric change can be calculated using Eq. (3.2.1.2). These model equations are presented in the same form in both FDDM/F and Kovacs (1981).

Table 3.2.1.3. Dimensional measurement of fuel compacts: cell 2 of capsule R2-K13 (from Myers et al., 1985c)
(Measuring instrument: dial gauges; accuracy of measurement: ± 0.01 mm)

3-11

Capsule No.	Rod No.	Preirradiation ^(a) Diameter (mm)		Postirradiation Diameter (mm)		Change In Diameter % Change In Diameter		Preirradiation ^(a) Length (mm)		Postirradiation Length (mm)		Change In Length (mm) % Change In Length		
2	2A1	12.48	Upper	12.38	12.35	0.12	0.92	25.542	25.30	25.36	0.21	0.83		
			Middle	12.37	12.37	0.11	0.88							
			Lower	12.38	12.36	0.11	0.86							
	2A2	12.48	Upper	12.38	12.39	0.10	0.76	25.623	25.37	25.31	0.28	1.10		
			Middle	12.37	12.39	0.10	0.80							
			Lower	12.36	12.39	0.11	0.84							
	Average						0.85	Average						0.97
	2	2B1	12.48	Upper	12.35	12.36	0.13	1.00	25.452	25.27	25.27	0.18	0.72	
				Middle	12.36	12.37	0.12	0.92						
				Lower	12.35	12.39	0.11	0.88						
2B2		12.48	Upper	12.38	12.37	0.11	0.84	25.643	25.31	25.24	0.37	1.43		
			Middle	12.38	12.36	0.11	0.88							
			Lower	12.38	12.37	0.11	0.84							
Average						0.89	Average						1.08	

^(a) Determined from QC fuel rods during rod manufacture.

Table 3.2.1.4. Dimensional measurement of fuel compacts: cell 3 of capsule R2-K13 (from Myers et al., 1985c)
(Measuring instrument: dial gauges; accuracy of measurement: ± 0.01 mm)

3-12

Capsule No.	Rod No.	Preirradiation ^(a) Diameter (mm)		Postirradiation Diameter (mm)		Change In Diameter (mm)	% Change In Diameter	Preirradiation ^(a) Length (mm)	Postirradiation Length (mm)		Change In Length (mm)	% Change In Length
3	3A1	12.48	Upper	12.36	12.37	0.12	0.92	25.482	25.36	25.28	0.16	0.64
			Middle	12.37	12.41	0.09	0.72					
			Lower	12.38	12.38	0.10	0.80					
	3A2	12.48	Upper	12.38	12.39	0.10	0.76	25.874	25.61	25.60	0.27	1.04
			Middle	12.39	12.37	0.10	0.68					
			Lower	12.40	12.39	0.09	0.68					
				Average			0.78				Average	0.84
3	3B1	12.48	Upper	12.35	12.36	0.13	1.00	25.633	25.46	25.46	0.17	0.67
			Middle	12.34	12.38	0.12	0.96					
			Lower	12.36	12.37	0.12	0.92					
	3B2	12.48	Upper	12.37	12.37	0.11	0.88	25.573	25.37	25.31	0.23	0.91
			Middle	12.39	12.41	0.08	0.64					
			Lower	12.39	12.39	0.09	0.72					
				Average			0.85				Average	0.79

^(a) Determined from QC fuel rods during rod manufacture.

Range of validity

Neither Kovacs (1981) nor FDDM/F discusses the range of validity or experimental basis of this model. Apparently the model can be assumed to apply over all irradiation conditions. The experimental range of the data upon which this model is based is unknown.

Assumptions

Neither Kovacs (1981) nor FDDM/F discusses the assumptions relevant to derivation of this model.

Uncertainty

FDDM/F states that the standard deviation in the strain anisotropy is given by:

$$\sigma(\Delta\epsilon) = 0.34 \quad (3.2.2.4)$$

MODEL CHRONOLOGY

These model equations originated from studies of dimensional changes of fuel compacts in accelerated irradiation capsules, before data from Fort St. Vrain fuel compacts became available. The source reference for this model has not been determined.

DISCUSSION

The experimental data for strain anisotropy upon which Eq. (3.2.2.3) is based are shown in Figure 3.2.2.1, taken from Kovacs (1981). The source reference for this data is unknown. The discussion in §3.2.1 regarding the difference in particle size between NP-MHTGR particles and those upon which this data is based may also be relevant to the model equation for strain anisotropy, Eq. (3.2.2.3).

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

As additional data become available for NP-MHTGR-design compacts, that data should be compared to Eq. (3.2.2.3) to verify the equation's accuracy.

DATABASE USED IN MODEL DEVELOPMENT

Refer to Figure 3.2.2.1 for data on the fuel compact strain anisotropy as a function of fast fluence.

Fig. 3.2.2.1. Empirically determined fuel compact strain anisotropy versus fluence (from Kovacs, 1981).

3.3 FUEL COMPACT MECHANICAL PROPERTIES

function	The models for the modulus of elasticity under compression, ultimate compressive strength, and ultimate tensile strength for the fuel compact are given as functions of the volume fraction of graphite shim in the compact.
present status	Absolute values for ultimate tensile strength, ultimate compressive strength, and modulus of elasticity were obtained from Fort St. Vrain-vintage fuel compacts. Recent model revisions determine polynomial approximations of these data as a function of the volume fraction of graphite shim in the fuel compact.
model uncertainty	The available data was taken on unirradiated compacts typical of 1976-vintage fuel compacts. The experimental uncertainty is given below with the experimental values. The actual uncertainty with respect to modern compacts is unknown.
references	FDDM/F; General Atomic (1976b)

MODULUS OF ELASTICITY UNDER COMPRESSION: model equation

The model equation for the elastic modulus in compression of the fuel compact is given in FDDM/F as:

$$E = e_1 + e_2 S_v + e_3 S_v^2, \quad (3.3.1)$$

E = elastic modulus in compression (GPa),
 S_v = volume fraction of graphite shim in the compact,
 e_i = constants, for $i = 1, 2, 3$.

Values for the coefficients are given in Table 3.3.1. The source references for this model equation are given in FDDM/F as General Atomic (1976b) and an internal GA memorandum which has not been reviewed by this writer.

ULTIMATE COMPRESSIVE STRENGTH: model equation

The model equation for the ultimate compressive strength of the fuel compact is given in FDDM/F as:

$$UCS = a_1 + b_1 S_v, \quad (3.3.2)$$

UCS = ultimate compressive strength (MPa),
 S_v = volume fraction of graphite shim in the compact,

$a_1, b_1 = \text{constants.}$

Values for the coefficients are given in Table 3.3.1. The source references for this model equation are given in FDDM/F as General Atomic (1976b) and an internal GA memorandum which has not been reviewed by this writer.

ULTIMATE TENSILE STRENGTH: model equation

The model equation for the ultimate tensile strength of the fuel compact is given in FDDM/F as:

$$UTS = a_2 + b_2 S_v, \quad (3.3.3)$$

UTS = ultimate tensile strength (MPa),
 S_v = volume fraction of graphite shim in the compact,
 a_2, b_2 = constants.

Values for the coefficients are given in Table 3.3.1. The source references for this model equation are given in FDDM/F as General Atomic (1976b) and an internal GA memorandum which has not been reviewed by this writer.

Table 3.3.1. Coefficients for use in the model equations for the elastic modulus under compression, ultimate compressive strength, and ultimate tensile strength, Eqs. (3.3.1) through (3.3.3) (from FDDM/F)

Property	Coefficient	Units	Value
Elastic modulus in compression	e_1	GPa	0.813000
	e_2	"	-2.16246
	e_3	"	2.24266
Ultimate compressive strength	a_1	MPa	6.200
	b_1	"	-4.136
Ultimate tensile strength	a_2	MPa	0.8700
	b_2	"	-0.9300

Range of validity

Due to the limited database, these models must be considered applicable to all conditions, by necessity. Experimentally, measurements were performed on compacts with shim volume fractions of 0, 23, and 36%.

Assumptions

1. The mechanical properties of unirradiated compacts should approximate those of irradiated compacts.
2. The "prototype" fuel compacts used for these measurements are representative of the behavior of modern reference compacts.

Uncertainty

Values for the mechanical property uncertainties are given in FDDM/F in terms of the standard deviation in the property:

$$\sigma(E) = 1.0 \text{ GPa} , \quad (3.3.4)$$

$$\sigma(UCS) = 1.1 \text{ MPa} , \quad (3.3.5)$$

$$\sigma(UTS) = 0.17 \text{ MPa} , \quad (3.3.6)$$

E = elastic modulus in compression (GPa),
UCS = ultimate compressive strength (MPa),
UTS = ultimate tensile strength (MPa).

MODEL CHRONOLOGY

The original model equations recommended a single value for each property for both shimmed and unshimmed compacts, apparently based on a single set of experiments in the mid-1970s. Rather than including the data for all shimmed compacts in a single average value, the recent model revision developed polynomial approximations to describe the original data as a function of the volume fraction of graphite shim

DISCUSSION

The original design values for the mechanical properties of fuel compacts were obtained by averaging the data obtained for unshimmed and for shimmed compacts. These earlier design values are presented in Table 3.3.2 (General Atomic, 1976b).

Table 3.3.2. Mechanical properties of fuel compacts (from General Atomic, 1976b)

Mechanical property	Unshimmed compacts	Compacts with 23 to 36 v/o ^(a) shim
Modulus of elasticity under compression (GPa)	0.813 ± 0.063	0.385 ± 0.123
Ultimate compressive strength (MPa)	6.54 ± 0.91	4.75 ± 1.38
Ultimate tensile strength (MPa)	0.86 ± 0.21 $(0.93 \pm 0.35)^{(b)}$	0.60 ± 0.16

(a) v/o = volume %.

(b) Result calculated from raw data.

Analysis of the data presented by General Atomic (1976b) provides a different average value for the UTS of unshimmed compacts than the value specified by General Atomic (1976b) and given in Table 3.3.1. However, the average UTS of 0.86 MPa is mentioned twice by General Atomic (1976b); therefore, we must assume that to be the correct average.

General Atomic (1976b) mentions that failure of compacts under compressive loads is reflected by slow crumbling of the compact at the fracture surface rather than brittle fracture, and that the compacts could support loads at 40% of ultimate compressive strain up to compressive strains of 2 to 3 times that at failure. This reference also speculates that the decrease in strength and modulus of elasticity of shimmed compacts may result from either: (1) the matrix pitch may not be properly wetting the shim, resulting in poor bond strength, or (2) the compact matrix is weakened by absorption of matrix pitch binder by the shim particles.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Due to the limited data available, model revision cannot be pursued until NP-MHTGR-specific data has been obtained and compared to these model equations.

DATABASE USED IN MODEL DEVELOPMENT

The data upon which the model equations are based are given in Table 3.3.3, taken from General Atomic (1976b).

Table 3.3.3. Mechanical properties of HTGR fuel compacts (from General Atomic, 1976b)

Fuel Rod			Tensile Properties				Compressive Properties							
Type	Shim Vol. (Vol %)	Specimen	Failure Load		Ultimate Strength		Ultimate Strength		Modulus ^(a)		Failure Load		Compression at Failure (10 ⁻⁴ m)	Length (10 ⁻² m)
			(N)	(lb)	(10 ⁶ Pa)	(psi)	(10 ⁶ Pa)	(psi)	(10 ⁸ Pa)	(10 ⁵ psi)	(10 ³ N)	(lb)		
A3	0	4003-3	173.5	39	0.89	130	6.44	934	8.09	1.17	1.25	282	1.7	2.143
		4004-1	142.3	32	0.73	106	5.30	768	--	--	1.03	232	--	2.170
		4004-3	129.0	29	0.66	96	7.24	1050	8.77	1.27	1.41	317	2.0	2.423
		4005-2	222.4	50	1.44	166	7.19	1043	7.52	1.09	1.40	315	2.0	2.092
		Mean			0.86 ± 0.21	124 ± 31	6.54 ± 0.91		8.13 ± 0.63					
C3	23	4021-3	146.8	33	0.75	109	6.01	871	5.79	0.84	1.17	263	3.2	3.082
		4021-4	111.2	25	0.57	83	2.12	308	--	--	0.41	93	--	3.019
		4022-1	142.3	32	0.73	106	5.21	755	4.55	0.66	1.01	228	3.5	3.074
		4022-2	120.1	27	0.62	89	4.00	580	2.81	0.41	0.78	175	4.3	3.018
		Mean			0.67 ± 0.09	97 ± 13	4.32 ± 1.70		4.38 ± 1.5					
D2	36	4025-3	133.4	30	0.68	99	6.12	888	3.97	0.58	1.19	268	3.5	2.275
		4026-1	115.7	26	0.59	86	4.52	656	3.60	0.52	0.88	198	3.3	2.627
		4026-2	53.4	12	0.27	40	5.28	765	2.37	0.34	1.03	231	6.0	2.693
		Mean			0.52 ± 0.22	75 ± 31	5.31 ± 0.80		3.31 ± 0.84					

(a) Modulus measured as compressive stress at failure divided by compressive strain at failure.

3.4 FUEL COMPACT THERMAL PROPERTIES

3.4.1 FUEL COMPACT THERMAL CONDUCTIVITY

function	This model calculates the compact's thermal conductivity as a function of irradiation temperature, fast neutron fluence, and the volume fraction of graphite shim and weight fraction of coke in the compact.
present status	A recursive relation has been derived to include the effects of fast fluence and temperature on the thermal conductivity over time. This model is probably based on data from the early to mid-1970s.
model uncertainty	The uncertainty of this model has not been evaluated (FDDM/F).
references	FDDM/F; Harmon et al. (1975); Shenoy et al. (1974)

Model equations

The model equation for the thermal conductivity of the fuel compact is given in FDDM/F, in a form that is "calculated incrementally in n time steps by using the following recursive relation":

$$\lambda(t_i) = \lambda(\gamma_i, T_i) + \left[\kappa(\gamma_{i,i-1}) + \frac{k_2(\gamma_i)}{k_2(\gamma_{i-1})} \lambda(t_{i-1}) - \lambda(\gamma_i, T_i) \right] e^{-\omega \Delta \gamma_i}, \quad (3.4.1.1)$$

$$\lambda(\gamma_i, T_i) = k_1(\gamma_i) + k_2(\gamma_i) T_i, \quad (3.4.1.2)$$

$$\kappa(\gamma_{i,i-1}) = k_1(\gamma_i) - \frac{k_1(\gamma_{i-1}) \cdot k_2(\gamma_i)}{k_2(\gamma_{i-1})}, \quad (3.4.1.3)$$

$$k_j(\gamma_i) = \alpha_j + \beta_j e^{-\gamma \gamma_i}, \quad j = 1, 2, \quad (3.4.1.4)$$

$$\Delta \gamma_i = \gamma_i - \gamma_{i-1}, \quad (3.4.1.5)$$

$\lambda(t_i)$ = thermal conductivity at i th time step ($\text{W m}^{-1} \text{K}^{-1}$),
 $\lambda(t_i, T_i)$ = thermal conductivity isotherm ($\text{W m}^{-1} \text{K}^{-1}$),
 t_i = time at the i th time step (arbitrary units),

γ_i = fast neutron fluence at the i th time step [10^{25} n m^{-2} , ($E > 29 \text{ fJ}$)_{HTGR}],
 T_i = temperature at the i th time step (K),
 ω = constant [$(10^{25} \text{ n m}^{-2})^{-1}$],
 α_j, β_j = coefficients ($\text{W m}^{-1} \text{ K}^{-1}$) for $j = 1, 2$, given by:

$$\alpha_1 = C_1 + C_2 S_v + C_3 C_w, \quad (3.4.1.6)$$

$$\beta_1 = C_5 + C_7 S_v + C_8 C_w + C_9 S_v^2, \quad (3.4.1.7)$$

$$\alpha_2 = C_4, \quad (3.4.1.8)$$

$$\beta_2 = C_6 + C_{10} S_v + C_{11} S_v^2, \quad (3.4.1.9)$$

S_v = volume fraction of graphite shim in the compact,
 C_w = weight fraction of coke in the compact,
 C_i = coefficients ($\text{W m}^{-1} \text{ K}^{-1}$),
 τ = constant [$(10^{25} \text{ n m}^{-2})^{-1}$].

Values for the coefficients and constants are given in Table 3.4.1.1. The source references for this model equation are given in FDDM/F as a GA document (J. W. Ketterer, "Reference HTGR Fuel Compact Thermal Conductivity Data Base and Model," GA Document 907591/A, 1986) and an internal GA memorandum which have not been reviewed by this writer.

Range of validity

The model equation can model both constant and changing temperature conditions, but temperature variations must be approximated as a series of step changes. The model equation can be applied to both NOC and AC regimes but requires the assumption that no annealing of irradiation damage occurs during AC transients (FDDM/F).

The source data have not been evaluated in detail but are reported (Harmon et al., 1975) to encompass the temperature range of 950 to 1250°C and a fractional shim content of 0 to 36 v/o. Experimental determinations of the effect of irradiation on thermal conductivity had not been conducted as of 1975.

Assumptions

The assumptions which were employed in the derivation of the model equations may be stated explicitly in the source documents, but they are unknown to this writer except for Assumption 1. Whether Assumption 2 was employed for the model equations is uncertain.

Table 3.4.1.1. Coefficients for use in the model equations for the thermal conductivity of the fuel compact, Eqs. (3.4.1.1) through (3.4.1.7) (from FDDM/F)

Coefficient	Units	Value
ω	$(10^{25} \text{ n m}^{-2})^{-1}$	6.0
τ	$(10^{25} \text{ n m}^{-2})^{-1}$	0.50
C_1	$\text{W m}^{-1} \text{ K}^{-1}$	0.7008326
C_2	$\text{W m}^{-1} \text{ K}^{-1}$	10.91361
C_3	$\text{W m}^{-1} \text{ K}^{-1}$	-9.103535
C_4	$\text{W m}^{-1} \text{ K}^{-1}$	0.005334483
C_5	$\text{W m}^{-1} \text{ K}^{-1}$	17.28523
C_6	$\text{W m}^{-1} \text{ K}^{-1}$	-0.0087609808
C_7	$\text{W m}^{-1} \text{ K}^{-1}$	-16.36312
C_8	$\text{W m}^{-1} \text{ K}^{-1}$	5.671053
C_9	$\text{W m}^{-1} \text{ K}^{-1}$	61.04872
C_{10}	$\text{W m}^{-1} \text{ K}^{-1}$	0.02361024
C_{11}	$\text{W m}^{-1} \text{ K}^{-1}$	-0.07228171

1. Irradiation damage will not anneal out during high-temperature accident conditions.
2. Estimating the effect of irradiation on compact thermal conductivity based on the effects of irradiation on the individual components (Harmon et al., 1975) provides an acceptable approximation.

Uncertainty

The uncertainty for these model equations has not been evaluated (FDDM/F).

MODEL CHRONOLOGY

During the 1970s a single constant value of the thermal conductivity was recommended for use in design calculations. Information on the development of the model equations presented here is unknown to this writer, but the source data are probably the same as that referred to by Shenoy et al. (1974) and Harmon et al. (1975) and presented in Fig. 3.4.1.1.

Fig. 3.4.1.1. Thermal conductivity of typical HTGR fuel compacts as a function of temperature (from Shenoy et al., 1974).

DISCUSSION

Shenoy et al. (1974) and Harmon et al. (1975) both suggest the use of a conservative value for thermal conductivity of 4.0 Btu/hr-ft-°F (6.9 W/m-K) for all compact and irradiation conditions and temperatures. The following discussion will be limited to the information on thermal conductivity which is available in the open literature, from the mid-1970s.

The most detailed data available for the thermal conductivity of fuel compacts apparently was presented by Johnson (1974) as reported by Shenoy et al. (1974) and Harmon et al. (1975). Some of the data obtained by Johnson is presented in Figure 3.4.1.1, taken from Shenoy et al. (1974). As the contents of Johnson (1974) have not been evaluated, the conclusions paraphrased in Harmon et al. (1975) will be quoted below.

"The thermal conductivity of four types of unirradiated prototype LHTGR fuel [compacts] containing different fuel and shim particle compositions was measured in the temperature range 950 to 1250°C ... The thermal conductivity values ranged from 9.8 Btu/ft-hr-°F at 975°C for the [compacts] containing 36 vol % shim particles to 4.0 Btu/ft-hr-°F at 1250°C for unshimmed fuel [compacts]. The lowest thermal conductivity observed for the [compact] containing 23 vol % shim particles, which is representative of the "average" composition of LHTGR fuel [compacts], was about 6.0 Btu/ft-hr-°F at 1250°C. The data indicated that fuel [compact] thermal conductivity increased with increasing shim content and decreased with increasing temperature.

"The effect of irradiation on the thermal conductivity of fuel [compacts] has not been experimentally determined; however, an estimate of the effects of irradiation was made by evaluating thermal conductivity changes of fuel [compact] components ... Based on the changes in thermal conductivity of each component, the thermal conductivity of fuel [compacts] may be expected to decrease with irradiation in the low temperature range 600 to 1000°C and to increase or remain constant in the higher temperature range (1000 to 1400°C) of operation."

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Little justification exists for refining the existing model unless data from NP-MHTGR-design compacts becomes available.

DATABASE USED IN MODEL DEVELOPMENT

Refer to Figure 3.4.1.1.

3.4.2 FUEL COMPACT THERMAL EXPANSION

function	This model calculates the compact's thermal expansion during irradiation as a function of the unirradiated coefficient of thermal expansion and the fast neutron fluence.
present status	A polynomial approximation is derived from the results of a mid-1970s capsule irradiation to incorporate the dependency on fast fluence. Little variation in the thermal expansion was observed for a variety of compacts and fabrication techniques, although the particle loading volume fractions were limited to the range 33 to 39 v/o. No temperature-dependence is incorporated into the model.
model uncertainty	Although the experimental uncertainty based on the results from twelve compacts is not large, the model uncertainty in using data from Fort St. Vrain-vintage compacts relative to NP-MHTGR-design compacts should be determined.
references	FDDM/F; General Atomic (1976d)

Model equations

The model equation for the thermal expansion of the fuel compact is given in FDDM/F as:

$$\alpha_i = (1 + a\gamma + b\gamma^2 + c\gamma^3) \alpha_o, \quad (3.4.2.1)$$

- α_i = coefficient of thermal expansion for irradiated compacts (K^{-1}),
 α_o = coefficient of thermal expansion for unirradiated compacts (K^{-1}),
 γ = fast neutron fluence [10^{25} n m^{-2} , ($E > 29 \text{ fJ}$)_{HTGR}],
 a, b, c = coefficients (units given in Table 3.4.2.1).

Values for the model parameters are given in Table 3.4.2.1. The source reference for this model equation is given in FDDM/F as an internal GA memorandum which has not been reviewed by this writer.

Range of validity

The model equation can be applied to both NOC and AC regimes, but requires the assumption that no annealing of irradiation damage occurs during AC transients. The equation is also stated to apply "to both the axial and radial components of thermal expansion ... for all temperatures of interest for fast neutron fluences up to $8.0 \times 10^{25} \text{ n/m}^2$ " (FDDM/F).

Table 3.4.2.1. Parameters for use in the model equation for the coefficient of thermal expansion of the fuel compact, Eq. (3.4.2.1) (from FDDM/F)

Parameter	Units	Value
α_o	K^{-1}	4.85×10^{-6}
a	$(10^{25} \text{ n m}^{-2})^{-1}$	-0.1384516
b	$(10^{25} \text{ n m}^{-2})^{-2}$	0.02080897
c	$(10^{25} \text{ n m}^{-2})^{-3}$	-0.001020047
σ_{α_o}	Dimensionless	0.900

The irradiated compacts in the P13Q capsule irradiation were subjected to fast neutron fluences of 4.2 to $9.4 \times 10^{25} \text{ n m}^{-2}$ ($E > 29 \text{ fJ}$)_{HTGR}, at irradiation temperatures of 860 to 1160°C . The particle loading volume fractions ranged from 33 to 39 v/o . The compacts were fabricated by injection molding and by admix compaction, and they were cured by cured-in-place and packed-bed methods. Measurements of the coefficient of thermal expansion (CTE) were conducted between room temperature and 800°C .

Assumptions

1. Irradiation damage will not anneal out during high-temperature accident conditions.
2. The particle loading volume fractions of the compacts used for measurements of the CTE are comparable to those of NP-MHTGR-design compacts.
3. The values for the CTE are applicable to irradiation temperatures outside those at which the experiments were conducted.
4. Compacts containing UCO fuel should exhibit comparable thermal expansion as those containing UC_2 fuel.

Uncertainty

The uncertainty in the CTE is given as (FDDM/F):

$$\sigma(\alpha_i) = \sigma_{\alpha_o} (1 + a\gamma + b\gamma^2 + c\gamma^3) , \quad (3.4.2.2)$$

- $\sigma(\alpha_i)$ = standard deviation in the CTE, α_i ,
 σ_{α_o} = standard deviation in the CTE for unirradiated compacts, α_o ,
 γ = fast neutron fluence [10^{25} n m^{-2} , ($E > 29 \text{ fJ}$)_{HTGR}],
 a, b, c = coefficients (units given in Table 3.4.2.1).

The values for σ_{α_o} , a , b , and c are given in Table 3.4.2.1.

MODEL CHRONOLOGY

The only referenced experiments for determination of the CTE values were conducted as part of the P13Q capsule irradiation in the mid-1970s. Earlier models recommended using two constant values for the thermal conductivity, one for unirradiated compacts and another for irradiated compacts. The recent model revision employs a polynomial approximation to incorporate the fast fluence dependence of the data into the model equation.

DISCUSSION

In the P13Q capsule irradiation, six fuel compacts fabricated by several methods were irradiated, and their postirradiation thermal expansion compared to six companion unirradiated compacts. The mean CTE from room temperature to 800°C was found to be independent of relative fuel/inert particle fractions and compact fabrication and curing technique (General Atomic, 1976d). The decrease in thermal expansivity with irradiation (approximately 30%) was found to be independent of total neutron fluence and irradiation temperature (suggesting a saturation effect for the neutron fluence). In the 1970s the recommended values for the CTE within the range of room temperature to 800°C were stated to be:

unirradiated compacts: $4.86 \pm 0.21 \times 10^{-6} \text{ K}^{-1}$
irradiated compacts: $3.44 \pm 0.15 \times 10^{-6} \text{ K}^{-1}$

The experimental results for irradiation-induced thermal expansion are summarized in Fig. 3.4.2.1.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Confirmation should be made that the particle volume fractions upon which the data is based (33 to 39 v/o) is typical of that for NP-MHTGR compacts. The model should be compared to any data which might become available for compacts of NP-MHTGR design.

DATABASE USED IN MODEL DEVELOPMENT

Details of the fuel compacts used in the P13Q capsule test are given in Table 3.4.2.2, and the CTE data are given in Table 3.4.2.3 (both taken from General Atomic, 1976d).

Fig. 3.4.2.1. Axial thermal expansion of HTGR fuel compacts in P13Q experiment (from General Atomic, 1976d).

Table 3.4.2.2. Thermal expansivity specimens from capsule P13Q fuel compacts (from General Atomic, 1976d)

Rod Location	Average Irrad. Temp. (K)	Total Neutron Fluence (10^{25} n/m ²) (E > 29 fJ) _{HTGR}	Volume Fraction Particle Loadings (Z)				Fabrication ^(a)	Curing ^(b)
			Fertile	Fissile	Inert DISO	Inert TRISO		
G1-1B	1435	9.4	2	6	19	12	I	C
G1-2A	1380	9.0	2	7	17	9	C	P
G2-1A	1180	7.2	2	10	13	8	C	C
G3-1B	1155	5.6	3	15	8	8	C	C
G3-2B	1155	5.6	3	15	8	8	C	C ^(c)
G3-3A	1130	4.2	-(d)	-	-	-	I	C

(a) Fabrication symbols: I = injection molded, C = admix compaction

(b) Curing symbols: C = cured-in-place, P = packed bed.

(c) Fired at 1773 K.

(d) Thermocouple rod; relative volume fraction unknown.

Table 3.4.2.3. Thermal expansivity of HTGR fuel compacts in capsule P13Q
(from General Atomic, 1976d)

Rod Type	$\bar{\alpha}_{(298-1073)}$ (10^{-6} K^{-1})		$\Delta\bar{\alpha}$ (%)	$\bar{\alpha}_{(298-773)}$ (10^{-6} K^{-1})		$\Delta\bar{\alpha}$ (%)
	Unirrad.	Irrad.		Unirrad.	Irrad.	
G1-1B	5.05	3.42	-32	4.60	2.98	-35
G1-2A	4.87	3.44	-29	4.48	3.04	-32
G2-1A	4.50	3.17	-30	3.95	2.46	-38
G3-1B	5.06	3.54	-30	4.63	2.96	-36
G3-2B	4.75	3.58	-25	4.31	2.85	-34
G3-3A	4.95	3.51	-29	4.44	2.89	-35
Mean	4.86	3.44	-29	4.40	2.86	-35
Std. dev.	0.21	0.15	2.3	0.25	0.21	2

3.4.3 FUEL COMPACT SPECIFIC HEAT CAPACITY

function	This model calculates the compact's specific heat capacity as a function of temperature and the volume fraction of graphite shim in the compact.
present status	Apparently, data for the specific heat capacity do not exist, rather the model is based on a mid-1970s approach which sums the specific heats for the individual components of the fuel compact. The model equation is expressed as a polynomial approximation with dependencies on temperature and shim volume fraction.
model uncertainty	According to FDDM/F, the uncertainty of the model equation has not been evaluated. In practice, some uncertainty is known to exist in the material parameters used as input to the model, for both unirradiated and irradiated conditions (Shenoy et al., 1974, Amendment 1).
references	Shenoy et al. (1974), and Amendment 1

Model equations

The model equation for the specific heat capacity of the fuel compact is given in FDDM/F as:

$$C_p = C_1 + C_2 S_v + C_3 T + C_4 S_v^2 + C_5 (1 + S_v) T^{-1} + C_6 T^{-2} + C_7 T^{-3} \quad , \quad (3.4.3.1)$$

- C_p = specific heat capacity ($10^3 \text{ J kg}^{-1} \text{ K}^{-1}$),
 S_v = volume fraction of graphite shim in the compact,
 T = temperature (K),
 C_i = coefficients (units given in Table 3.4.3.1).

Values for the coefficients are given in Table 3.4.3.1. The source reference for this model equation is given in FDDM/F as Shenoy et al. (1974), plus an internal GA memorandum which has not been reviewed by this writer.

Range of validity

According to FDDM/F, the model equation is applicable at temperatures greater than 327°C. As of 1976, no program to measure the specific heat of fuel compacts was planned, thus Kopp's additivity rule (see "Discussion" below) must be assumed to be valid over the range of reactor conditions encountered. Based on the application of Kopp's rule to experimental determinations of specific heat of cermet samples, the model can be considered to be generally valid (Shenoy et al., 1974, Amendment 1).

Table 3.4.3.1. Coefficients for use in the model equation for the specific heat capacity of the fuel compact, Eq. (3.4.3.1) (from FDDM/F)

Coefficient	Units	Value
C_1	$10^3 \text{ J kg}^{-1} \text{ K}^{-1}$	1.003910
C_2	$10^3 \text{ J kg}^{-1} \text{ K}^{-1}$	1.106288
C_3	$10^3 \text{ J kg}^{-1} \text{ K}^{-2}$	6.494645×10^{-5}
C_4	$10^3 \text{ J kg}^{-1} \text{ K}^{-1}$	0.6052790
C_5	$10^3 \text{ J kg}^{-1} \text{ K}^{-2}$	-1.182767
C_6	$10^3 \text{ J kg}^{-1} \text{ K}^{-3}$	614.9928
C_7	$10^3 \text{ J kg}^{-1} \text{ K}^{-4}$	-7.025196×10^7

Assumptions

As the model equations are apparently formulated based on the model presented by Shenoy et al. (1974), the model assumptions as stated in or deduced from Shenoy et al. are presented below.

1. Kopp's additivity rule (Darken et al, 1953) is approximately valid for representing the total compact specific heat as the sum of its parts (i.e., each component contributes independently to the total specific heat).
2. The specific heats of the pyrocarbon, compact matrix material, and graphite shim are the same as that of the graphite.
3. All compact components are assumed to be at the same temperature in calculating the compact specific heat as a function of temperature.
4. Use of specific heat values for unirradiated materials is conservative (i.e., the specific heats of SiC , UC_2 , and ThO_2 are expected to increase with irradiation analogous to that of graphite).
5. The specific heat of UCO approximates that of UC_2 and ThO_2 , and the total volume fraction of UCO in modern compacts approximates that of UC_2 and ThO_2 in the calculations, or else any difference is negligible with respect to the non-kernel volume fraction within the compact.

Uncertainty

The uncertainty for the specific heat capacity has not been evaluated (FDDM/F).

MODEL CHRONOLOGY

Figure 3.4.3.1 is presented in Shenoy et al. (1974) as the result from application of their model. FDDM/F presents a similar figure but based on the above model equation, with results portrayed at the same shim contents as Fig. 3.4.3.1 (i.e., 0, 11, 23, and 36 v/o). One can conclude the FDDM/F model is developed from that presented by Shenoy et al. (1974) but with more detailed numerical approximation for intermediate values of shim content.

DISCUSSION

Model equations per se have not been presented prior to FDDM/F in the open literature. Apparently, the only relevant information was a figure presented by Shenoy et al. (1974), which shows the calculated specific heat of a compact as a function of temperature and shim content, and reproduced as Fig. 3.4.3.1. This figure is calculated "by summing the contributions of individual fuel [compact] components (matrix, SiC, PyC, etc.) according to Kopp's additivity rule". The values of specific heat used for SiC, UC_2 , and ThO_2 were obtained from Touloukian (1970, vol. 5), and those for the carbonaceous materials were obtained from Butland et al. (1973). Values of compact specific heat for shim contents other than those in Figure 3.4.3.1 were obtained by extrapolation.

As no measurements were reported of the specific heat of fuel compacts through 1976, some justification of the use of Kopp's additivity rule was given by comparison of predictions with the measured specific heat of several cermet (see Table 3.4.3.2), with variations of less than 10% (Shenoy et al., 1974, Amendment 1).

The results of a sensitivity study presented by Shenoy et al. (1974, Amendment 1) on the relative effect of each component on total compact specific heat are shown in Table 3.4.3.3. These results show the presence of ThO_2 makes a significant contribution to the compact specific heat. Use of the model equations represented by Figure 3.4.3.1 may require consideration of the actual shim content and the presence or absence of ThO_2 in the compact for realistic specific heats.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The design curves of Figure 3.4.3.1 could be recalculated using the parameters of the modern compacts, particularly the actual shim content and the relative volume fraction of fissile vs. fertile kernels. Data on the specific heat of UC_2 vs UO_2 should be considered, and modified to reflect the carbon-to-oxygen ratio in the UCO kernel. If possible, more accurate data on the specific heat of PyC, H-451 graphite, etc. should be considered rather than a single average value. The expectation that irradiation should increase the specific heat of the nongraphitic components should be confirmed, if possible.

DATABASE USED IN MODEL DEVELOPMENT

Refer to Tables 3.4.3.2 and 3.4.3.3.

Fig. 3.4.3.1. Specific heat of graphite and fuel compacts as a function of temperature (from Shenoy et al., 1974).

Table 3.4.3.2. Comparison of calculated and experimental values for the specific heat of cermets (from Shenoy et al., 1974, Amendment 1)

CERMET (COMPONENTS IN WT %)	SPECIFIC HEAT (cal/gm-°K)			
	EXPERIMENTAL 373°K	EXPERIMENTAL 1073°K	CALCULATED 373°K	CALCULATED 1073°K
78% SiC/20% C/1% SiC/ 1% other ^(b)	0.207	0.323	0.198-0.204	0.289-0.312
50% SiC/46% C/4% Si ^(b)	0.207	0.373	0.205-0.217	0.330-0.353
43% SiC/57% C ^(c)	0.206	0.365	0.207-0.221	0.361-0.371
23% SiC/77% C ^(c)	0.230	0.398	0.211-0.231	0.380-0.400
57.6% BeO/42.4% Mo ^(d)	0.188	0.285	0.195-0.202	0.290-0.307

(a) Calculated from components using Kopp's law. Component data from Touloukian (1970), vol. 5 (SiC, C, and BeO), vol. 4 (Si and Mo).

(b) Data from Touloukian (1970), vol. 5.

(c) Data from Touloukian (1970), vol. 5.

(d) Data from Touloukian (1970), vol. 5.

Table 3.4.3.3. Relative effect of fuel compact component specific heats on total (calculated) fuel compact specific heat (from Shenoy et al., 1974, Amendment 1)

Temperature (°C)	Shim Content (vol %)	CONTRIBUTION OF COMPONENT SPECIFIC HEAT TO TOTAL FUEL ROD SPECIFIC HEAT (%)			
		Pyrocarbon + Matrix + Shim	SiC	UC ₂	ThO ₂
200	0	74.9	4.5	0.8	19.8
200	0	80.3	3.5	0.6	15.6
200	23	85.6	2.6	0.5	11.3
200	36	91.1	1.6	0.3	7.0
500	0	79.2	4.0	0.7	16.1
500	0	83.9	3.1	0.5	12.5
500	23	88.3	2.3	0.2	9.2
500	36	92.8	1.4	0.3	5.5
1000	0	80.2	4.0	0.6	15.2
1000	0	84.7	3.0	0.5	11.8
1000	23	89.0	2.2	0.3	8.5
1000	36	93.2	1.4	0.2	5.2
1800	0	80.1	4.1	0.6	15.2
1800	0	84.6	3.1	0.5	11.8
1800	23	88.9	2.4	0.3	8.4
1800	36	93.2	1.4	0.2	5.2

3.4.4 FUEL COMPACT EMISSIVITY

function	This model provides a value for the thermal emissivity of the fuel compact to be used in heat transfer calculations.
present status	No data for the thermal emissivity of the fuel compact is presented in FDDM/F. Although this potential mechanism of heat transfer from the compact to the graphite was presented by Shenoy et al. (1974), its relevance to present methods of thermal analysis is not known to this writer. This model is presented here for the sake of completeness.
model uncertainty	As discussed below, the uncertainty in the recommended design value for the emissivity is approximately 10 to 15% that of the experimental values. The significance of this uncertainty to overall core design and modelling is unknown to this writer.
references	Shenoy et al. (1974)

Model equations

Shenoy et al. (1974) state that the spectral emissivities from the compact surface have been measured in the range of 0.86 to 0.92. A design value of 0.8 is recommended as a conservative value over the life of the compact.

Range of validity

The original data upon which this design value is based have not been reviewed, nor have the experimental conditions under which the data were obtained.

Assumption

The emissivity of the compact will change little over the lifetime of the compact.

Uncertainty

The experimental values are reported to vary 10 to 15% from the recommended design value.

MODEL CHRONOLOGY

FDDM/F presents no discussion of the emissivity of fuel compacts. The only apparent reference to this data is that by Shenoy et al. (1974), who reference Johnson (1974) as providing the source data.

DISCUSSION

This writer is unaware whether thermal emissivity is considered significant for current core thermal design methods. This mechanism for heat transfer was considered relevant in 1974 and was included in core thermal design calculations. If the compact shrinkage is greater than the core graphite shrinkage, then consideration of thermal emissivity from the compact should be justified.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Deemphasis of this thermal property in FDDM/F suggests that further analysis and development of this model is not justified. If relevant, the source data reported to be in Johnson (1974) should be reviewed.

DATABASE USED IN MODEL DEVELOPMENT

The source data is reported to be in Johnson (1974). This reference has not been reviewed by this writer.

3.4.5 PARTICLE KERNEL AND COATING THERMAL CONDUCTIVITIES

function	These values for the thermal conductivity of the fuel particle materials are taken from published reports and are listed here for informational purposes.
present status	No reference is made to these thermal properties in FDDM/F. These values as reported in the early 1980s are included for reference with minimal discussion.
model uncertainty	Some reported values for thermal conductivity vary by factors of two to four.
references	McElmury et al. (1975a); Myers (1981a); Becker et al. (1983)

Model equations

Values for the thermal conductivities of kernel materials and particle coatings as given by Becker et al. (1983) and others are listed in Table 3.4.5.1. The thermal conductivities are employed in standard heat transfer and temperature distribution calculations. No temperature dependence of the thermal conductivities was presented or discussed.

Table 3.4.5.1. Thermal conductivities of fuel particle components

Material	Thermal conductivity (W m ⁻¹ K ⁻¹)	Reference	Source reference
Kernel:			
UO ₂	3.0	Becker et al. (1983)	Touloukian (1970, vol. 2)
UC ₂	13.8	Becker et al. (1983)	McElmury et al. (1975)
UCO	3.0 ^(a)	Becker et al. (1983)	Montgomery (1983)
ThO ₂	2.5	Myers (1981a)	McElmury (1975b)
Coating:			
buffer	2.3	Becker et al. (1983)	Myers (1981a)
PyC	9.1	Becker et al. (1983)	Myers (1981a)
SiC	8.4	Becker et al. (1983)	Myers (1981a)
Buffer-IPyC gap	0.024 ^(b)	McElmury et al. (1975a)	Cook (1961)

(a) Assumed to be the same as UO₂ (i.e., the final kernel material after burnup of the UC₂).

(b) Value for 100% xenon in gap.

Range of validity

No discussion of the range of validity is given in the main references. Values may represent room-temperature conditions. Any variation as a function of temperature is unknown to this writer except for SiC (discussed below).

Assumptions

The only assumptions known to this writer are the following.

1. The thermal conductivity of UCO is assumed to be the same as that of UO₂.
2. The value for the buffer-IPyC gap with 100% xenon in the gap is also representative for helium.

Uncertainties

Some reported values of thermal conductivity vary as much as a factor of four. The dependence of the non-SiC values in Table 3.4.5.1 on temperature is unknown to this writer.

MODEL CHRONOLOGY

Most of the values for thermal conductivity have been taken from source data, with some values approximated. The values have changed little from McElmury et al. (1975a), except Myers (1981a) averaged some of the reported values to obtain new values.

DISCUSSION

As the most recent source among the references presented, Becker et al. (1983) must be considered to provide the reference values until more recent values are located. Becker et al. (1983) obtained the values for the particle coatings from Myers (1981a). The table from Myers (1981a) is presented as Table 3.4.5.2, which indicates the averaging or selecting of values to obtain a reference value. Most of the values attributed to McElmury (1975b) in Table 3.4.5.2 (a GA Technologies internal document) are also presented in McElmury et al. (1975a). Two sets of values are given by McElmury et al. (1975a): one set reported to be the "more recent values", based on data from the particle components and used for most of the calculations in that report; and the second set used in calculational comparisons of "single-particle" and "two-particle" models. These two sets of values are listed in Tables 3.4.5.3(a) and 3.4.5.3(b). Comparison with Table 3.4.5.2 shows that Myers selected the values used for the calculational comparisons rather than the values reported to be "more recent." The rationale in determining which reference values were chosen is not stated.

Use of a single value for the thermal conductivity also introduces uncertainty. Figures 3.4.5.1 and 3.4.5.2 are taken from publications of R. J. Price (1977 and 1973, respectively), and show significant variation of thermal conductivity with irradiation and irradiation temperature. The data shown in Fig. 3.4.5.2 indicate the thermal conductivity of SiC irradiated at temperatures above 1000°C can vary significantly from the value reported by Myers. One might expect the other materials to also exhibit a temperature-dependent thermal conductivity.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

This summary provides a cursory review of the thermal conductivity data for the particle as provided by the major references. Further investigation into the original data and references would be required for reevaluation of the values suggested by Becker et al. (1983). In the case of SiC, Figures 3.4.5.1 and 3.4.5.2 suggest a dependence of the thermal conductivity on fast neutron fluence and on irradiation temperature. Refinement of the reference value for SiC might need to take these dependencies into consideration. Such

Table 3.4.5.2. Thermal conductivities for fuel particle materials (from Myers, 1981a)

Material	Thermal Conductivity (W/m·K)			Selected Value
	Ref. (a)	Ref. (b)	Ref. (c)	
ThO ₂	2.5	--	--	2.5
Buffer	2.1	2.5	--	2.3
PyC	3.56	14.6	8.4	9.1
SiC	18.8	8.4	8.4	8.4

(a) S. S. McElmury, "The Effect of Uncertainty and Known Variations in Coating Dimensions and Properties on Temperatures in Coated Fuel Particles," SSM:020:FMB:75, 27 May 1975.

(b) S. S. McElmury and O. M. Stansfield, "An Analysis of the Effect of Buffer-IPyC Coating Separation on the Temperature Distribution in TRISO UC₂ Fuel Particles," GA-A13500, General Atomic Company, December 1, 1975.

(c) J. Kaae, private communication.

Table 3.4.5.3.a. Thermal conductivity of particle components (from McElmury et al., 1975a)

Particle Component	Model Nomenclature	Thermal Conductivity (cal/sec-cm-°C)
Kernel	k_1	0.033
Buffer	k_2	0.005
Gap (100% Xe)	k_3	0.000058
Inner pyrocarbon (IPyC)	k_4	0.018
SiC	k_5	0.045
Outer pyrocarbon (OPyC)	k_6	0.018

Table 3.4.5.3.b. Particle dimension and component thermal conductivity used for comparing single-particle and two-particle models (from McElmury et al., 1975a)

Model Nomenclature	Particle Component	Outer Radius (μm)	Thermal Conductivity (cal/cm-sec-°C)
a	Kernel	100	0.0529
b	Buffer	150	0.0060
c	IPyC	170	0.0350
d	SiC	190	0.0200
e	OPyC	230	0.0350

(a) Thermal conductivity values were approximations derived from unpublished data.

Fig. 3.4.5.1. Thermal conductivity of unirradiated SiC and irradiated SiC at the irradiation temperature as a function of temperature (fluences between 10^{25} and 10^{26} n m⁻²) (from Price, 1977).

Fig. 3.4.5.2. Room-temperature thermal conductivity of pyrolytic B-SiC irradiated to $2.7 - 7.7 \times 10^{25} \text{ n m}^{-2}$ ($E > 0.18 \text{ MeV}$), as a function of irradiation temperature. ○: material deposited at 1400°C, Δ: material deposited at 1750°C (from Price, 1973).

dependencies might also be expected for the other materials within the particle, provided data exist which could provide information on such dependencies.

DATABASE USED IN MODEL DEVELOPMENT

Some of the database for SiC is indicated in Figures 3.4.5.1 and 3.4.5.2. Additional information on the database can be obtained from the references listed in the tables and in the figure captions.

3.5 UPDATE

The following references have been suggested as providing information on the Japanese program relevant to this chapter.

Minato, K., and K. Fukuda, "Strength and Young's modulus of silicon carbide layers of HTGR fuel particles at high temperatures," *J. Nucl. Mater.*, 182 (1991) 6-10.

Minato, K., K. Fukuda, and K. Ikawa, "Strength of Silicon Carbide Coating Layers of Fuel Particles for High Temperature Gas-Cooled Reactors," *J. Nucl. Sci. Technol.*, 19 (1982) 69-77.

T. D. Burchell et al. at ORNL have used a laser flash method to obtain thermal conductivity data on NPR fuel compacts. The reported results were not consistent with the reference models, particularly with respect to the temperature dependence of the thermal conductivity. This work is expected to be documented in a final report.

Other PIE data and analysis of the NPR and HRB-21 irradiation capsules should be reviewed as appropriate.

4. FISSION GAS TRANSPORT WITHIN THE FUEL PARTICLE

4.1 INTRODUCTION

Analyses of fission gas release focus on the short-lived isotopes of krypton and xenon. Iodine is also a concern, and is typically included as a fission gas because of the similarity of its release profiles from the particle with that of Xe. These three elements are the greatest contributors to the activity levels in the primary coolant (Nabielek et al., 1982). Although fission gas release from intact particles is insignificant, release from failed particles (typically referred to as "exposed kernels") and from heavy-metal contamination (§7) are of significant concern. Analyses of fission gas behavior generally assume that iodine and tellurium release is similar to xenon, and selenium and bromine release is similar to krypton. Existing data supports the analogy between iodine and xenon, although the analogy weakens for transport through graphitic components of the reactor core.

The only barriers to fission gas release considered by reference models are the kernel and the SiC and OPyC layers. The buffer and IPyC layers sometimes provide resistance to gas release, as discussed below, but normally are not considered in safety calculations. An intact SiC layer is considered to be impermeable to most fission products except for some metallic species at high temperatures. Fission gases are assumed to diffuse through the OPyC layer after SiC failure.

Exposed kernels are particles whose coating layers are no longer intact and provide no effective resistance to gas release from the kernel. Data on gas release from exposed kernels is normally obtained from laser-failed particles; i.e., particles which have been laser-drilled to the surface of the kernel, leaving a hole through the coating layers of approximately 10 μm diameter. Laser-failed particles are used as the reference for exposed kernels, although the relationship of their FP release to particles which may have interconnected porosity through coating layers of submicron dimensions has not been well defined.

Normal operating conditions

Several processes are involved in the release of fission gas from kernels: the gas atoms diffuse to the grain surfaces, where they accumulate in the porosity and form bubbles, and are finally released by bubble migration and interconnection of the porosity. According to Myers (1988) the predominant mechanisms of gas atom transport within the grains are: (1) athermal, neutron-irradiation-enhanced diffusion (at temperatures below 600°C); (2) diffusion enhanced by the neutron-generated vacancies (between 600 and 1000°C); and (3) thermally-induced gas atom diffusion (above 1000°C). Additional mechanisms for release are recoil of fission fragments from the near-surface region of the kernel, and knockout of FP atoms from the surface by collisions with fission fragments and reactor radiation.

The model developed for NOC fission gas release is semi-empirical and largely based on TRIGA reactor experiments, although the model is supported by other reactor

experiments (Myers, 1988). The model must simulate the release of both diffusing and of stored (i.e., trapped) gas from the kernel. A similar model format is employed for all NOC scenarios of gas release. The general NOC model equations are presented below, followed by the specific models.

Accident conditions

All NOC models (hydrolyzed and nonhydrolyzed kernels) simulate steady-state release of fission gas from the kernels. Transient release is simulated by the applicable AC models. A fundamental distinction between NOC and AC models is the absence of a neutron flux under AC which removes an important mechanism for athermal enhancement of diffusion, as well as limiting the gas release to that previously stored in the kernel structure during irradiation.¹ Accident condition models consider much shorter time scales than those considered for steady-state NOC release. Unlike the NOC models, the AC models for hydrolyzing vs nonhydrolyzing conditions are quite different.

Hydrolysis and oxidation

Hydrolysis describes the reaction of the particle and core materials with water vapor, while oxidation describes their reaction with molecular oxygen (FDDM/F). The mechanisms of reaction are not completely independent, as water has some oxidizing effect due to the inherent presence of oxygen. Oxygen and water are always present as impurities in the helium coolant. Nominal impurity levels have been given as 126 μatm of water and <630 μatm of all oxidants (O_2 , CO , CO_2) (CEGA, 1990). Myers (1986) quotes R. D. Burnette for a NOC oxygen concentration on the order of 10^{-9} (i.e., 1 ppbv). The possible large-scale ingress of water and steam during an accident raise much more serious concerns than the ambient impurity levels.

Only exposed kernels are considered in these models for hydrolysis and oxidation. Hydrolysis- and oxidation-induced failure of defective particles is not considered. Both hydrolysis and oxidation result in enhanced release of fission gas from the exposed kernel. The NOC models for hydrolyzing conditions presented below apply to gas release from completely hydrolyzed kernels. The AC models consider the transient effects induced by both gradual hydrolysis of the fuel kernel and by the sudden ingress of water or oxidant under accident conditions. A small but steady influx of water vapor results in an equilibrium enhancement of fission gas release, while a large influx induces rapid release of fission gas. For reference UCO fuel, the UC_2 portion of the kernel hydrolyzes quickly to form UO_2 , while the original UO_2 component of the fuel hydrolyzes slowly. The fertile ThO_2 fuel only hydrolyzes if it has previously been converted to the carbide at high temperatures. Oxidation of the carbide component of UCO progresses more rapidly than does the oxide component.

¹In MHTGR AC modeling, accident conditions are considered to be synonymous with reactor shutdown (zero flux). As such, transient overpower events are not analyzed in the context of AC modeling.

General model equations

The NOC model equations for steady-state short-lived¹ fission gas release from exposed kernels under both nonhydrolyzing and hydrolyzing conditions are similar and differ only in an additional multiplicative parameter used for hydrolyzing conditions. The governing equation has the functional form (Myers, 1985b, 1983b, 1981d):

$$\left(\frac{R}{B}\right)_{kjiHTFS} = \frac{\left(\frac{R}{B}\right)_{kji} \cdot f(T) \cdot f(F) \cdot f(H) + f_s}{1 + f_s}, \quad (4.1.1)$$

with the functional parameters defined to be:

$$\left(\frac{R}{B}\right)_{kji} = 3 \left(\frac{\xi_H}{\lambda_i}\right)^n, \quad n = 0.5, \quad (4.1.2)$$

$$f(T) = \frac{(R/B)_T}{(R/B)_o} = \frac{(R/B)_m}{(R/B)_o} + \left(1 - \frac{(R/B)_m}{(R/B)_o}\right) e^{Q/RT_o} e^{-Q/RT}, \quad (4.1.3)$$

$$f(H) = \frac{(R/B)_H}{(R/B)_o} = h, \quad (4.1.4)$$

$$f_s = e^{a(T-T_o)}. \quad (4.1.5)$$

For unhydrolyzed fuel:

$$f(F) = \frac{(R/B)_F}{(R/B)_o} = 1 + SF^{0.9}, \quad (4.1.6)$$

while for completely hydrolyzed fuel:

¹For discussion of models relevant to kernel release of stable fission gases see Nabielek et al. (1982) and Myers et al. (1977). Also, Myers (1985b) briefly discusses such a model.

$$f_H(F) = 1 + \frac{S_H F}{1 + F}, \quad (4.1.7)$$

$(R/B)_{kjiHTFS}$	=	steady-state fractional release for fuel type k , short-lived isotope i of element j , under hydrolysis H at temperature T and burnup F ,
$(R/B)_{kji}$	=	steady-state fractional release at the reference temperature ($T_o = 1373$ K) and negligible burnup,
$(R/B)_o$	=	same definition as for $(R/B)_{kji}$ above,
$(R/B)_T$	=	steady-state fractional release at temperature T ,
$(R/B)_F$	=	steady-state fractional release at burnup F ,
$(R/B)_m$	=	curve-fitting parameter,
$f(x)$	=	some function of the variable x , where $x = H, T$, or F .
T	=	temperature (K),
F	=	burnup (% FIMA).
H	=	hydrolyzing conditions,
f_s	=	factor related to structural changes in the fuel at high temperatures,
ξ_{kj}	=	reduced diffusion coefficient for element j in fuel type k (s^{-1}),
λ_i	=	radioactive decay constant of isotope i of element j (s^{-1}),
Q	=	activation energy for steady-state fission gas release ($J\ mol^{-1}$),
R	=	ideal gas constant ($8.314\ J\ mol^{-1}\ K^{-1}$),
T_o	=	reference temperature for steady-state fractional release (1373 K),
T_s	=	reference temperature for structural changes in the fuel (≈ 1750 K),
a	=	constant (K^{-1}),
S	=	constant (% FIMA) $^{-0.9}$,
h, S_H	=	constants (dimensionless).

Note that $(R/B)_{kji}$ and $(R/B)_o$ appear to be identical terms (Myers, 1983b). For nonhydrolyzing conditions, the parameter $f(H)$ is not included in Eq. (4.1.1) which then defines the term $(R/B)_{kjiTFS}$.

General assumptions

1. The model equations are specified to be valid for short-lived fission gases only, not for long-lived gaseous species.
2. Release of iodine and tellurium isotopes from exposed kernels can be modelled using the model parameters for xenon.
3. Release of bromine and selenium isotopes from exposed kernels can be modelled using the model parameters for krypton.

Discussion of model equations

This modelling approach takes the data for experimental gas release at 1100°C as the reference, and then attaches multiplicative terms to account for gas release dependencies

on temperature, burnup, and hydrolysis. Myers (1988) describes the model as containing "a diffusion parameter $[(R/B)_{kji}]$, multiplicative temperature $[f(T)]$ and burnup $[f(F)]$ functions and an ad hoc factor $[f_s]$. The function containing the diffusion parameter comes from a solution to the diffusion equation for release from a sphere. Very roughly, one might consider the diffusion parameter to account for the vacancy motion, the temperature function for the athermal mechanism as well as the overall temperature dependence, the burnup function for the developing pore structure and the ad hoc factor for the high temperature diffusion of gas atoms in grains as well as any bubble diffusion contribution at the highest temperatures of interest under normal operating conditions. This mishmash model is based mainly on TRIGA reactor experiments but has been roughly confirmed in other reactor experiments, the latest being HRB-17/18." According to Myers (1983b), the burnup-dependent term is considered to include irradiation effects in general and to subsume the effects of, for example, fission fragments and fast neutrons.

The reference fractional release curves, $(R/B)_{kji}$, for 1100°C and insignificant burnup ($F \approx 0$) are given in Fig. 4.1.1, as calculated from Eq. (4.1.2) (reference parameter values will be provided in §4.1.2 below). In Fig. 4.1.1, steady-state fractional gas release is shown to be a function of the kernel material, and the lower release curves of "as-manufactured fuel" (intact particles) represent release observed from fuels in the early 1970s and attributed to heavy-metal contamination (Haire et al., 1974).

A temperature-dependent term is combined with the reference fractional steady-state release according to (Myers, 1981d):

$$\left(\frac{R}{B}\right)_{kjiT} = \left(\frac{R}{B}\right)_{kji} \left[\frac{(R/B)_T}{(R/B)_o} \right], \quad (4.1.8)$$

with the multiplicative temperature-dependent function [Eq. (4.1.3)] described by Fig. 4.1.2 (reproduced from Myers, 1981d). Likewise, the dependence on burnup can be represented by:

$$\left(\frac{R}{B}\right)_{kjiF} = \left(\frac{R}{B}\right)_{kji} \left[\frac{(R/B)_F}{(R/B)_o} \right], \quad (4.1.9)$$

with the multiplicative burnup-dependent function [(Eq. (4.1.6))] described by Fig. 4.1.3 (Myers, 1981d). For hydrolyzed kernels, the corresponding temperature- and burnup-dependencies are represented by Figs. 4.1.4 and 4.1.5, respectively (Myers, 1981d). The effect of hydrolysis on the reference fractional steady-state release can be represented as $(R/B)_{kjiH}$ and defined analogously to Eqs. (4.1.8) and (4.1.9) by applying Eq. 4.1.4.

Fig. 4.1.1. Fission gas release curves at 1100°C for fuel particles with failed coatings (upper curves) and for as-manufactured fuel (lower two curves). Solid curves are for krypton, and dashed curves are for xenon (from Myers, 1981d). UO_2^* refers to a UO_2 kernel with a ZrC coating.

Fig. 4.1.2. Temperature dependence of normalized fractional release, $(R/B)_T / (R/B)_0$, for fission gas products from nonhydrolyzed as-manufactured fuel and fuel with failed coatings (from Myers, 1981d).

Fig. 4.1.3. Burnup factors for laser-failed particles as a function of burnup at 1100°C (from Myers, 1981d).

Fig. 4.1.4. Temperature dependence of normalized fractional release, $(R/B)_T / (R/B)_0$, for fission gas release from hydrolyzed, laser-failed fuel particles (from Myers, 1981d).

Fig. 4.1.5. Burnup factors for hydrolyzed, laser-failed particles as a function of burnup at 1100°C (from Myers, 1981d).

4.2 RELEASE FROM EXPOSED KERNELS: NORMAL OPERATING CONDITIONS, NO HYDROLYSIS

function	This model calculates the steady-state fission gas release from exposed kernels during irradiation as a function of temperature, kernel material and burnup, and isotope half-life.
present status	Although the model is semi-empirical, combining several assumed functional parameters and based mostly on results obtained from TRIGA reactor irradiations, predictions of gas release from kernels appear to be acceptable (Myers, 1988).
model uncertainty	Although significant uncertainty exists in one of the assumed functional parameters and in the diffusion coefficients of the gases in the kernel, the overall accuracy of the predictions are reasonable, and "the R/B values have not differed by more than, and in many cases, have differed by less than a factor of two" (Myers, 1988).
references	Myers (1985b, 1983b, 1981d)

Model equations

The model for fractional steady-state fission gas release from exposed kernels under nonhydrolyzing conditions is given by Eqs. (4.1.1) through (4.1.6) in §4.1, except the hydrolysis term, $f(H)$, is not included. Equation (4.1.1) thus takes the general form:

$$\left(\frac{R}{B}\right)_{kjITFS} = \frac{\left(\frac{R}{B}\right)_{kji} \cdot f(T) \cdot f(F) + f_s}{1 + f_s}, \quad (4.2.1)$$

and the detailed form:

$$\left(\frac{R}{B}\right)_{kjITFS} = \frac{3 \sqrt{\xi_{kj} / \lambda_i}}{1 + e^{a(T - T_s)}} \cdot \left\{ \left[\frac{(R/B)_m}{(R/B)_o} + \left(1 - \frac{(R/B)_m}{(R/B)_o}\right) e^{Q/RT_o} e^{-Q/RT} \right] \cdot (1 + SF^{0.9}) + e^{a(T - T_s)} \right\}, \quad (4.2.2)$$

with all parameters and variables as defined in §4.1.

The parameters for krypton and xenon release for use in Eq. (4.2.2) are listed in Table 4.2.1.

Table 4.2.1. Parameters for use in the design equation for fission gas release from unhydrolyzed exposed kernels, Eq. (4.2.2)

Parameter	UCO _{1.6} ^(a)		ThO ₂		UC ₂ ^(b)		UO ₂ ^(c)		UCO _{1.1} ^(c)		Ref.
	Kr	Xe	Kr	Xe	Kr	Xe	Kr	Xe	Kr	Xe	
ξ_H (s ⁻¹)	1.31 x10 ⁻¹⁰	1.35 x10 ⁻¹¹	8.17 x10 ⁻¹²	8.44 x10 ⁻¹³	1.23 x10 ⁻¹⁰	1.26 x10 ⁻¹¹	3.90 x10 ⁻¹¹	4.02 x10 ⁻¹²	1.62 x10 ⁻¹⁰	1.67 x10 ⁻¹¹	Myers (1981d)
(R/B) _∞ /(R/B) ₀	0.073	0.21	0.073	0.21	0.073	0.21	0.073	0.21	0.073	0.21	Myers (1981d)
Q (kJ mol ⁻¹)	53.1	45.2	53.1	45.2	53.1	45.2	53.1	45.2	53.1	45.2	Myers (1981d)
S (%FIMA ^{-0.9})	0.0	0.0	1.43	1.43	0.0	0.0	0.17	0.17	0.0	0.0	Myers (1981d)
a (K ⁻¹)	0.0128	0.0128	0.0186	0.0186	0.0133	0.0133	U ^(d)	U ^(d)	U ^(d)	U ^(d)	Myers (1985b)
T _i (K)	1800	1800	1790	1790	1700	1700	U ^(d)	U ^(d)	U ^(d)	U ^(d)	Myers (1985b)
T ₀ (K)	1373	1373	1373	1373	1373	1373	1373	1373	1373	1373	Myers (1981d)

(a) Parameters given here for UCO_{1.6} are used for the reference UCO fuel in FDDM/F.

(b) FDDM/F states that parameter values for UC₂ also apply to (Th,U)C₂ and ThC₂ kernels.

(c) Kernel materials not presented by FDDM/F or Myers (1985b).

(d) U = unknown, i.e., no parameters found in the literature; values for UCO_{1.6} might be used as an approximation.

Range of validity

This model is applicable to steady-state release under NOC (in the presence of a neutron flux) throughout the operating temperature range of the reactor. The model considers only short-lived fission gases (half-life < 5.3 d) in its derivation (Myers, 1981d). [Refer to Nabielek et al. (1982) and Myers et al. (1977) for discussion of a model relevant to kernel release of stable fission gases. Also, Myers (1985b) seems to imply that the model for release of the short-lived gases can also be applied to model release of long-lived gases by incorporation into the model equation recommended by Haire et al. (1974) for fractional release of radionuclides; however, this implication is not stated unambiguously.]¹

The experimental conditions under which the data used in model development were obtained are listed in Table 4.2.2 (Myers, 1981d) and compared to expected in-reactor conditions. The data were obtained from individual laser-failed particles (i.e., a hole burned through all coating layers using a laser). Data for gas release from fuel compacts was excluded because it was unexpectedly higher than that for the loose particles (Myers, 1981d). Most of the experimental data has been obtained at 1100°C, but some data has been obtained over the temperature range of 600 to 1300°C and a few data points near room temperature. Most of the data is obtained for burnups under 10% FIMA, with additional data up to 30% FIMA and a few data up to 60% FIMA. Gas release data was obtained from both BISO and TRISO particles for a variety of kernel materials [ThO_2 , $(8\text{Th},\text{U})\text{O}_2$, $(\text{Th},\text{U})\text{C}_2$, UO_2 , UC_2 , and UCO]. The gas release data obtained from the TRIGA irradiations does not truly represent steady-state release (Myers, 1981d).

Assumptions

1. Release of iodine and tellurium isotopes from exposed kernels can be modelled using the model parameters for xenon.
2. Release of bromine and selenium isotopes from exposed kernels can be modelled using the model parameters for krypton.
3. Fission gas release from laser-failed particles is comparable to release from particles with failed SiC, PyC, and buffer coating layers.
4. Fission gas release is a function of only temperature, burnup, and kernel material.
5. The burnup factor is independent of temperature (Myers, 1983b), and no synergism exists between the temperature and burnup dependencies of fission gas release.
6. The non-steady-state release of fission gas from TRIGA irradiations can be used to simulate steady-state release by the use of a constant correction factor (Myers, 1981d).
7. In Eq. (4.1.2) the exponent n is a constant of value 0.5 and remains constant for all irradiation and heating conditions.

¹In review, B. F. Myers comments that the reference formulation does account for both short- and long-lived isotopes, and that the other model for long-lived isotopes is not used at present.

Table 4.2.2. Comparison of TRIGA-test and reactor normal operating conditions
(from Myers, 1981d)

	TRIGA Test	Reactor NOC
Pressure (MPa)	0.24	5.0
Temperature (°C)	1100	700 to 1400
Temp. Gradient	No	Yes
Configuration	Loose, laser-failed particles	Particles failed in fuel rods in graphite core
Irradiation damage-annealing interaction	No	Yes
Time	Non-steady state (a) (short time)	Steady state (long time)
Neutron Flux	Low	Normal
Gas	Static	Flowing
Failure	Laser Hole	Particle and fuel rod cracking, induced porosity

(a) Except for hydrolyzed fuel

Uncertainties

The uncertainties in the model parameters are given in terms of the standard deviation of the natural logarithm of the parameter. The values as given by Myers (1981d) and FDDM/F are listed in Table 4.2.3.

MODEL CHRONOLOGY

An early analytical model was presented for fission gas release by Haire et al. (1974), which included the term $(R/B)_{kij}$. Myers et al. (1977) developed this model in more detail, but the modern version of this model did not appear until 1981 (Myers, 1981d). The only modification to the 1981 model was the introduction of the structure term (Myers, 1985b) to better simulate the enhanced gas release above 1100°C.

DISCUSSION

According to CEGA (1990), the current database relevant to this model for gas release from failed particles is derived primarily from the above-mentioned TRIGA measurements on laser-failed fuel particles. Although the results for gas release from unhydrolyzed fuel in the recently-completed HFR-B1 capsule should also be relevant to this model, analysis of that data has not yet been reported.

In comparison with Myers (1981d), it appears the parameters specified for UCO fuel in FDDM/F are actually based on calculations for $UCO_{1.6}$ rather than the reference $UCO_{1.7}$ fuel. In "Assumptions" above, reference is made to the use of two correction factors in using TRIGA data to simulate HTGR-like steady-state release. Reference should be made to Myers (1981d) for further discussion of the derivation and use of these correction factors. The need to use these correction factors introduces some uncertainty in using this TRIGA data for model development.

Table 4.2.3. Uncertainties in the parameters for NOC fission gas release from exposed kernels, no hydrolysis, Eq. (4.2.2)

Parameter ^(a)	Krypton	Xenon
ξ	0.94	1.40
Q	0.20	0.35
f(F)	0.5	0.5

(a) Uncertainty given in terms of the standard deviation of the natural logarithm of the parameter.

Other models for gas release used in the FRG and Great Britain are qualitatively described and contrasted with this GA model by Myers (1983b). Myers (1985b) describes differences in experimental gas release between GA and FRG data, some of which he ascribes to intact buffer layers on the FRG particles. Myers (1983b) states that the difference between laser-failed FRG and U.S. particles is that the buffer layers remain intact on the FRG particles but the hole is drilled to the kernel surface in the U.S. particles. If buffer layers do in fact remain intact on particles with failed SiC and OPyC layers within the reactor, the question then arises whether gas release from laser-failed particles will accurately represent what one would see under reactor conditions. This buffer effect is discussed in more detail in §4.8.2.

Another unresolved question in this model is the actual value of the exponent n in Eq. (4.1.2). A value of 0.5 is typical of diffusive release while a value of 1.0 is indicative of the release of stored gas (Myers, 1985b). Because some data provide a value of $n \approx 0.5$, the assumption is made that $n = 0.5$ under all conditions. The data do not unequivocally support this assumption. Myers (1981d) comments that for some data "the exponent n is found to be closer to 0.35 than 0.5. However, mechanisms leading to a lower value of n are not well established so that no generally acceptable expression for R/B incorporating such mechanisms is available. Therefore, the square root relation ($n = 0.5$) is used in the absence of any other." Myers (1981d) also comments that "the half-life dependence becomes weaker with increasing burnup, i.e., the value of n decreases. This can be shown by the data in Table [4.2.4]. A description of these data can be roughly given by the relation $n = 4.76/(14 + F)$ where F is in % FIMA. The form of this relation also fits data from long-term TRIGA experiments on laser-failed ThO_2 fuel ... although here the absolute values of n are lower at a given burnup as shown in Table [4.2.4]." Other data relevant to this issue is provided by Fig. 4.2.1 (from Myers, 1985b) which indicates a temperature-dependence of n , and it "is the change in n values in going from 1100°C to 1300°C that is the indicator of the release of stored gas [rather than a value of n close to one]. Unfortunately, there is no theoretical framework to quantitatively account for the specific n values found."

Thus, the square root dependence for $(R/B)_{ki}$ is actually an experimental parameter which is assumed to be 0.5 in agreement with the analytical model. FDDM/F gives the uncertainty of this value of n in terms of the standard deviation of $\ln n$. For Kr:

$$\sigma(\ln n) = 0.19 \quad , \quad (4.23)$$

and for Xe:

$$\sigma(\ln n) = 0.24 \quad . \quad (4.24)$$

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

A general question raised above is whether the gas release from laser-failed particles is the same as from particles with defective outer layers but intact buffer layers. Indications that densification of an intact buffer layer can have a significant effect on kernel gas release

Table 4.2.4. Dependence of the exponent n on burnup for unhydrolyzed laser-failed particles at 1100°C (from Myers, 1981d)

Fuel	Unirradiated	Irradiated	
	n	n	% FIMA
UC ₂	0.34	0.11	28
UCO _{1.6}	0.34	0.15	22
UO ₂	0.33	0.07	18
UO ₂ [*]	0.36	0.13	23
ThO ₂	-	0.23	1.2
ThO ₂	-	0.16	6
ThO ₂	-	0.098	11.7

Fig. 4.2.1. Fractional gas release vs decay constant at 850, 1100, and 1300°C for UCO particles with exposed kernels (18.5% FIMA) (from Myers, 1985b).

will be presented in §4.8.2. This question is irrelevant if the buffer layers of NP-MHTGR particles fail during irradiation, but if they remain intact this issue should be kept in mind in model analysis and revision.

From the above discussion, it is apparent that not all the questions about gas release from the kernel have been answered by the model. Myers (1981d) mentioned an effort to develop a better model and references several internal GA memoranda which were to be issued in a GA document (B. F. Myers, "Fission Gas Release Model," GA Document No. 906036). This document has not been reviewed by this writer and might be considered for its approach to revising the models for gas release from exposed kernels.

The existing data for gas release from exposed kernels has been analyzed in detail in derivation of this reference model, and the fact that predictions of gas release from kernels appear to be acceptable (Myers, 1988) suggests that further detailed analysis of the existing data may not be justified. However, CEGA (1990) states: "... the temperature dependence of gas release from both unhydrolyzed and hydrolyzed fuel has been addressed in the recently completed HFR B1 test, test results from these experiments are still being evaluated." The analysis of gas release from this experiment should be reviewed as it becomes available to determine its consistency with this existing model.

DATABASE USED IN MODEL DEVELOPMENT

Much of the database used in the model development is given by Myers (1981d, 1985b) with earlier data compilation by Myers et al. (1977). Figure 4.2.2 (Haire et al., 1974) shows some of the data used in early calculations of fractional kernel release vs nuclide half-life, which formed the basis of Fig. 4.1.1. Figure 4.2.3 (Myers et al., 1977) shows the effect of burnup on the reduced diffusion coefficient in ThO_2 kernels, while Table 4.2.5 (Myers, 1981d) also provides data on the burnup dependence for several kernel materials. Figure 4.2.4 (Myers et al., 1977) shows the temperature dependence of (R/B) for ^{85}Kr in a Fort St. Vrain-type fuel compact, while Fig. 4.2.5 (Myers et al., 1977) contrasts (R/B) for UO_2 vs $(\text{Th,U})\text{C}_2$ as a function of temperature. Figure 4.2.6 (Myers, 1983b) gives (R/B) data as a function of temperature and burnup for ^{85}Kr release from TRISO ThO_2 and $(8\text{Th,U})\text{O}_2$ particles. Figure 4.2.7 (Myers, 1985b) shows data for the temperature dependence of (R/B) for ^{85}Kr release from laser-failed UCO fuel particles. Figure 4.2.8 (Myers, 1983b) shows (R/B) for ^{85}Kr at 1100°C as a function of burnup for several kernel materials. Table 4.2.6 (Myers, 1981d) tabulates (R/B) data for ^{85}Kr release from laser-failed UC_2 particles at 1100°C as a function of burnup, while Table 4.2.7 (Myers, 1981d) calculates the burnup parameter, S , for several kernel materials and several fission gas isotopes.

In addition to Myers et al. (1977), other references for source data are Montgomery et al. (1982a) and Burnette et al. (1981). Montgomery et al. (1982a) provide data specifically for gas release from UCO fuel. Refer to these sources for more experimental detail and source data.

Fig. 4.2.2. Bases for reference R/B curves (from Haire et al., 1974).

Fig. 4.2.3. Average effective reduced diffusion coefficient in ThO_2 kernels at 1400°C vs percent FIMA (from Myers et al., 1977).

Table 4.2.5. Calculated diffusion parameters for unirradiated, loose, laser-failed particles at 1373 K (from Myers, 1981d; references available therein)

Kernel	Isotope	%R/B $\pm$ SD	(b) (%R/B) CORR	λ (1/s)	ξ_{kj} (1/s) (c)	Ref. 2 Run Nos.
UC ₂	Kr85m	0.60 $\pm$ 0.18	0.96	4.35(-5)	4.45(-10)	(d)
UC ₂	Kr85m	1.00 $\pm$ 0.5	1.60	4.35(-5)	1.24(-9)	-49 -88
	Kr87	0.87 $\pm$ 0.4	0.78	1.52(-4)	1.02(-9)	
	Kr88	0.84 $\pm$ 0.6	1.08	6.90(-5)	8.94(-10)	
	Kr89	0.70 $\pm$ 0.3	0.35	3.63(-3)	4.94(-9)	
UCO _{1.1}	Kr85m	0.69(e)	1.10	4.35(-5)	5.85(-10)	-48
	Kr87	0.64	0.58	1.52(-4)	5.68(-10)	
	Kr88	0.61	0.79	6.90(-5)	4.78(-10)	
	Kr89	0.57	0.29	3.63(-3)	3.39(-9)	
UCO _{1.6}	Kr85m	0.62(f)	0.99	4.35(-5)	4.74(-10)	-89
	Kr87	0.55	0.50	1.52(-4)	4.22(-10)	
	Kr88	0.59	0.74	6.90(-5)	4.20(-10)	
	Kr89	0.41	0.21	3.63(-3)	1.78(-9)	
UO ₂	Kr85m	0.34 $\pm$ 0.02	0.54	4.35(-5)	1.41(-10)	-40
	Kr87	0.28 $\pm$ 0.02	0.25	1.52(-4)	1.06(-10)	-46
	Kr88	0.27 $\pm$ 0.03	0.35	6.90(-5)	9.39(-11)	-60
	Kr89	0.24 $\pm$ 0.05	0.12	3.63(-3)	5.80(-10)	-91
UO ₂ *	Kr85m	0.084 $\pm$ 0.043	0.134	4.35(-5)	8.68(-12)	-41
	Kr87	0.063 $\pm$ 0.035	0.057	1.52(-4)	5.49(-12)	-47
	Kr88	0.056 $\pm$ 0.044	0.072	6.90(-5)	3.97(-12)	-90
	Kr89	0.063 $\pm$ 0.034	0.032	3.63(-3)	4.13(-11)	-61 -112
ThO ₂	Kr85m		0.13(g)	4.35(-5)	8.17(-12)	

(a) The original computer calculations of R/B used different intensity

Table 4.2.5 (continued)

factors for the Kr88 spectral peak in determining the disintegrations/minute (DPM) for the sample (correctly) and the DPM for the reference stearate sample (incorrectly). The Kr88 data in the tables of this memorandum as well as in Ref. 2 have been corrected (by hand) by dividing the R/B values based on the original computer calculations by 1.44. The value 1.44 represents the ratio of the old intensity factor to the new one (see Table of Isotopes, seventh edition. John Wiley, 1978, p 331; new value of intensity at 0.196320 MeV is 26.3% of total emission.)

- (b) Column 3 multiplied by $1/2 \operatorname{erf} \sqrt{\lambda t}$, $t = 1800s$.
- (c) $\xi_{kj} = \lambda(R/B)^2/9.10^4$.
- (d) Ref. 11, see text.
- (e) Only one run.
- (f) One of two runs; the other run has R/B factors of 50 to 60 smaller, and the particles used are thought to be improperly failed.
- (g) Ref. 3, this value represents long-term run data and no correction as in (a) above needed to be applied.

Fig. 4.2.4. Temperature profile of R/B for ^{85m}Kr release from fuel rod CR-12 (from Myers et al., 1977).

Fig. 4.2.5. Comparison of temperature profiles of R/B for $^{85\text{m}}\text{Kr}$ between matrix-dispersed bare kernels of $(\text{Th,U})\text{C}_2$ and UO_2 (from Myers et al. 1977).

Fig. 4.2.6. Fission gas (^{85}mKr) release measurements from laser-failed, TRISO-coated ThO_2 and $(8\text{Th},\text{U})\text{O}_2$ particles at 600 ($\circ$), 1050 ($\bullet$), and 1250 $^{\circ}\text{C}$ ($\square$) as a function of (a) burnup and (b) temperature (from Myers, 1983b).

Fig. 4.2.7. R/B vs $10^4/T$ for ^{85m}Kr in failed UCO fuel particles (from Myers, 1985b; references available therein).

Fig. 4.2.8. The dependence of R/B on burnup for ThO_2 , $(8Th,U)O_2$, $(2Th,U)O_2$ and UC_2 laser-failed fuel particles (from Myers, 1983b).

THE DEPENDENCE OF R/B ON BURNUP FOR Kr-85m AT 1100°C
IN LASER-FAILED, (2Th,U)O₂ PARTICLES

Fig. 4.2.8 (continued)

Table 4.2.6. *R/B* data on laser-failed UC₂ fuel particles for ⁸⁵Kr at 1100°C
(from Myers, 1981d)

(R/B)	% FIMA	Kernel Type
0.005	1.6	ThC ₂
0.008	1.6	ThC ₂
0.008	1.2	ThC ₂
0.014*	1.2	ThC ₂
0.008	1.8	ThC ₂
0.0048	0	UC ₂
0.0056	63	UC ₂
0.0066	8	UC ₂
0.0042	21	UC ₂
0.0057	30	UC ₂
0.0026	25	UC ₂
0.0038	30	UC ₂
0.0072	54	UC ₂
0.015*	0	UC ₂
0.005	0	UC ₂
0.005	28	UC ₂
0.0069	28	UC ₂

With all data:

$$R/B = 0.0078 - 5.89 \cdot 10^{-5} F$$

$$SR/B = 0.00318 (0.1065 - 0.0055 F + 1.59 \cdot 10^{-4} F^2)$$

Without * data:

$$R/B = 0.0060 - 1.38 \cdot 10^{-5} F$$

$$SR/B = 0.00169 (0.134 - 0.0069 F + 1.77 \cdot 10^{-4} F^2)$$

where *R/B* is for Kr85m at 1100°C and *F* is burnup in % FIMA.

Table 4.2.7. Calculated coefficients of burnup for burnup dependence of R/B
(from Myers, 1981d; references available therein)

Kernel/ % FIMA	Isotope	(a) %R/B±SD	(b) (%R/B) _{corr}	(c) S	Run No.
UC ₂ /28	Kr85m	0.60±0.10	0.96	0.0	(e)
	Kr87	0.49±0.07	0.96	(d)	-142
	Kr88	0.44±0.04	0.57	(d)	-143
	Kr89	0.29±0.01	0.15	(d)	
UCO _{1.1} /-(f)					
UCO _{1.} /22	Kr85m	0.53	0.85	-0.0 (g)	-85
	Kr87	0.49	0.44	-0.0	
	Kr88	0.40	0.52	-0.0	
	Kr89	0.33	0.17	-0.0	
UO ₂ /18	Kr85m	0.97±0.18	1.55	0.14	-76
	Kr87	0.85±0.16	0.77	0.15	-87
	Kr88	0.74±0.96	0.13	0.13	-115
	Kr89	0.83±0.16	0.42	0.26	
UO ₂ /23	Kr85m	0.82±0.09	1.31	0.52	-86
	Kr87	0.81±0.17	0.73	0.70	
	Kr88	0.61±0.12	0.79	0.59	
	Kr89	0.51±0.06	0.26	0.52	
ThO ₂ (h)	-	-	-	1.43	

(a) SD = standard deviation; no value indicates only one measurement was made.

(b) Column 3 multiplied by $1/2 \operatorname{erf} \sqrt{\lambda t}$, $t = 1800s$.

$$(c) S = \left[\frac{(\%R/B)_{F=F}}{(\%R/B)_{F=0}} - 1 \right] / F^{0.9}, \quad F = \% \text{ FIMA.}$$

Table 4.2.7 (continued)

- (d) See discussion in Section 3.1.1. The data of Ref. 2 alone are not adequate to determine the coefficient of burnup so that all data available on carbide kernels were used to determine the burnup dependence.
- (e) See Section 3.1.5.
- (f) The datum for $UCO_{1.1}$ has a very large value and is suspect.
- (g) See discussion in Section 3.1.5.
- (h) S determined in Ref. 3.

4.3 RELEASE FROM EXPOSED KERNELS: NORMAL OPERATING CONDITIONS, COMPLETE HYDROLYSIS

function	This model calculates the steady-state fission gas release from exposed kernels during irradiation after complete hydrolysis of the kernel, as a function of temperature, kernel material and burnup, and isotope half-life.
present status	The model for NOC release after complete hydrolysis of the kernel differs from the model for nonhydrolyzing conditions only in having an additional multiplicative hydrolysis factor and in modified values for some of the model parameters. Recent and current analyses of the data from the HRB-17/18 and HFR-B1 irradiation experiments will be relevant to this model.
model uncertainty	The uncertainty in the hydrolysis factor employed by the model is given a value of 3.4 (Myers, 1988) and is attributed to potential changes in kernel configuration under hydrolysis (swelling, cracking, etc.).
references	Myers (1981d, 1983b); Myers et al. (1977); Montgomery et al. (1982a)

Model equations

The model for fractional steady-state fission gas release from exposed and completely hydrolyzed kernels, $(R/B)_{kjiHTFS}$, is described by Eq. (4.1.1) in §4.1:

$$\left(\frac{R}{B}\right)_{kjiHTFS} = \frac{\left(\frac{R}{B}\right)_{kji} \cdot f(T) \cdot f_H(F) \cdot f(H) + f_s}{1 + f_s}, \quad (4.3.1)$$

which takes the detailed form:

$$\left(\frac{R}{B}\right)_{kjiHTFS} = \frac{3 \sqrt{\xi_k / \lambda_i}}{1 + e^{a(T - T_o)}} \cdot h \cdot \left\{ \left[\frac{(R/B)_m}{(R/B)_o} + \left(1 - \frac{(R/B)_m}{(R/B)_o}\right) e^{Q/RT_o} \cdot e^{-Q/RT} \right] \cdot \left(1 + \frac{S_H F}{1 + F}\right) + e^{a(T - T_o)} \right\}, \quad (4.3.2)$$

with parameters as defined in §4.1. This model equation differs from that for unhydrolyzed fuel only in having an additional hydrolysis factor, $f(H)$, and a modified burnup parameter, $f_H(F)$. The parameters for krypton and xenon release for use in Eq. (4.3.2) are listed in Table 4.3.1. The values for the variables ξ_k , a , T_o , and T_o are the same for both hydrolyzed

Table 4.3.1. Parameters for use in design equation for gaseous release from exposed kernels with complete hydrolysis, Eq. (4.3.2)

Parameter	UCO _{1.6} ^(a)		ThO ₂ ^(b)		UC ₂ ^(c)		UO ₂ ^(d)		UCO _{1.1} ^(d)		Ref.
	Kr	Xe	Kr	Xe	Kr	Xe	Kr	Xe	Kr	Xe	
ξ_{ij} (s ⁻¹)	1.31 x10 ⁻¹⁰	1.35 x10 ⁻¹¹	-	-	1.23 x10 ⁻¹⁰	1.26 x10 ⁻¹¹	3.90 x10 ⁻¹¹	4.02 x10 ⁻¹²	1.62 x10 ⁻¹⁰	1.67 x10 ⁻¹¹	(i)
(R/B) _∞ /(R/B) ₀	0.83	0.87	-	-	0.83	0.87	0.83	0.87	0.83	0.87	(i)
Q (kJ mol ⁻¹)	10.2	8.08	-	-	10.2	8.08	10.2	8.08	10.2	8.08	(i)
S _H	-0.40	-0.40	-	-	2.4	2.4	5.1	5.1	-0.40	-0.40	(i)
a (K ⁻¹) ^(e)	0.0128	0.0128	-	-	0.0133	0.0133	U ^(f)	U	U	U	(j)
T _i (K) ^(e)	1800	1800	-	-	1700	1700	U	U	U	U	(j)
T ₀ (K)	1373	1373	-	-	1373	1373	1373	1373	1373	1373	(i)
h	1.70 ^(g)	1.70 ^(g)	-	-	1.70 ^(g)	1.70 ^(g)	1.7	1.7	4.9 ^(h)	4.9 ^(h)	(i)

(c) Parameters given here for UCO_{1.6} are used for the reference UCO fuel in FDDM/F.

(b) Parameters for ThO₂ are given by Myers (1981d), but FDDM/F states that hydrolysis of ThO₂ does not occur unless it has first been converted into ThC₂, after which parameters for UC₂ hydrolysis should be used.

(c) FDDM/F states that parameter values for UC₂ also apply to (Th,U)C₂ and ThC₂ kernels.

(d) Kernel materials not presented in FDDM/F or Myers (1985b).

(e) Values reported by Myers (1985b) for nonhydrolyzed kernels, and used in FDDM/F for hydrolyzed kernel gas release.

(f) U = unknown (i.e., no parameters found in the literature); values for UCO_{1.6} might be used as an approximation.

(g) Value from FDDM/F, and different from that given by Myers (1981d).

(h) Myers (1981d) also mentions a value of 24.

(i) Myers (1981d).

(j) Myers (1985b).

and unhydrolyzed conditions, but all other parameters are different from the unhydrolyzed case.

Range of validity

As in §4.2, the model is applicable to steady-state NOC gas release throughout the operating temperature range of the reactor. The model considers only short-lived fission gases (half-life <5.3 d) in its derivation (Myers, 1981d). In addition, the model is valid for completely hydrolyzed kernels only.

The experimental range of validity for UC_2 kernels as reported by Myers et al. (1977) includes heating temperatures from 300 to 900°C and 100 ppm water vapor pressure. The experimental range of validity for $UCO_{1.6}$ kernels as reported by Montgomery et al. (1982a) includes temperatures of 850 to 1300°C, for burnups of 18.5 and 24.5% FIMA.

Assumptions

The same assumptions apply as are listed in §4.2. In addition, the hydrolysis factor is assumed to be a constant independent of irradiation or heating conditions, with no synergism between the temperature, burnup, and hydrolysis dependencies of fission gas release. Apparently the hydrolysis factor for UO_2 kernels is assumed to apply to all kernel materials (see Table 4.3.2).

Uncertainties

The uncertainties in the model parameters are given in terms of the standard deviation of the natural logarithm of the parameter. The values as given by FDDM/F are listed in Table 4.3.3.

MODEL CHRONOLOGY

The model presented here was developed by Myers (1981d) and is present in largely the same form in FDDM/F except for the introduction of the high-temperature structure factor (Myers, 1985b).

DISCUSSION

Table 4.3.2 lists experimental hydrolysis factors for several kernel materials. The value for UO_2 is applied to all kernel materials by the model (Table 4.3.1). CEGA (1990) states that this model is derived from a database consisting of laboratory measurements and short-term TRIGA tests, and that isothermal, in-pile hydrolysis tests were conducted on reference UCO fuel in the HRB-17/18 capsule tests and that data from hydrolyzed fuel is also available from the recently completed HFR-B1 capsule test.

Table 4.3.2. Hydrolysis factors for unirradiated, loose, laser-failed particles at 1373 K
(from Myers, 1981d; references available therein)

Kernel	Isotope	(% R/B) _u (a)	(%R/B) _h (b)	Run No (c)	H (d)
UC ₂	Kr85m	0.96	6.0 (e)		39
UCO _{1.1}	Kr85m	1.1	(f)		24 (g)
	Kr87	0.58	(f)		
	Kr88	0.79	(f)		
	Kr89	0.29	(f)		
UCO _{1.6}	Kr85m	0.99	4.9		24
	Kr87	0.50	3.7	{ -105 }	
	Kr88	0.74	4.6		
	Kr89	0.21	2.8		
UO ₂	Kr85m	0.54	0.49		1.7 (h)
	Kr87	0.25	0.42	{ -104 }	
	Kr88	0.35	0.59		
	Kr89	0.12	0.44		
UO ₂ *	Kr85m	0.134	0.19 (i)		2.0
	Kr87	0.057	0.14	{ -106 }	
	Kr88	0.072	0.17		
	Kr89	0.032	0.13		
ThO ₂	Kr85m	0.13	-		1.0 (j)

- (a) These data are taken from Table 16.
- (b) These data are taken from Ref. 2; no steady-state correction has been applied.
- (c) These run numbers refer to the experiments listed in Ref. 2.
- (d) Calculated from the ratio $\{(\%R/B)_h / (\%R/B)_u\}^2$ for Kr85m.
- (e) This value is taken from Refs. 19 and 20.

Table 4.3.2 (continued)

- (f) No data on hydrolyzed, unirradiated, loose, laser-failed $\text{UCO}_{1.1}$ fuel particles in Ref. 2.
- (g) Based on Kr85m; in accordance with procedure described in Section 3.1.1.
- (h) Averaged over the H values for Kr85m, Kr87, and Kr88.
- (i) These values differ from those in Ref. 2, Table 1 since here, as stated at the beginning of Section 3, data on fuel rods are not used.
- (j) Assumed to be 1.0 in the absence of data for the case of hydrolysis.

Table 4.3.3. Uncertainties in the parameters for NOC fission gas release from exposed kernels, complete hydrolysis, Eq. (4.3.2)

Parameter ^(a)	Krypton	Xenon
ξ	0.94	1.40
Q	0.78	0.78
$f_H(F)$	0.5	0.5
$f(H)^{(b)}$	0.63	0.63
$n^{(c)}$	0.19	0.24

- (a) Uncertainty given in terms of the standard deviation of the natural logarithm of the parameter (FDDM/F).
- (b) Values differ from those given by Myers (1981d).
- (c) Although n [Eq. (4.1.2)] is assumed to be a constant ($n = 0.5$), n was found to vary in experiment; refer to "Discussion" in §4.2.

Myers (1988) discusses this model and these experiments in more detail. He states that most of the uncertainty in the model "arises from the possible change in particle configuration during hydrolysis. If the hydrolysis occurs rapidly, the kernel expands and could possibly enlarge the pore or cracks through which the water vapor reached the kernel. This matter can be addressed more thoroughly after completion of the detailed analysis of the HRB-17/18 experiment and related data ... Also, when the HFR-B1 experiment and the analysis are completed, the description of hydrolysis on smaller time scales will be possible. The data derived from these two reactor experiments cover the temperature range between 700 and 1100°C and the water vapor concentration range is adequate for application of the model to normal operating conditions but for water vapor concentrations, extrapolation to lower levels is required and this introduces some uncertainty."

Myers et al. (1977) analyzed the gas release from hydrolyzed UC_2 kernels. The data is presented in Table 4.3.4. Some of the conclusions of Myers et al. are quoted here. "Hydrolysis tests on unirradiated [i.e., very lightly irradiated], exposed carbide particles in fuel rods and slightly irradiated compact material show that R/B initially increases to 20% to 60%, then declines to approximately 10% after about 1200 h of annealing. In one hydrolysis test on an irradiated fuel rod, the apparent R/B of hydrolyzed carbide particles was estimated to be 1.35%. The recommended R/B for Kr-85m at 1100°C for failed, hydrolyzed carbide particles in fuel rods is $10\% \pm 4\%$. This value is based on data from the unirradiated fuel rods ... The large values for R/B encountered during fuel hydrolysis indicate a change in the mechanism of release for the short-lived isotopes as compared with the recoil-type release deduced for the case of unhydrolyzed failed fuel in fuel rods ... Diffusive

Table 4.3.4. $R/B^{(a)}$ vs hydrolysis time for UC_2 particles in compacts exposed to 100 ppm H_2O in helium (from Myers et al., 1977)

Time (h)	300°C		400°C		500°C		700°C		800°C		900°C	
	Laser- Drilled ^(b)	Bare Kernel ^(c)	Laser- Drilled	Bare Kernel	Laser- Drilled	Bare Kernel	Laser- Drilled	Bare Kernel	Laser- Drilled	Bare Kernel	Laser- Drilled	Bare Kernel
0	0.8	1.5	1.5	1.7 ^(d)	0.7	2.2	0.3	2.9	0.2	4.1	0.2	5.6
7											2.4	23.0
10							2.5	24.0	6.7	31.0		
15	1.5	3.2	6.6	16.0	1.5	14.0						
20											1.5	50.0
30							3.1	23.0	9.6	36.0		
50			6.6	21.0	2.4	39.0	2.4	24.0	8.7	43.0		
60	3.2	7.0									11.0	63.0
90								33.0				
100			6.2	25.0	3.6	29.0					11.0	12.0
110	2.7	16.0					2.1		11.0	42.0		
200							6.1	42.0	18.0	41.0	14.0	14.0
300	7.4	39.0	9.9	19.0	6.3	23.0	38.0	35.0	25.0	34.0	5.7	14.0
400							32.0	17.0	27.0	31.0	4.5	26.0
455												
560							25.0		27.0	32.0	8.3	11.0
630	21.0	23.0	12.0	17.0	10.0	22.0						
670								22.0				
780							16.0		30.0	32.0	9.1	21.0
1185								12.0				
1216			6.5 ^(d)	8.6 ^(d)	5.3 ^(d)	9.4 ^(d)						
1226	12.6 ^(d)	7.2 ^(d)										
1292							10.0					
1315									13.0	16.0	4.2	10.0

(a) Kr-85m R/B values (percent) at 1100°C, corrected for steady state (i.e., multiplied by 1.9).

(b) Fuel rods prepared from laser-drilled UC_2 TRISO-coated particles.

(c) Fuel rods prepared from bare kernel UC_2 particles.

(d) Average of two successive measurements.

release from the hydrolyzed fuel during the peak release is apparently contributing significantly to release. This can be understood on the basis of a greatly reduced diffusion distance for the hydrolyzed fuel, which is in a powder form; thus, the short-lived isotopes as well as the long-lived and stable isotopes diffusively escape before they decay. Also, as a result of the change in structure of the fuel during hydrolysis, the recoil fraction may be expected to increase. The relative changes in recoil and diffusive release as a function of annealing time are not known. However, with increased annealing time and possibly the onset of a slow sintering process, the fraction release, R/B decreases."

Montgomery et al. (1982b) analyzed the fission gas release from hydrolyzed $UCO_{1.6}$ kernels. Their results are summarized in Table 4.3.5 and the data tabulated in Table 4.3.6. They summarize their data as follows. "At 850°C the increase caused by hydrolysis of $UC_{0.4}O_{1.6}$ irradiated to 18.5% FIMA is ~6. When the sample is irradiated to 24.5% FIMA, the ratio of the fractional release from hydrolyzed fuel to that from unhydrolyzed fuel is ~4.0." Additional interpretation of the results with respect to release mechanisms is provided.

The model equations simulate gas release from completely hydrolyzed kernels. No discussion is presented of release for partially hydrolyzed kernels or the presence of small concentrations of water. No model is presented to consider release for intermediate conditions of hydrolysis. One would assume that insufficient data exist to consider this regime.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The "Additional Considerations" mentioned in §4.2 are also relevant here. In particular, the data from the HRB-17/18 and HFR-B1 experiments must be evaluated and compared to this model for consistency.

If a model for gas release from incompletely hydrolyzed kernels would be useful for expected NP-MHTGR conditions, such a model might be developed by interpolation between the models of §4.2 and §4.3 (i.e., between no kernel hydrolysis and total hydrolysis).

DATABASE USED IN MODEL DEVELOPMENT

Some of the relevant database was presented above in Tables 4.3.2 and 4.3.4 through 4.3.6. In addition, experimentally determined values of n , Q , and S_H for hydrolyzed kernels are presented in Tables 4.3.7, 4.3.8, and 4.3.9, respectively (taken from Myers, 1981d). Myers (1981d) makes reference to additional General Atomic documents which contain gas release data used in the model development, but these documents have not been reviewed for inclusion here.

Table 4.3.5. Summary table of results from 28-hour irradiation of failed Si-BISO $UC_{0.4}O_{1.6}$ (from Montgomery et al., 1982a)

Fuel Condition	Experimental Observation					Remarks
	Time for Kr-85m to Reach Equilibrium at 850°C	Kr-85m Correction Factor at 850°C(a)	Decay Constant Dependence	Temperature Dependence(b)	Possible Mechanism	
Unirradiated/unhydrolyzed	2-4 hr	1.9	Ambient-850°C: <0.3 1100°-1300°C: 0.5	Expected Expected	Recoil Diffusion/ recoil	• High λ dependence at 1100°-1300°C suggests diffusion but not compatible with short equilibrium time.
Unirradiated/hydrolyzed	>16 hr	3	850°-1300°C: 0.37-0.45	Expected	Pseudo recoil/ diffusion	• First time that time dependent release observed in failed hydrolyzed fuel. • Activation energy probably too low for bulk diffusion. • Pseudo recoil mechanism questionable.
Irradiated/unhydrolyzed	0.5-2 hr	1.2-1.4	Ambient-1100°C: <0.3 1300°C: 0.5	Expected Unexpected(c)	Recoil Recoil	• High release at 1300°C due to stored fission gas. • Activation energy too low for bulk diffusion. • Irreversible structural change at 1300°C.
Irradiated/hydrolyzed	6-8	1.3-1.5	850°-1300°C: 0.13-0.23	Expected	Pseudo recoil	• Low λ dependence not compatible with time dependent release and bulk diffusion mechanism. • Pseudo recoil mechanism questionable.

(a) Not the same factor used to correct standard 1100°C TRICA test (STT) for steady-state, since STT collects gas for additional 15 min after reactor scram.

(b) Expected refers to temperature dependence reported in Fuel Design Data Manual; a factor of 2-3 for temperature jump of ~200°C between 800°-1300°C.

(c) Unexpected refers to an apparent increase in R/B of >10 between 1100° and 1300°C.

Table 4.3.6. Summary of krypton isotope release from failed Si-BISO LEU $UC_{0.4}O_{1.6}$ during 28-hour irradiation tests (from Montgomery et al., 1982a)

Sample	Temperature (°C)	R/B x 10 ²			
		Kr-85m	Kr-88	Kr-87	Kr-89
Nonirradiated	R.T.	0.066	0.055	0.052	0.023
Nonhydrolyzed	850	0.4	0.3	0.3	0.1
8489-28	1100	2.1	1.8	1.4	0.3
	1300	5.4	4.8	3.7	0.7
Irradiated	R.T.	0.067	0.056	0.059	0.028
18.5% FIMA	850	0.3	0.2	0.2	0.1
Nonhydrolyzed	1100	0.4	0.4	0.5	0.2
8489-34	1300	15.1(a)	11.0(a)	8.3(a)	1.5(a)
Irradiated	R.T.	0.16	0.15	0.14	0.062
24.5% FIMA	850	0.7	0.6	0.6	0.3
Nonhydrolyzed	1100	1.3	1.1	0.9	0.4
8489-46	1300	25.4(a)	18.8(a)	14.0(a)	2.1(a)
Nonirradiated	850	4.0	3.1	2.3	0.8
Hydrolyzed	1100	9.5	7.5	5.6	1.3
8489-30	1300	16.0	13.0	10.8	2.8
Irradiated	850	1.6	1.3	1.3	0.8
18.5% FIMA	1100	2.3	2.0	1.7	1.0
Hydrolyzed	1300	2.6	2.3	2.0	1.0
8489-36					
Irradiated	850	2.9	2.5	2.6	1.6
24.5% FIMA	1100	5.0	4.4	4.1	2.4
Hydrolyzed	1300	9.1	8.0	6.8	3.2
8489-48					

(a) These values are influenced by release of stored fission gas and are not equilibrium R/B values: see Discussion 6.1.3 "Temperature Dependence."

Table 4.3.7. Values of the exponent n for unirradiated and irradiated hydrolyzed laser-failed particles at 1100°C (from Myers, 1981d)

Fuel	Unirradiated	Irradiated	
	n	n	% FIMA
UC ₂	0.11	0.07	28
UCO _{1.6}	0.13	0.10	22
UO ₂	0.06	0.08	18
UO ₂ *	0.09	0.09	23

Table 4.3.8. Activation energies for the temperature dependence of R/B for hydrolyzed fuel (from Myers, 1981d)

Isotope	$Q(\text{cal/mol})$ (a)	$Q(\text{cal/mol})$ (b)	$Q(\text{cal/mol})$ (c)
Kr85m	2493	2555	
Kr87	3750	3776	
Kr88	2275	2258	
Kr89	1083	1346	
Average	2400	2483	2443 $\pm$ 972
Xe135	3949	3650	
Xe138	1561	1531	
Xe139	453	433	
Average	1988	1871	1930 $\pm$ 1533

(a) Determined from absolute R/B values.

(b) Determined from R/B values relative to stearate R/B values

(c) Average overall data with standard deviation.

Table 4.3.9. Calculated coefficients of burnup for burnup dependence of R/B in hydrolyzed fuels (from Myers, 1981d; references available therein)

Kernel/ % FIMA	Isotope	$(\%R/B)_{F=0}$ (a)	$(\%R/B)_{F=F}$ (b)	S_H (c)
UC ₂ /23 (e)	Kr85m	6.0	20.0	2.4
UCO _{1.1} /- (f)				
UCO _{1.6} /22	Kr85m	4.9	2.7	-0.47
	Kr87	3.7	2.4	-0.37
	Kr88	3.2	1.9	-0.41
	Kr89	2.8	1.9	-0.34
UO ₂ /18	Kr85m	0.49	2.9	5.2
	Kr87	0.42	2.5	5.2
	Kr88	0.41	2.4	5.0
	Kr89	0.44	2.5	4.9
UO ₂ [*] /23	Kr85m	0.19	1.2	5.5
	Kr87	0.14	0.95	6.0
	Kr88	0.12	0.76	5.7
	Kr89	0.13	0.84	5.7
ThO ₂ (g)	Kr85m	-	-	0.0

(a) $(\%R/B)_{F=0}$ = the percent R/B at zero burnup

(b) $(\%R/B)_{F=F}$ = the percent R/B at burnup F (F given in Column 1)

(c) $S_H = \left\{ \frac{(\%R/B)_{F=F}}{(\%R/B)_{F=0}} - 1 \right\} \left(\frac{1+F}{F} \right)$ where F is % FIMA.

(d) Run Nos. for data in Column 4.

(e) The values of $(\%R/B)$ were taken from Refs. 19 and 20.

(f) No data on UCO_{1.1} for the burnup dependence of R/B; assume values to be the same as for UCO_{1.6}.

(g) No data on ThO₂ fuel; assume no burnup dependence for R/B of hydrolyzed fuel.

4.4 RELEASE FROM EXPOSED KERNELS: ACCIDENT CONDITIONS, NO HYDROLYSIS

function	This model calculates the time-dependent fission gas release from exposed kernels during accident conditions (no neutron flux) with no water vapor present, as a function of gas species, kernel material and burnup, and temperature.
present status	The analytical framework of the model is well established using data for UC_2 and ThO_2 , but the database for fission gas release from UCO consists of only two experiments (Myers, 1988). ¹
model uncertainty	"No uncertainty analysis has been performed but an estimate of the uncertainty is less than a factor of 2 except for the UCO case where 3 is more appropriate" (Myers, 1988).
references	Myers et al. (1980); Myers (1988)

Model equations

The time-dependent fractional release of fission gas from exposed kernels under nonhydrolyzing accident conditions (no neutron flux present) is given by (Myers et al., 1980; FDDM/F):

$$f(t) = f_{\alpha} (f_{\beta_1} + f_{\beta_2}) + S \cdot t \quad , \quad (4.4.1)$$

$$f_{\alpha} = \sqrt{1 - e^{-\alpha t}} \quad , \quad (4.4.2)$$

$$f_{\beta_1} = \frac{1 - C}{1 + \delta_1} \quad , \quad (4.4.3)$$

$$f_{\beta_2} = \frac{C}{1 + \delta_2} \quad , \quad (4.4.4)$$

¹B. F. Myers comments that the model has also been successfully applied to German data.

$$S = S^{\circ} e^{-\sigma/T} (1 - f_{\beta_1} - f_{\beta_2}) \quad , \quad (4.4.5)$$

$$\alpha = a_1 g_1 + a_2 (1 - g_1) e^{-a_3/T} \quad , \quad (4.4.6)$$

$$\delta_i = \exp \left[\beta_i \left(\frac{10^4}{T} - \tau_{\beta_i} \right) \right] \quad , \quad i = 1, 2 \quad , \quad (4.4.7)$$

$$g_1 = \frac{f_{\beta_1}}{f_{\beta_1} + f_{\beta_2}} \quad , \quad (4.4.8)$$

- $f(t)$ = transient fractional gas release, no hydrolysis,
 T = temperature (K),
 t = time (h), for $t \leq (1 - f_{\beta_1} - f_{\beta_2})/S$,
 $f_{\beta_i}, f_{\beta_i}, g_1, \delta_i, C$ = burnup-dependent parameters, $i = 1, 2$ (dimensionless),
 $\alpha, S, S^{\circ}, a_i$ = burnup-dependent parameters, $i = 1, 2$ (h^{-1}),
 τ_{β_i} = burnup-dependent parameters, $i = 1, 2$ (K^{-1}).
 β_i = burnup-dependent parameter (K),
 σ, a_3, β_2 = constants (K).

Combination of Eqs. (4.4.1) through (4.4.8) gives the overall model equation:

$$f(t) = S^{\circ} e^{-\sigma/T} (1 - f_{\beta_1} - f_{\beta_2}) t + \quad (4.4.9)$$

$$(f_{\beta_1} + f_{\beta_2}) \sqrt{1 - \exp \left[- \left(\frac{a_1 f_{\beta_1}}{f_{\beta_1} + f_{\beta_2}} + \frac{a_2 f_{\beta_2}}{f_{\beta_1} + f_{\beta_2}} e^{-a_3/T} \right) t \right]} \quad .$$

For those parameters which vary linearly with burnup, the following form for the functional dependence is used:

$$p = c + dF \quad , \quad (4.4.10)$$

- p = general parameter representing $a_1, a_3, C, \beta_1, \tau_{\beta_1}$, and τ_{β_2} ,
 F = burnup (% FIMA),
 c, d = constants.

The parameter S° varies nonlinearly with burnup, and the following equations are used to represent this dependence:

$$S^o = S_o^o \quad , \quad F < 1.0 \quad , \quad (4.4.11)$$

$$S^o = S_o^o F^n \quad , \quad F \geq 1.0 \quad , \quad (4.4.12)$$

S_o^o, n = constants.

Values for the above parameters for UC_2 and ThO_2 kernels and krypton and xenon isotopes are given in Table 4.4.1, taken from Myers et al. (1980). These values are identical to those given in FDDM/F, the only difference being that Myers et al. (1980) represented the parameter a_3 as α_2 .

FDDM/F recommends using the same parameters for UCO that are given in Table 4.4.1 for ThO_2 . FDDM/F also recommends that iodine and tellurium release be modelled identically to that for xenon, except that the parameter values $a_1 = a_2 = 10$ and $a_3 = 0$ be used for tellurium instead of those for xenon.

Range of validity

The model is applicable for nonhydrolyzing conditions, in the absence of a neutron flux. Myers et al. (1980) state that the model was derived from FP release data from "laser-failed BISO ThO_2 and highly enriched (HEU) TRISO UC_2 particles that had been irradiated to a range of kernel burnups. The burnups were 0.25, 1.4, and 15.7% FIMA for ThO_2 particles and 23.5 and 74% FIMA for UC_2 particles ... Fission product release was measured in isothermal and temperature rise experiments. The range of the temperatures was from 1200° to 2300°C. In the temperature rise experiments, the heating rates were between 50° and 450°C/h."

Assumptions

1. The model parameters for ThO_2 can also be used to represent fission gas release from exposed UCO kernels.
2. The model parameters for Xe can also be used to model the release of Te and I from exposed kernels (except for modification in the values of a_1 , a_2 , and a_3).
3. The model derived from data for HEU kernels is also applicable to LEU kernel materials.

Uncertainties

According to FDDM/F, the uncertainties for fission gas release from exposed kernels have not been quantified. The only quantification is that provided by Myers (1988) and quoted above in "model uncertainty".

Table 4.4.1. Recommended values of the model parameters for fission gas release from exposed kernels under accident conditions, no hydrolysis (from Myers et al., 1980)

Parameters (p)	ThO ₂		UC ₂	
	Xe	Kr	Xe	Kr
Independent of burnup p = constant				
a ₃	2.96(4) ^(a)	2.91(4)	5.59(4) ^(b)	5.37(4)
β ₂	11.81	11.81	10.3	10.3
σ ²	3.44(4)	4.08(4)	4.92(4)	5.84(4)
Linearly dependent on burnup p = c + dF				
	c	d	c	d
a ₁	2.13	0.403	1.31	0.169
a ₂	3.33(5)	1.93(5)	5.02(5)	3.94(4)
c ²	0.9968	-3.62(-3)	0.980	-2.52(-3)
β ₁	1.23	-2.10(-2)	1.56	-4.20(-2)
τβ ₁	4.68	7.13(-2)	5.31	3.15(-2)
τβ ₂	4.49	1.26(-2)	4.58	4.90(-3)
Non-linearly dependent on burnup S^o = S_o^o Fⁿ				
	S _o ^o	n	S _o ^o	n
S ^o	8.42(3)	1.38	3.82(6)	0.298

(a) 2.96(4) = 2.96 × 10⁴.

(b) Average of values given in Table 6-1.

(c) The value of a₂ at 23.5% FIMA has been increased to avoid obtaining negative numbers with the recommended function for p (i.e., a₂).

MODEL CHRONOLOGY

The model as presented in FDDM/F is virtually identical to that presented by Myers et al. (1980). The values of the model parameters given in Table 4.4.1, taken from Myers et al. (1980), are the same as those given in FDDM/F. The model of Myers et al. (1980) was published earlier with the same model parameters in Myers et al. (1978).

DISCUSSION

Myers et al. (1980) states: "The central feature of the release model is a fractional release function which describes the release as a function of time, temperature, and burnup. This function was formulated as semiempirical but, for specific conditions, was shown to be equivalent to a corresponding function derivable from a diffusion equation which accounts for trapping ... The releases predicted with the model and the observed releases were in agreement. In the case of xenon and krypton nuclides, the predicted and observed releases differed by less than 18%, well within the associated uncertainties. Iodine and tellurium nuclides were found to behave like xenon nuclides except in a few instances."

Figures 4.4.1 and 4.4.2 (from Myers et al., 1980) show the relationship of the model to the measured Xe and Kr releases, respectively. Figure 4.4.3 indicates the similarity of release of Xe and I. Figure 4.4.4 indicates one instance in which the release of Xe and I are not similar, with the explanation that "the mechanism of release for iodine in UC_2 at high burnup is clearly different from that for xenon."

For detailed discussion of the derivation and logic of the model, one should refer to Myers et al. (1980). Details of the model and the physical interpretation of the model parameters will not be discussed here. In lieu of analysis, the general discussion of the model and some of the relevant data by Myers (1988) will be presented. "The US model ... is fairly well established, having also been used successfully by the Germans. The model involves a diffusion-trapping mechanism which is applied to gas atom migration at temperatures below the range 1700 to 2000 K and to gas bubble migration above this range, the particular temperature depending on the composition of the kernel. The parameters of the model have been determined mainly for ThO_2 and UC_2 and only two experiments have been conducted with the reference fissile fuel, UCO ... For the important case of iodine, US experiments have shown that above 1200°C, it can be treated as xenon, except in carbide kernels at temperatures of 1740°C and higher. Furthermore, there are German data on the release of iodine that we in the US have not yet incorporated into our data base. The US experiments also show that tellurium can be treated as xenon above 1200°C."

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Myers (1988) suggests incorporation of the German data for fission gas release from exposed kernels into the US database. Analysis of this German data for its relevance to model revision should be considered. Specifically, the recent work of W. Schenk and coworkers in the FRG should be reviewed (e.g., Schenk and Nabielek, 1988).

Fig. 4.4.1. Comparison of measured and calculated cumulative number of xenon atoms released in temperature rise experiments (from Myers et al., 1980).

Fig. 4.4.2. Comparison of measured and calculated cumulative number of krypton (^{85}Kr , ^{87}Kr , and ^{83}Kr) atoms released in temperature rise experiments (from Myers et al., 1980).

Fig. 4.4.3. Comparison of fractional release of xenon and iodine nuclides between 1200 and 2300°C (from Myers et al., 1980).

Fig. 4.4.4. Fractional release curves for xenon and iodine in Exp. 7240-92 at 2013 K with laser-failed UC_2 particles at 74% FIMA (from Myers et al., 1980).

Myers et al. (1980) comment that "model parameters that will conservatively predict release of fission products from the kernels of failed LEU fissile particles are developed from the HEU UC_2 data" in their work, and that the "model parameters will be confirmed when irradiated LEU particles become available." If relevant data exist, confirmation should be made that the release from LEU kernels does in fact confirm the validity of this model.

DATABASE USED IN MODEL DEVELOPMENT

Much of the database relevant to the derivation of this model is represented by Figs. 4.4.1 through 4.4.4. In addition, Table 4.4.2 provides data on the fractional release of I and Te isotopes during the temperature rise experiments. Additional details of the database can be obtained from Myers et al. (1980).

4.5 RELEASE FROM EXPOSED KERNELS: ACCIDENT CONDITIONS, WITH HYDROLYSIS

function	This model calculates the time-dependent fission gas release from exposed kernels during accident conditions (no neutron flux) in the presence of water vapor, as a function of initial UO_2/UC_2 ratio, burnup, temperature, and water vapor pressure.
present status	The presence of water increases the release of fission gas. For UCO fuel the "mechanisms have been established ... and the model is in good agreement with the available data in the range of temperatures 700 to 900°C for hydrolysis." However, data for UC_2 must be used for higher and lower temperatures, for the dependence of the hydrolysis rate coefficient on water vapor pressure, and for the retention of iodine from 300 to 800°C (Myers, 1988). The model should be reconsidered based on the recently published analysis of the HRB-17/18 irradiation capsule data (Myers, 1991). Additional details on the model for hydrolysis of kernel materials can be obtained in §11.2.
model uncertainty	"No uncertainty analysis of the total model has been made, but uncertainties, between 5 and 10 cannot be ruled out without some further analysis" (Myers, 1988).
references	Myers (1986, 1988)

Table 4.4.2. Fractional release of ^{131}I , ^{133}I , ^{135}I , and ^{132}Te in temperature rise experiments (from Myers et al., 1980)

Exp. No.	Temp Range (K)	Burnup (Z FIMA)	L (h)	Fractional Release			
				I-131	I-133	I-135	Te-132
7240-108	1270-2250	1.4	3.35	1.1(-2) (a)	8.1(-3)	1.0(-2)	3.4(-2)
		1.4	4.43	6.0(-1)	4.2(-1)	4.5(-1)	7.8(-2)
		1.4	4.43 MB (b)	3.4(-1)	5.9(-1)	5.1(-1)	7.7(-1)
7240-76	1250-2280	1.4	4.43	(c)	(c)	(c)	9.0(-1)
7240-78	1250-2240	15.7	2.13	2.9(-2)	1.3(-2)	1.3(-2)	1.1(-1)
		15.7	4.83	4.8(-1)	8.3(-1)	7.2(-1)	2.0(-1)
		15.7	4.83 MB	9.2(-1)	9.7(-1)	9.3(-1)	9.7(-1)
7240-106	1250-2280	15.7	4.63	(d)	8.8(-1)	7.5(-1)	3.7(-1)
		15.7	4.63 MB	(d)	8.8(-1)	9.3(-1)	9.6(-1)
7240-80	1270-2280	23.5	1.93	(e)	2.7(-2)	3.3(-2)	6.1(-2)
		23.5	4.37	(e)	8.2(-1)	8.6(-1)	6.0(-1)
		23.5	4.37 MB	(f)	(f)	(f)	9.6(-1)
7240-110	1270-2250	74.0	3.33	(d)	(g)	(g)	1.1(-1)
		74.0	4.55	(d)	(g)	(g)	1.6(-1)
		74.0	4.55 MB	(d)	(g)	(g)	5.6(-1)

(a) $1.1(-2) = 1.1 \times 10^{-2}$.

(b) MB represents mass balance; the fractional release entries in this row have been obtained from measurements of the particle activity before and after the experiment.

(c) Measurements not made in latter part of run.

(d) Measurement on initial particle inventory not available.

(e) Mass balance in error by factor of two.

(f) Measurement on final particle inventory not available.

(g) A very large uncertainty in initial particle activity measurements makes release calculations totally unreliable.

(h) Analysis incomplete.

Model equations: fissile particle under isothermal conditions

Accident conditions imply the absence of a neutron flux, therefore any fission gas release from exposed kernels represents release of stored gas only. For isothermal conditions, the fraction of gaseous inventory released due to hydrolysis, $f_h(t)$, is given by Myers (1986):

$$f_h(t) = \left(1 - \frac{\delta_{gJ}}{1 + e^{-b\Delta_i}} \right) \quad (4.5.1)$$

$$\left\{ \left(\frac{X}{1 + e^{C_1 F}} \right) (1 - e^{-\Delta_i^3}) + \left(\frac{(1 - X) + e^{C_1 F}}{1 + e^{C_1 F}} \right) \left(\frac{1 + C_0 e^{d\Delta_i}}{1 + e^{d\Delta_i}} \right) (1 - e^{-\Delta_i^3}) \right\} ,$$

$$\Delta_i = \int_0^t k_i [p_{H_2O}(\zeta), T] d\zeta \quad , \quad (4.5.2)$$

$$k_i = k_{o,i} (1 - e^{-a p_{H_2O}}) e^{-Q/RT} \left\{ 1 + \frac{C_2 e^{Q'/RT}}{1 + e^{C_3(T - T_{ok})}} \right\} \quad , \quad (4.5.3)$$

$f_h(t)$	=	fractional release of fission gas inventory from the hydrolyzed kernel,
t	=	time (h),
i	=	c for UC_2 or o for UO_2 ,
$\delta_{g,i}$	=	Kronecker delta, with $\delta_{g,i} = 1$ if the gas (g) released is iodine or $\delta_{g,i} = 0$ for other gases (Kr, Xe, etc.),
Δ_i	=	$10^4/T - 10^4/T_{o,i}$ (K^{-1}),
Δ_u	=	$10^4/T - 10^4/T_{o,u}$ (K^{-1}),
T	=	temperature (K),
$T_{o,i}, T_{o,k}$	=	constants (K),
X	=	twice the as-manufactured molar fraction of UC_2 in the UCO kernel, ¹
F	=	burnup (% FIMA),
$k_{o,i}$	=	constant (h^{-1}),
p_{H_2O}	=	water vapor pressure at the kernel (Pa),
$Q/R, Q'/R$	=	temperature coefficients (K),
Q	=	activation energy ($J \text{ mol}^{-1}$),
R	=	ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$),
a	=	constant (Pa^{-1}),

¹Myers (1986) defines X to be the "as manufactured" molar fraction of UC_2 in the UCO kernel.

b, d	=	constants (K),
C_o, C_2	=	constants (dimensionless),
C_1	=	constant (% FIMA ⁻¹),
C_3	=	constant (K ⁻¹),
ζ	=	dummy variable.

Values for the parameters are given in Table 4.5.1 (reproduced from Myers, 1986).

Model equations: fissile particles under nonisothermal conditions

If the fuel temperatures vary with time, Eq. (4.5.2) becomes:

$$\Delta_i = \int_0^t k_i [p_{B_2O}(\zeta), T(\zeta)] d\zeta, \quad (4.5.4)$$

the temperature in Eq. (4.5.3) also becomes dependent on the time, and the other model equations remain valid for short time increments over which the temperature remains approximately constant. Equation (4.5.1) can then be expressed in the general form (Myers, 1986):

$$f_h(t) = \sum_{j=0} \Delta_j [f_h(t)] , \quad (4.5.5)$$

$$\Delta_j [f_h(t)] = \left(1 - \frac{\delta_{g,j}}{1 + e^{-b\Delta_j}} \right) \cdot \left\{ \left(\frac{X}{1 + e^{C_1 F}} \right) \Delta_j \alpha_c + \left(\frac{(1 - X) + e^{C_1 F}}{1 + e^{C_1 F}} \right) \left(\frac{1 + C_o e^{d\Delta_j}}{1 + e^{d\Delta_j}} \right) \Delta_j \alpha_o \right\} , \quad (4.5.6)$$

$$\begin{aligned} \Delta_j \alpha &= \alpha(j+1) - \alpha(j), \\ j &= \text{index for the time interval,} \\ \alpha(j) &= 1 - \exp [-\Delta_j^3(j)]. \end{aligned}$$

Transient evaluations require solution of Eq. (4.5.6) over each of these short-time increments, and the fractional release over each of these increments is summed to give the total fractional release as a function of time. Myers (1986) provides details for such transient calculations and recommends approximations for the numerical evaluation of specific situations. This discussion should be referred to for relevant information on the computational implementation of the model into design codes.

Table 4.5.1. Values of the model parameters for fission gas release from exposed UCO kernels under accident conditions, with hydrolysis (from Myers, 1986)

Parameter	Value		
	Composition Independent	Composition Dependent	
		UC ₂	UO ₂
b	1.46		
T _{o,i} (K)	943.		
X	0.3		
C ₁	0.09		
d		NA	1.51
T _{o,u} (K)		NA	943.
C _o		NA	0.045
k _{o,i} (1/h)		236.	3.38
a (1/Pa)		5.99(-3)	3.65(-3)
Q/R (T)		4371.	4371.
C ₂		14.1	14.1
Q'/R(T)		1382.	1382.
C ₃ (1/K)		0.0443	0.0443
T _{o,k} (K)		413.	413.

Model equations: fertile particles

ThO_2 is not susceptible to hydrolysis and oxidation unless it first undergoes carbothermic reduction to thorium carbide. Such reduction will only take place at temperatures above 1400°C and under conditions which promote carbothermic reduction. Hydrolysis and oxidation of the carbide is modelled identically to that of UC_2 (Myers, 1986). Model equations for UC_2 hydrolysis and oxidation can be obtained in §11.2.5.

Range of validity

The model is valid in the absence of a neutron flux. According to Myers (1988) the available data for the hydrolysis of UCO is limited to the temperature range of 700 to 900°C , but data for UC_2 has been obtained at higher temperatures. Details on the range of validity of the models for hydrolysis of kernel materials can be obtained in §11.2.3.

Assumptions

The next seven assumptions are stated explicitly by Myers (1986).

1. The partial pressure of water vapor at the kernel can be accurately approximated.
2. Effects of the graphite and fuel compact matrix on the mass transfer of water vapor to the kernel are not significant.
3. The response of the UC_2 and UO_2 portions of the UCO kernel to hydrolysis are distinct.
4. Hydrolysis of the UC_2 portion of the UCO nears completion before hydrolysis of UO_2 begins.
5. Complete release of the fission gas stored in the UC_2 portion of the UCO is concurrent with the complete hydrolysis of the UC_2 portion.
6. For complete hydrolysis of the UO_2 portion of the UCO kernel, the release of the stored fission gas is dependent on the temperature.
7. The significant variables in AC gas release during hydrolysis are the water vapor pressure, temperature, and time of hydrolysis; any effects due to previous irradiation are insignificant.

In addition, the following assumptions are stated in FDDM/F.

8. In Table 4.5.1, the values of the parameters Q/R , Q'/R , C_2 , C_3 , and $T_{o,k}$ for UO_2 are assumed to be the same as for UC_2 due to the lack of data.
9. The parameters of Table 4.5.1 are assumed to be valid for all common fission gases (Kr, Xe, I, Te).

Uncertainties

According to FDDM/F and Myers (1988) no uncertainty analysis of this model has been performed. Myers (1988) estimates that "uncertainties, between 5 and 10 cannot be ruled out without some further analysis."

MODEL CHRONOLOGY

The same model and parameter values are given in both FDDM/F and Myers (1986). The existence of any related model prior to 1986 is unknown.

DISCUSSION

The original definition of X as noted in the footnote above appears to be an error, which was subsequently corrected in FDDM/F. Equation (4.5.1) represents the summation of two terms which reflect the fractional hydrolysis of the carbide and oxide portions of the kernel. More information on the kinetics and mechanisms of kernel hydrolysis can be obtained in §11.2.

Myers (1988) comments on this model for gas release during kernel hydrolysis. "The models are based on studies of the hydrolysis of UC_2 , UO_2 , and UCO ... The mechanisms have been established for the reference fissile particle and the model is in good agreement with the available data in the range of temperatures 700 to 900°C for hydrolysis ... However, in extending the results to lower temperatures in the case of hydrolysis, only data for UC_2 are available and the uncertainty associated with their use is unknown. Also, in accounting for (1) the retention of iodine by the reacting fuel over the range 300 to 800°C and (2) the dependence of the rate coefficient for hydrolysis on the water vapor pressure, data for UC_2 have to be used. The extrapolation of the model for hydrolysis and oxidation to temperatures above 900°C introduces an additional uncertainty of unknown magnitude."

A simplified approach to gas release during hydrolysis is presented by General Atomics (1989): hydrolysis of UCO kernels is assumed to result in the rapid release of 6% of the stored gases, hydrolysis of UO_2 kernels results in no rapid release, and hydrolysis of UC_2 results in the rapid release of 100% of the stored gases.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Myers (1986) states the assumption that this model "will be coupled with other models which account for the interactions of the oxidants with graphite and fuel [compact] matrix material." Whether this coupling has in fact been made in the relevant computer codes should be determined. If not implemented, such a coupling should be significant for the analysis of data from, for example, capsule HFR-B1.

Myers (1986) presents a model to take into account the effects of partial hydrolysis during NOC on the subsequent AC release. This model could be considered for refinement of the AC models and coupling with the previous NOC fuel environment.

Myers (1988) makes an interesting comparison of the NOC and AC models for fission gas release under hydrolysis. "The model for normal operating conditions describes the steady-state release whereas the model for accident conditions describes the transient release of fission gas. The former model is applied to large time scale events in the presence of a neutron field and the latter to small time scale events in the absence of a neutron field ... the two models must be related in the sense that as the time scale is reduced or the resolution increased under normal operating conditions, the transient behavior becomes

evident and has to be taken into account in a complete description." Whether this linkage between the two models has been achieved is doubtful.

Extensive analysis of the hydrolysis data from irradiation capsules HRB-17 and -18 was recently published (Myers, 1991a). The reference model given above should be revised to include this data from representative UCO kernels and the resulting changes in the mechanistic understanding of the hydrolysis process.

DATABASE USED IN MODEL DEVELOPMENT

The database for gas release has not been reviewed in detail. Figures 4.5.1 and 4.5.2 (from Myers, 1986) represent some of the data relevant to this model. The database relevant to the model for fractional hydrolysis of the kernel materials is presented in §11.2. The hydrolysis data from the HRB-17/18 irradiation capsules represent an expansion of the relevant database.

4.6 RELEASE FROM EXPOSED KERNELS: ACCIDENT CONDITIONS, TRANSITION FROM HYDROLYZING TO NONHYDROLYZING CONDITIONS

function	This model amends the previous AC hydrolysis model to consider gas release from exposed kernels under partially hydrolyzing conditions, as a function of fractional kernel hydrolysis as well as initial UO_2/UC_2 ratio, burnup, temperature, and water vapor pressure.
present status	This model considers an accident with limited water ingress which only partially hydrolyzes the exposed kernels before the water is depleted. This model is presented only in Myers (1986) and is not included in FDDM/F. It is included here for the sake of completeness.
model uncertainty	The uncertainty of this component of the gas release model is not discussed.
references	Myers (1986)

Model equations

An additional term is added to the time-dependent model equation for AC gas release from exposed kernels during hydrolysis, Eq. (4.5.5), to treat the gas release from the nonhydrolyzed portion of the fuel kernel during and after hydrolysis as the water vapor is depleted:

$$\bar{S}_T = S_0 \sum_j e^{-\sigma_j T_j} \Delta t_j (1 - f_H) \quad , \quad (4.6.1)$$

Fig. 4.5.1. The time profile of ^{133}Xe release from UCO fuel at 800°C under hydrolysis conditions of 18 Pa water vapor over the first nine hours (from Myers, 1986; references available therein).

Fig. 4.5.2. The time profile of ^{133}Xe release from UCO fuel at 800°C under hydrolysis conditions of 18 Pa water vapor over 93 hours (from Myers, 1986).

$$S_o = S_o^\circ F^n , \quad (4.6.2)$$

σ = temperature coefficient (K),
 T_j = temperature (constant) over time interval j (K),
 Δt_j = time interval j (h),
 f_H = fraction of fuel hydrolyzed,
 F = burnup (% FIMA),
 S_o, n = constants.

This modification converts Eq. (4.5.5) into the form:

$$f_h(t) = \sum_{j=0} \Delta_j [f_h(t)] + S_o e^{-\sigma/T_j} \Delta t_j (1 - f_H) , \quad (4.6.3)$$

with $\Delta_j[f_h(t)]$ defined by Eq. (4.5.6) and all terms defined as in §4.5. The fraction of fuel hydrolyzed, f_H , can be calculated using the model equations of §11.2.3. Values for the constants are given in Table 4.6.1, as provided by Myers (1986). Calculations involving Eq. (4.6.3) should be performed as discussed in §4.5.

Range of validity

Refer to Assumption 3 below for the model's range of validity. The experimental data are those of xenon and are the same data as those used to derive the model parameters of §4.4. Refer to §4.4 for additional experimental details.

Assumptions

Myers (1986) states the following assumptions.

1. The gas release under hydrolysis conditions is more rapid than the f_g -release (see "Discussion" below).

Table 4.6.1. Parameters for calculation of release of fission gas from the nonhydrolyzed portion of the exposed UCO kernel, Eq. (4.6.1)

Parameter	Units	Value
σ	K	3.44×10^4
S_o°	h^{-1}	8.42×10^3
n	-	1.38

2. The S -release is not retarded by a hydrolyzed surface layer of fuel material (see "Discussion" below).
3. Extrapolation of the linear time dependence of release beyond the range of times involved in the experiments on which this dependence is based, is conservative.

In addition, the assumptions stated in §4.4 are also applicable here.

Uncertainties

The uncertainty of this model is not discussed in Myers (1986).

MODEL CHRONOLOGY

All information on this model is taken from Myers (1986). This model is not mentioned in FDDM/F and is probably not discussed elsewhere.

DISCUSSION

The values in Table 4.6.1 are taken from Myers et al. (1978) and are the same as those listed for Xe in Table 4.4.1 of §4.4. The terms f_0 and S mentioned in "Assumptions" are explained by reference to Fig. 4.6.1, taken from Myers et al. (1978): f_0 represents the y-axis intercept of the extrapolated linear portion of the curve, while S represents the slope of the linear portion of the curve. Myers (1986) states that Eq. (4.6.1) is added to the model equation for AC hydrolysis gas release to "treat the release of fission gas from the non-hydrolyzed portion of the exposed fuel kernel during and after hydrolysis," which seems to indicate Eq. (4.6.3) could also be used prior to termination of the water ingress into the fuel. This point is not discussed further.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

To evaluate this model further, data relevant to the situation would be required for comparison. The analysis of the HRB-17/18 capsule hydrolysis data may be relevant here (Myers, 1991a).

DATABASE USED IN MODEL DEVELOPMENT

The database used in deriving the model parameters of Table 4.6.1 is the same as that discussed in §4.4 for Xe.

Fig. 4.6.1. Fractional release profile for ^{135}Xe at 1430°C from laser-failed ThO_2 particle with 0.25% FIMA (from Myers et al., 1978).

4.7 RELEASE FROM EXPOSED KERNELS: ACCIDENT CONDITIONS, WITH OXIDATION

function	This model calculates the time-dependent fission gas release from exposed kernels during accident conditions (no neutron flux) in the presence of free oxygen, as a function of oxygen vapor pressure and temperature.
present status	For UCO fuel the "mechanisms have been established ... and the model is in good agreement with the available data ... in the range 500 to 800°C for oxidation." However, data for UC_2 must be used for higher temperatures and for the retention of iodine from 300 to 800°C (Myers, 1988).
model uncertainty	"No uncertainty analysis of the total model has been made, but uncertainties between 5 and 10 cannot be ruled out without some further analysis" (Myers, 1988).
references	Myers (1986, 1988)

Model equations

The model for the oxidation of the UCO fuel kernel in the absence of a neutron flux is given by Myers (1986):

$$f_o(t) = \left(1 - \frac{\delta_{sI}}{1 + e^{-b\Delta_{ox}}} \right) (1 - e^{-\Delta_{ox}}) , \quad (4.7.1)$$

$$\Delta_{ox} = \int_{t_1}^t k_{ox} [p(\zeta), T(\zeta)] d\zeta , \quad (4.7.2)$$

$$k_{ox} = k_{ox,0} (1 - e^{-a_2 p_{O_2}}) e^{-Q''/RT} , \quad (4.7.3)$$

$$t_1 = \frac{t_1' e^{Q''/RT}}{1 - e^{-a_1 p_{O_2}}} , \quad (4.7.4)$$

$f_o(t)$ = fractional release of fission gas inventory from the oxidized kernel,
 t = time (h),

$\delta_{g,i}$	= Kronecker delta, with $\delta_{g,i} = 1$ if the gas (g) released is iodine or $\delta_{g,i} = 0$ for other gases (Kr, Xe, etc.),
Δ_i	= $10^4/T - 10^4/T_{a,i}$ (K^{-1}),
T	= temperature (K),
$T_{a,i}$	= constant (K),
$k_{a,o}$	= constant (h^{-1}),
p_{O_2}	= oxygen vapor pressure at the kernel (Pa),
Q''/R	= temperature coefficient (K),
Q''	= activation energy ($J\ mol^{-1}$),
R	= ideal gas constant ($8.314\ J\ mol^{-1}\ K^{-1}$),
a_1, a_2	= constants (Pa^{-1}),
b	= constant (K),
t'_i	= constant (h),
ζ	= dummy variable.

Values for the parameters are given in Table 4.7.1, taken from Myers (1986).

Range of validity

No limitations of the applicability of the model are stated by Myers (1986). Experimentally, data for UCO are limited to the temperature range of 500 to 800°C and data for UC_2 must be used outside that range (Myers, 1988).

Assumptions

The following model assumptions are stated in Myers (1986).

1. No distinction needs to be made between the UC_2 and UO_2 components of the fuel.
2. The oxidation rates of UC_2 and UO_2 are comparable.
3. The rate of kernel oxidation can be described by first order kinetics.
4. The release of stored gas is complete upon complete oxidation of UO_2 and UC_2 .

Uncertainties

No uncertainty analysis has been performed for this model (Myers, 1986; FDDM/F). According to Myers (1988), the "extrapolation of the model for ... oxidation to temperatures above 900°C introduces an additional uncertainty of unknown magnitude ... uncertainties between 5 and 10 cannot be ruled out without some further analysis."

MODEL CHRONOLOGY

This model was presented by Myers (1986) and incorporated into FDDM/F. Values for the model parameters are the same in both references.

Table 4.7.1. Values of the model parameters for fission gas release from exposed UCO kernels under accident conditions, with oxidation (from Myers, 1986)

<u>Parameter</u>	<u>Value</u>
b	1.46
$T_{o,I}(K)$	943.
$k_{ox,o}(1/h)$	9.96 (6)
$a_2(1/Pa)$	2.07 (-3)
$Q''/R(K)$	1.08 (4)
$t'_I(h)$	3.03 (-8)
$a_1(1/Pa)$	9.51 (-5)

DISCUSSION

The model equations presented above are similar to those of kernel hydrolysis, except that oxidation is considered to proceed rapidly and at comparable rates for the carbide and oxide portions of the UCO kernel. The kernel can therefore be considered as a single material. The model incorporates the expression for the fractional oxidation of the UCO kernel in §11.2.4; reference can be made to that section for additional information on the oxidation mechanism.

Myers (1986) comments on the oxygen concentrations to which the fuel might be exposed. "The oxygen concentrations during accident conditions are expected to be very low, although no specification is available. Under normal reactor operating conditions, the estimated concentration ... is of the order of 10^{-9} (1 ppbv). Under these conditions ... the oxidation of UCO can be neglected. Not until the pressure of oxygen is greater than 0.1 Pa does the induction period [for oxidation] become much less than 100 h." Additional information on the model derivation can be obtained from Myers (1986).

Information on the oxidation of UO_2 kernels and the associated release of FP can be obtained from Wood et al. (1985).

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Myers (1991) comments on some FRG calculations for UO_2 kernels "which show that, at temperatures greater than 700°C , the H_2 generated by the oxidation of graphite retards the oxidation of UO_2 , leading to the deduction that fission product release is thereby excluded. This calculation also depends on the questionable assumption of a linear relation between the fission gas release and the stoichiometry of uranium dioxide. However, recent experiments in the U.S., experiments HRB-17 and -18, demonstrate that only a small degree of oxidation ($<10^{-5}$) is required to promote the release of significant amounts of fission gases, albeit under irradiation conditions ..." If further investigation supports this suggestion that graphite oxidation may slow the oxidation of UO_2 , then this interrelationship might be considered in the future.

DATABASE USED IN MODEL DEVELOPMENT

Refer to §11.2.4 for information on the database for fractional oxidation of kernel material. Information on FP release from oxidized UO_2 kernels is available from Wood et al. (1985). The database for fission gas release used in the derivation of this model has not been reviewed in detail.

4.8 FISSION GAS TRANSPORT IN THE PARTICLE COATING LAYERS

4.8.1 INTRODUCTION

The diffusive model is assumed to apply to the transport of fission gas only through the OPyC layer. The buffer layer is assumed to have no effect on retention of fission gas, the IPyC layer is assumed to fail during irradiation, and the SiC layer is assumed to be impermeable to fission gas until some mechanical failure of the SiC occurs (i.e., via particle or SiC failure as discussed in §2).

No effects due to sorption or other trapping effects within the layers are considered. The partition coefficients between layers are "assumed to be unity" due to the "lack of data" (Acharya, 1984). In other words, FP concentration profiles are continuous across the interfaces between layers, and no layer exhibits preferential retention of the FP. Partition coefficients are discussed in more detail in §5.3 with respect to transport of metallic FP across the coating layers.

For diffusive FP transport in PyC, the dependence of transport on temperature is implicit in the model, and no data exist which would justify a separate AC transport model. The same lack of data apply to AC transport through the other coating layers; therefore, the models presented below are assumed to apply to both NOC and AC.

Design Data Need 11.47 (CEGA, 1990) comments on the present limitations of the database relevant to the following models. "The present data base resulted largely from diffusivity measurements for various fission products in SiC and pyrocarbon coatings in a laboratory environment ... There are limited and highly variable data on the diffusive release of fission gases from BISO particles, but the relevance of these data to the transport of gases in the OPyC coatings of TRISO particles is questionable ... The effective diffusivities of key radionuclides in particle coatings are needed as a function of temperature and, as required, of fluence, irradiation history, and as-manufactured coating attributes for normal operation and for core conduction cooldown conditions; specifically ... the diffusivities of key fission gases (Kr, Xe, I, and Te) in pyrocarbon coatings."

4.8.2 FISSION GAS TRANSPORT IN THE BUFFER LAYER

function	This model provides a simplified analysis of fission gas transport through the buffer, with no functional dependencies.
present status	The buffer layer is presently assumed to provide no retention of fission gas (i.e., transport through the buffer is instantaneous upon release from the kernel) (Myers, 1988). Although a conservative oversimplification, the effects of the buffer are insignificant relative to the influence of the SiC coating layer on gas transport and release.

model uncertainty "The uncertainty associated with the transport in and release from the buffer of fission products is very large but is not significant for core calculations" (Myers, 1988).

references Myers (1988); FDDM/F; EG&G (1992); Myers (1983b)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

Transport from the kernel to the IPyC layer (or vice versa) is considered to be instantaneous (Myers, 1988). This model is stated in a different form by EG&G (1992): "Fission products released from the kernel are assumed to be uniformly distributed throughout the buffer." In effect, the buffer is not considered in transport considerations, and only the void volume it contributes for the storage of fission gas is considered significant in relation to particle performance models (§2.3).

Provided fission gas can readily escape from the particle (i.e., failed coating layers), a model equation for release of fission gas from the buffer can be postulated as:

$$f = 1.0 \quad \text{at } t = 0, \quad (4.8.2.1)$$

f = fractional release of fission gas from the buffer with respect to that released from the kernel at $t = 0$,

t = time after fission gas release from the kernel (arbitrary units).

If gas transport through the particle coatings is modelled using a diffusional approach, the equation for the diffusion coefficient:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right), \quad (4.8.2.2)$$

can be simplified to (FDDM/F):

$$D = \infty, \quad (4.8.2.3)$$

D = diffusion coefficient of fission gas in the buffer layer ($\text{m}^2 \text{s}^{-1}$),

D_0 = pre-exponential factor ($\text{m}^2 \text{s}^{-1}$),

Q = activation energy (J mol^{-1}),

T = temperature (K),

R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

However, if the particle coating layers are intact an equilibrium pressure will be maintained inside the particle and the fission gas will not be immediately transported

through the buffer. Such an equilibrium situation requires a model equation consistent with the above statement by EG&G (1992):

$$C(r) = \bar{C} , \quad (4.8.2.4)$$

$C(r)$ = concentration of fission gas at radial position r within the buffer (arbitrary units),
 $\bar{C}$ = average concentration of fission gas throughout the buffer (arbitrary units).

Range of validity

The model is considered valid over all temperatures and all conditions. Apparently some experimental data relevant to this model exist (Myers, 1988) but details of these experiments are unknown to this writer.

Assumptions

1. The buffer provides no significant retention of any gaseous FP (Kr, Xe, I, Te, Br, Se).
2. The porous buffer structure has no effect on mass transfer.
3. Densification of the buffer under irradiation has no significant effect on FP retention.

MODEL CHRONOLOGY

No background to the model is presented in the references. Source data used in development of this model have not been located.

DISCUSSION

In practical terms, the model is satisfactory because the delay of fission gas transport by the buffer layer is insignificant with respect to the delay by the PyC and SiC layers. Fission gases would be expected to encounter little resistance to mass transport across a porous layer. In fact, Myers (1988) comments on "data showing that ^{85}Kr passes through a buffer layer without decay of activity, although this is not a stringent test." The origin of this data is not stated and remains unknown to this writer.

With respect to the physical integrity of the buffer layer, Myers (1988) states: "If the buffer densifies without fracture so that the density is greater than 1.5 g/cm^3 , then fission product gases as well as metals are retained as demonstrated by experiments. If the buffer densifies and fractures, the void volume thereby created contributes to a reduction in the release of the short-lived fission gases. Advantage cannot be taken of the retentive possibilities since no model exists to predict the behavior of the buffer under irradiation." Again, no reference is made to the experiments from which this observation was made. The corollary effect would be higher retention of fission gases and greater inventory available for release during accident conditions.

The previous statement by Myers is apparently referring to the GA data represented by Fig. 4.8.2.1 (from Myers, 1983b). Myers (1983b) comments on these results: "[Buffer]

Fig. 4.8.2.1. Dependence of R/B for ^{86}Kr at 1100°C on buffer density (from Myers, 1983b; attributed to N. L. Baldwin of GA).

densification occurs during irradiation as a result of irradiation damage and kernel swelling. The densification would be expected to reduce fission gas release and thereby compensate for an increase in release from the kernel due to burnup. Indeed, a reduction in release is demonstrated in Fig. [4.8.2.1] by GA measurements ... Here kernels of UC_2 , coated with buffer layers of varying densities, show the consequent reduction in R/B as the density increases. Note that when the buffer is unirradiated, the R/B for laser-failed particles with holes extending to the buffer surface and to the kernel surface is the same ... Thus the unirradiated buffer is no barrier to fission gas release." However, Myers points out that contradictory data exist. "Another difficulty with the buffer densification hypothesis is encountered at temperatures between 1000 and 1500°C where enhanced fission gas release [from exposed kernels] occurs ... The magnitude of the fractional release becomes too large there to be compatible with the restrictions on release imposed by a densified buffer. This raises the question of how the enhanced fission gas release occurred ... did the buffers undergo structural changes associated with pore opening or microcracking?"

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

With the buffer hypothesized to play at most a minor role in fission gas release from the particle, significant effort in modelling of transport in the buffer layer is not justified. However, the above discussion suggests that densification and cracking of the buffer layer might be considered with respect to the added retentivity of fission gases and to the void volume available to distribute the gas pressure within the particle (§2.3). Such consideration presupposes the availability of sufficient information to analyze this phenomenon, which may not be the case.

DATABASE USED IN MODEL DEVELOPMENT

The source of the "data showing that ^{85}Kr passes through a buffer layer without decay of activity" (Myers, 1988) is not known. Fig. 4.8.2.1 represents data which might be considered for future model revision.

4.8.3 FISSION GAS TRANSPORT IN THE PyC LAYERS

function	This model calculates the diffusion of fission gases through intact PyC layers using a diffusion coefficient for krypton.
present status	Parameters for fission gas diffusion in PyC layers are derived predominantly from heating ramp tests to temperatures well above 2000°C. Diffusion data for only krypton has been obtained. "There are limited and highly variable data on the diffusive release of fission gases from BISO particles, but the relevance of these data to the transport of gases in the OPyC coatings of

TRISO particles is questionable" (CEGA, 1990). The IPyC layer is normally assumed to fail during irradiation (Goodin et al., 1985).

model uncertainty For krypton, the "uncertainty associated with the derived diffusion coefficient is large, being 100" (Myers, 1988). The transport of the other gaseous species such as iodine is at least as uncertain due to lack of data.

references Goodin et al. (1985); Goodin (1984a)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations: IPyC layer

Like the buffer, the "IPyC layer is assumed to fail during irradiation" (Goodin et al., 1985). If one needs to consider the transport of fission gas through a failed IPyC layer, one should apply the model for transport in the buffer layer, §4.8.2. If one assumes the IPyC layer is intact, then transport should be treated the same as for the OPyC layer (see below). The assumption of IPyC failure provides conservatism in modeling.

Model equations: OPyC layer

Fission gas transport through the OPyC layer (LTI structure) is modelled using the diffusive approach, with the diffusion coefficient given by:

$$D = D_0 e^{-Q/RT} , \quad (4.8.3.1)$$

D = diffusion coefficient of fission gas in the OPyC layer ($\text{m}^2 \text{s}^{-1}$),
 D_0 = pre-exponential factor ($\text{m}^2 \text{s}^{-1}$),
 Q = activation energy (J mol^{-1}),
 T = temperature (K),
 R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

FDDM/F recommends the use of Eq. (4.8.3.1) with the parameters for krypton gas:

$$D_0 = 2.90 \times 10^{-8} \text{ m}^2 \text{s}^{-1},$$

$$Q = 2.91 \times 10^5 \text{ J mol}^{-1}.$$

An alternative model equation for the diffusion coefficient has been recommended more recently by Goodin (1989):

$$D = D_{0,1} e^{-Q_1/RT} + D_{0,2} e^{-Q_2/RT} , \quad (4.8.3.2)$$

$$D_{0,1} = 2.90 \times 10^{-8} \text{ m}^2 \text{s}^{-1},$$

$$Q_1 = 2.91 \times 10^5 \text{ J mol}^{-1},$$

$$D_{\alpha 2} = 2.02 \times 10^{-5} \text{ m}^2 \text{ s}^{-1},$$

$$Q_2 = 9.23 \times 10^5 \text{ J mol}^{-1}.$$

These parameters were also recommended by Goodin et al. (1985) and by the FRG program (Moormann et al., 1987). Note that the parameters used in the first part of Eq. (4.8.3.2) are the same as those recommended for Eq. (4.8.3.1).

The parameters for Kr diffusion are also assumed to apply to the other gaseous FP (i.e., Xe, I, Te, Br, Se).

Range of validity

These parameters for the diffusion coefficient are apparently considered valid for any temperatures or reactor conditions. With respect to the experimental range of validity, the original source references for the data have not been reviewed by this writer. Goodin et al. (1985) state that the parameters "are based on the GA ramp heating release data, the GA ramp/hold heating data and only limited FRG tests at 1600°C." The GA ramp heating tests were generally continued until temperatures well above 2000°C were obtained (as much as 2300 to 2500°C). A statement by Myers (1986) suggests these parameters are valid for temperatures up to 2200°C.

Because of the high temperature range in which most of the data were apparently obtained, it is likely that the range of validity for these reference diffusion parameters may be well outside the range of temperatures under which the NP-MHTGR will operate.

Assumptions

1. The diffusive behavior of krypton can be used to predict the transport of other gaseous fission products (Xe, I, Te, Br, Se).
2. The IPyC layer is conservatively assumed to fail during irradiation, with no retention of fission gas.
3. The diffusion coefficient is not a function of irradiation conditions (e.g., temperature or fast neutron fluence) or of heating conditions (e.g., temperatures and heating ramps).
 - a. The diffusive behavior of krypton at extreme temperatures (well above 2000°C) can be extrapolated to model Kr diffusion at typical MHTGR temperatures.
 - b. The diffusion coefficients derived from ramp heatup tests at heatup rates several times greater than expected for NP-MHTGR accident conditions will accurately describe the gas diffusion under NP-MHTGR conditions.
 - c. The ramp heating tests at the given ramp rates can accurately approximate equilibrium diffusion conditions with respect to thermal, chemical, and transport properties.
 - d. Very high temperatures will not modify the diffusive mechanisms for Kr (i.e., temperatures well above 2000°C will have no significant structural effect on the PyC layers or microstructure).
4. No transport of fission gas through the OPyC layer occurs until mechanical failure of the SiC layer.

5. The retention capabilities of the SiC layer for fission gas quickly goes from complete retention to zero retention upon mechanical failure.

Uncertainties

Myers (1988) has stated that the uncertainty associated with the diffusion coefficient of ^{85}Kr is large, ≈ 100 . FDDM/F quantifies this uncertainty as:

$$\sigma(\ln D) = 2.4 \quad , \quad (4.8.3.3)$$

$\sigma(\ln D)$ = standard deviation of $\ln D$, Eq. (4.8.3.1).

With regard to the model for the IPyC layer, delamination and cracking of the IPyC layers are often observed in ceramographs of particles, but not always. Although the model is conservative, the model uncertainty is not significant relative to the importance of OPyC or SiC failure estimates.

MODEL CHRONOLOGY

Although a diffusive mechanism for transport in PyC is commonly accepted, the reference diffusion parameters for Kr in PyC have changed several times over the past decade. Goodin (1984a) presented a value for the diffusion coefficient, but many assumptions were used in the derivation. Goodin et al. (1985) presented a revised diffusion coefficient in the form of a summation of two terms [Eq. (4.8.3.2)]. The parameters in one of the terms are the same as those presented by Myers (1986) and FDDM/F, but neither of those references mentions the second term. Goodin (1989) continues to recommend the two-term model. The reason for this difference is not discussed by any of the references.

DISCUSSION

Lacking the source references for the experimental data, the most comprehensive statement regarding this model and derivation appears to be that of Goodin et al. (1985). "Based on heating results from testing programs at both GA and KFA, the OPyC layers of particles that have failed SiC layers are expected to remain intact. Thus, it becomes necessary to provide a description of the diffusive release of fission products through the remaining OPyC ... In the present work, data from the following samples are analyzed to provide diffusion coefficients for Kr in PyC:

1. GA TRISO fuel core heatup simulation test data ...
2. GA ramp/hold isothermal heating data ...
3. KFA TRISO fuel sphere data from ramps and isothermal heating ...

"Failure of the SiC is indicated by Cs-137 release. The appropriate corrections for the continuously increasing SiC failure during a heating ramp are made in each case ...

"Evaluation of the data from large HTGR accident simulation tests (diffusion at temperatures of 2300°C to 2500°C) reveals no systematic dependence of diffusion in

pyrocarbon on prior irradiation exposure. While surprising at first, this observation should not be unexpected given that the SiC failure does not normally occur in such ramp tests until temperatures are well in excess of 2000°C and the opportunity for significant annealing (or repair) of the earlier irradiation damage in the PyC is great. Thus, in effect, the PyC would lose its memory of the earlier irradiation exposure. The limited data available from modular reactor transient simulations (i.e., 1600°C) are not yet sufficient to define a dependence on irradiation exposure ... As additional data at temperatures of ~1600°C and various irradiation conditions become available, an irradiation exposure dependence for gaseous diffusion in pyrocarbon is expected to become evident." Figure 4.8.3.1 shows the derived diffusion coefficients referred to by Goodin et al. (1985).

The above statements by Goodin et al. (1985) seem to indicate the model parameters are based more on TRISO than on BISO particles, but insufficient information is provided for a definitive statement on this matter. This inference is in contradiction to the statements by CEGA (1990) (see "present status" above) and Myers (1988), who states: "The diffusion of ⁸⁵Kr through the PyC coatings has been measured at high temperatures with BISO particles and the results have been confirmed in core heatup experiments although the interpretation of the latter tests is ambiguous." With BISO particles often coated with HTI PyC and TRISO particles coated with LTI PyC, the diffusion coefficient derived by Goodin et al. (1985) is not unambiguously based only on LTI PyC coatings. Review of the source references mentioned by Goodin et al. (1985) could clarify this matter.¹

EG&G (1992) also states that measurements of noble gas transport in both LTI and HTI PyC have been made. Although HTI PyC is a better FP diffusion barrier than LTI PyC, the latter is used in TRISO particles because of its better resistance to irradiation. Shepherd et al. (1982) describe the two structures as "that derived from methane at relatively high temperatures 1700°C - 2000°C (HTI - PyC); the other derived from higher hydrocarbons at lower furnace temperatures (1200°C - 1400°C), in particular from propene (LTI - PyC). The latter class possesses a higher degree of initial isotropy than the former, and its properties are less sensitive to variations in coating furnace conditions."

With the lack of detailed information in Goodin et al. (1985) on the derivation of the latest model parameters, it seems likely that the same methodology was used to calculate the experimental diffusion coefficients as was used for previous calculations (Goodin, 1984a) involving similar ramp heating tests. If so, the following additional assumptions in model development should be stated.

1. SiC defect levels can be determined by inspection of the ⁸⁵Kr release profiles obtained from high-temperature ramp heating tests (i.e., by an inflection in the release vs temperature curve).
2. Kernel retention of the long-lived ⁸⁵Kr is negligible (not necessarily a true assumption; dependent on conditions).

¹B. F. Myers comments that these data were in fact obtained from BISO particles coated with LTI PyC.

Fig. 4.8.3.1. Diffusion coefficients of Kr in PyC resulting from analysis of heating data (from Goodin et al., 1985).

3. The validity of the previous assumptions allows the DIFSHL computer code to accurately reproduce the temperature-dependent diffusion coefficients for the ramp heating tests.

Goodin et al. (1985) state: "Failure of the SiC is indicated by Cs-137 release. The appropriate corrections for the continuously increasing SiC failure during a heating ramp are made in each case." One cannot unambiguously state whether these corrections correspond to the methodology used by Goodin (1984a).

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Although transport in the IPyC layer could be modelled assuming diffusion, the cracking or delamination of the IPyC layer often observed during irradiation encourages the assumption that all IPyC layers are effectively failed during irradiation. Some quantification of this IPyC failure fraction from ceramographs, if possible, might be considered.

Analysis of the model for diffusion in OPyC requires more rigorous evaluation of the source data and computational methodology. The references provided by Goodin et al. (1985) should be reviewed. The use of data from TRISO vs BISO particles (and LTI vs HTI PyC) should be clarified. The calculation of the diffusion coefficients from the experimental data should be reviewed, especially the assumptions used with respect to SiC failure and how that failure was approximated from the data [i.e., were the same approximations and approach used by Goodin et al. (1985) as were used by Goodin (1984a)?]. Unless these concerns are addressed, one cannot have a great deal of confidence in using the reference diffusion coefficient for Kr in PyC.

DATABASE USED IN MODEL DEVELOPMENT

The database for this model is represented by Fig. 4.8.3.1. Source data may be available in the following references provided by Goodin et al. (1985):

Smith, C. L. (1980), "HTGR Fuel Development Department Technical Status Report for the Period Ending June 20, 1980," General Atomic Document No. 904907/A.

Smith, C. L. (1980), "TRISO ThO₂ CHST Data Compilation," General Atomic Document No. 905061/1.

Goodin, D. T. (1981), "Candidate LEU Fissile Fuel CHST Data," General Atomic Document No. 905182/3.

4.8.4 FISSION GAS TRANSPORT IN THE SiC LAYER

function	This model assumes complete gas retention by an intact SiC layer, and no resistance to gas transport after SiC failure.
present status	For standard particles, the model assumes no transport of fission gas through an intact SiC layer. All gas retention is lost upon failure of the SiC as predicted by particle performance models.
model uncertainty	The transport of fission gas through high-quality SiC is known to be negligibly small. Although the uncertainty in this model is small, the major uncertainty arises from attempts to specify the point at which the SiC fails as opposed to considering a more gradual evolution of SiC permeability to gas transport.
references	Goodin et al. (1985); Schenk et al. (1988)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equation: intact SiC

As long as the SiC layer remains intact, no fission gas enters or goes through the SiC layer. Using the diffusional methodology, this behavior can be represented by (FDDM/F):

$$D = 0.0 \quad , \quad (4.8.4.1)$$

D = diffusion coefficient of fission gas in intact SiC ($\text{m}^2 \text{s}^{-1}$).

Model equation: failed SiC

After the SiC fails, no resistance is offered to gas transport:

$$D = \infty \quad . \quad (4.8.4.2)$$

Range of validity

This model is assumed to hold in general for nondefective SiC under all reactor conditions. The model is a logical extension of the experimental database for fission gas release from TRISO particles. Lacking detailed experiments which could confirm that no gas enters the SiC structure at any temperature, one must assume the experimental range of validity encompasses the wide range of particle release data.

Assumptions

1. No significant amount of fission gas enters the SiC structure via a diffusional or other process.
2. The ability of the SiC layer to retain fission gas is represented as a step function from complete retention to no retention, without temporal or microstructural dependence and without any transitional regime of increasing permeability.

Uncertainties

The significant uncertainty is not in the assumption of no transport under most conditions, but in the model assumption of abrupt mechanical failure of the SiC layer. Ceramographs (Schenk et al., 1988) usually show gradual deterioration of the SiC layer at high temperatures. As pores in the SiC form, grow, and become interlinked, the small tortuous pathways for gas release which evolve would not be expected to suddenly release the entire gas inventory within the particle (Myers, 1989). By not considering more realistic phenomena the model introduces inherent uncertainty, but quantification of this uncertainty has not been stated.

MODEL CHRONOLOGY

The good retention capability of the SiC layer has long been recognized. Voice (1968) stated that SiC "is highly resistant chemically, can sustain high temperatures for long periods and in theory has a compact isodesmic structure making it practically impermeable by diffusion." The assumption of impermeability until structural failure has been retained to the present as an essential component of the pressure-vessel model for simulation of fission gas release, as stated explicitly in the US/FRG accident condition model (Goodin et al., 1985).

DISCUSSION

The measured fission gas release from intact TRISO particles is negligible unless temperatures well above 1600°C are applied to modern particles for extended periods of time. For the temperatures characteristic of the NP-MHTGR, typical release is too small to obtain a meaningful diffusion coefficient, thus $D \approx 0$ in reality.

Release from particles without OPyC layers

A FP release measurement which would appear to provide strong evidence for a SiC failure model for gas release is provided by Fig. 4.8.4.1, taken from Nabielek et al. (1987) which shows that Kr and Cs release are virtually identical from a particle without an OPyC layer during a high-temperature ramp test. As Nabielek et al. (1986) state: "With particles where the outer pyrocarbon has artificially been removed, krypton is released at the same rate as cesium. From intact particles, however, Kr 85 release is further delayed by diffusion

The statistics of SiC failure determines Cs release

$$\Phi(t) = 1 - 2^{-(kt)^m}$$

Φ ... SiC failure fraction = Cs release fraction

t ... heating time

m ... Weibull modulus

Fig. 4.8.4.1. GA measurements during temperature ramps using irradiated particles without OPyC layers (from Nabielek et al., 1987).

through the outer PyC layer." Figure 4.8.4.2 indicates the effect of the presence of the OPyC layer. Obviously one mechanism dominates the release of both metal and gas when the OPyC cannot delay the Kr release, as in Fig. 4.8.4.1. One weakness of this argument is the very high temperatures to which the OPyC-less particle was subjected. Thermal decomposition of a bare SiC layer will be very rapid above 2000°C without a protective OPyC layer, and one could expect rapid mechanical failure followed by release of all mobile FP. Such evidence for mechanical failure of the SiC layer would be more convincing at lower temperatures where thermal decomposition of the SiC would not overwhelm all other related phenomena. If Kr and Cs release profiles were identical at temperatures of 1600°C and below in a similar experiment, the argument for mechanical failure of the SiC prior to release of all FP would be more convincing (note that in §5.6 this same model is also advocated by some for the release of metallic FP from SiC).

Ceramographic results

Evidence for a refined SiC failure mechanism is provided by the ceramographic results obtained by Schenk et al. (1989, 1990) for FRG particles annealed at high temperatures. Figure 4.8.4.3 shows the distinct development of porosity in the SiC layer at 1600°C as a function of both heating time and irradiation conditions. Figure 4.8.4.4 shows the qualitative change in SiC decomposition mechanisms as temperatures exceed 2000°C, with rapid gross deterioration of the SiC structure. A SiC failure mechanism for gas release is reasonable for temperatures such as those in Figs. 4.8.4.1 and 4.8.4.2, but a gradual deterioration of the SiC layer with slow development of porosity through the SiC structure is typical at more reasonable AC temperatures (~1600°C).

The ceramographs of Schenk et al. are supportive of an analysis by Myers (1989) which considered the potential effect of pores through the SiC structure on SiC defect characterization and fission gas release. Myers comments that: "Analysis of fission gas release under normal conditions in the presence of larger-radius pores (>50 nm) when particle interior and exterior gas pressures are equalized shows that ... stable fission gas release from the particles is the same as the release from the kernel ... The steady-state fission gas release from a small-radius pore (<25 nm) is negligible compared with that from a larger-radius pore but, given the distribution of pore radii, the contribution of a collection of small-radius pores to the total steady-state fission gas release cannot be neglected. Under accident simulation conditions and with good-quality particles, the gas release may be governed by transport through small-radius pores as demonstrated with sphere 1 of the German capsule in reactor experiment R2-K13. For cesium release under these conditions, the small-radius pores may also contribute significantly to release."

Diffusion models

In contrast to the SiC failure methodology for fission gas release, diffusion coefficients of fission gases in SiC have been reported in the scientific literature. Fukuda et al. (1982) recommends a diffusion coefficient for Kr in SiC which is based on earlier data for Xe diffusion in SiC. However, Martin (1990) reported that use of this diffusion coefficient

Diffusion of Kr through outer PyC after SiC failure

$$F_{\text{Kr}}(t) = \int_0^t \frac{d\Phi(t')}{dt'} F_{\text{PyC}}(t-t') dt'$$

F_{Kr} ... Kr release fraction from particles

F_{PyC} ... Kr diffusion fraction through outer PyC

Fig. 4.8.4.2. GA measurements during temperature ramps with intact particles (from Nabielek et al., 1987).

Fig. 4.8.4.3. Ceramographic sections through particles heated at 1600°C (complete particle followed by enlarged views from three different particles) (from Schenk et al., 1990).

Fig. 4.8.4.4. UO₂ TRISO particles from fuel spheres heated at different temperatures (from Schenk et al., 1989).

would underpredict the release of Kr from FRG fuel spheres in postirradiation heating. Additional experiments and discussion of Xe diffusion coefficients can be found in Fukuda et al. (1976, 1978). Modelling attempts using a diffusional approach to fission gas release from SiC are not common. Apparently only Fukuda et al. (1982) and Martin (1990) have considered the methodology of bulk diffusion, while Myers (1989) considered diffusion in pores.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Refinement of the present model should focus on a better understanding of the microstructural evolution of the SiC layer as it deteriorates. The absolute impermeability of the SiC layer to fission gas transport up to the point of failure could be considered an oversimplification. A more realistic model for gas release mechanisms might consider a gradual increase in the permeability of the SiC layer. A model such as this is analogous to a modified diffusion model, similar to that considered by Fukuda et al. and Martin. Detailed consideration of the report by Myers (1989) has the potential to develop into a modified diffusion/permeation model more logically consistent with the ceramographic results of Schenk et al. With the maximum NP-MHTGR AC temperatures much lower than those at which the SiC failure model is clearly valid, the consideration of a more realistic and evolutionary model for enhancement of SiC permeability to fission gas over time may be needed.

DATABASE USED IN MODEL DEVELOPMENT

Figures 4.8.4.1 and 4.8.4.2 can be considered part of the database for this model. Fission gas release measurements in general can be considered part of the database, although assumptions about the influence of the OPyC layer on gas release and SiC integrity during heating blur the direct applicability of the data to the model. The ceramographs shown in Figs. 4.8.4.3 and 4.8.4.4 might be considered part of the database relevant to model evaluation and possible revision.

4.9 UPDATE

The following reference has been suggested for additional relevant information.

Horsley, G. W., G. J. Weldrick, J. A. Turnbull, and R. Shipp, "Influence of Irradiation Temperature, Burnup, and Fuel Composition on Gas Pressure (Xe, Kr, CO, CO₂) in Coated Particle Fuels," *J. Am. Ceram. Soc.*, 59 (1976) 1-4.

The analysis of the HRB-17/18 moisture injection tests was recently published (Myers, 1991a) as well as comparable preliminary data on the HFR-B1 capsule. Both experiments contained UCO kernels, and the data should be reviewed for relevance to model revision. High-temperature heating tests of German fuel in the presence of moisture are also planned

to continue in Germany under W. Schenk. That data should also be evaluated for its relevance to these models when published.

The on-line gas release data for NPR and HRB-21 capsules are available in the irradiation reports, and some analysis has been performed to extract particle failure and gas release information from the on-line recording of ionization chamber spikes. TRIGA (R/B) data are also available for compacts containing failed fuel particles. The relevance of this information to model evaluation must be determined, although preliminary correlation of NPR (R/B) data with the approximate number of ionization chamber spikes suggests a greater steady-state fractional release of fission gas per failed HEU particle than existing models for LEU UCO fuel would indicate.

5. METALLIC FISSION PRODUCT TRANSPORT WITHIN THE FUEL PARTICLE

5.1 INTRODUCTION

The standard assumption of simple diffusive transport is employed for modelling of metallic FP transport throughout the particle. The diffusion coefficients in the coating layers are dependent on temperature only. Diffusion coefficients for the kernel also explicitly depend on the burnup (§5.2). The buffer layer is assumed to have no effect on retention of FP; the diffusive model simulates this by assuming a very large diffusion coefficient (§5.4). Although transport in the IPyC layer can be modelled assuming diffusion, cracking, or delamination of the IPyC layer introduces ambiguity into this approach (§5.5). Apparently, the IPyC is usually ignored as a barrier to transport and only retention by the OPyC (and SiC) layers are considered.

No effects due to sorption or other trapping effects within the layers are considered. The partition coefficients between layers are "assumed to be unity" due to the "lack of data" (Acharya, 1984) [i.e., fission product concentrations are continuous across the interfaces between layers, and no layer exhibits a preferential retention of the FP (§5.3)].

The temperature-dependency of transport is implicit in the diffusive model, and no data exist which would justify a separate AC transport model. The models presented below are assumed to apply to both NOC and AC.

5.2 METALLIC FISSION PRODUCT TRANSPORT IN THE FUEL KERNEL

function	This model provides metallic FP diffusion coefficients in the kernel as a function of kernel material, burnup, and temperature.
present status	The diffusion coefficients for FP atoms in the fuel kernel were largely derived from ThO ₂ data and accelerated test data, assume only temperature and burnup effects but no fluence or sorption effects and do not account for the significant difference in release from bare kernels vs kernels in intact particles. Few data at AC temperatures were considered in deriving the model parameters. Recent fuel performance and transport data should be used to update the model, and transport in HEU UCO kernels needs to be characterized (CEGA, 1990).
model uncertainty	The uncertainties in metallic FP diffusion coefficients in kernels are "exceedingly large" (Myers, 1988) due to extrapolation of diffusion data in ThO ₂ and lack of data on burnup and fluence effects. Accident condition models are extrapolated from NOC models and data, and the uncertainty "is unknown but is probably not significant" (Myers, 1988).

references Myers (1981b, 1981d, 1985e, 1988); General Atomic (1977b);
Acharya (1984, 1987)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The effective homogeneous diffusion coefficient is given by (Myers, 1981d; Acharya, 1987):

$$D = D' r^2 , \quad (5.2.1)$$

with the reduced diffusion coefficient in the kernel prior to irradiation given by:

$$D' = D'_0 \exp\left(-\frac{Q}{RT}\right) , \quad (5.2.2)$$

- D = effective homogeneous diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
- D' = reduced diffusion coefficient (s^{-1})
- r = kernel radius (m)
- D'_0 = pre-exponential factor (s^{-1})
- Q = activation energy (J mol^{-1})
- R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
- T = temperature (K).

During irradiation, the reduced diffusion coefficient changes with burnup according to:

$$D'_0 = C_1 [1 + (1 + n) C_2 F^n] , \quad (5.2.3)$$

- F = burnup (% FIMA)
- C_1 = constant (s^{-1})
- C_2, n = dimensionless constants.

Given the parameters C_1 , C_2 , n , and Q , the reduced diffusion coefficient can be calculated as a function of temperature and burnup. Values for C_1 , C_2 , n , and Q are given in Table 5.2.1 for the common metallic FP.

Range of validity

According to FDDM/F, this model applies to both NOC and AC regimes, therefore the range of validity of this model must be considered to include all temperature regimes representative of NOC and AC. The data relevant to metallic FP diffusion in kernels is chronicled in Myers (1981e); reference should be made to this document for the specifics of the experiments for each FP metal.

Table 5.2.1. Parameters for calculation of metallic fission product diffusion coefficients in kernels, Eqs. (5.2.2) and (5.2.3)

Kernel material	FP	C_1 (s^{-1})	C_2	n	Q ($J\ mol^{-1}$)	Ref.
UCO ($UC_{0.4}O_{1.6}$) ^(a)	Ag	8.2×10^{-4}	0.0104	3	174,200	(f)
	Cs	$1.6 \times 10^{-10(b)}$	0.164	4	77,800	(g)
	Rb	$1.6 \times 10^{-10(b)}$	0.164	4	77,800 ^(c)	(h)
	Sr	1.1×10^9	0.0197	4	594,000	(f)
	Eu	1.1×10^9	0.0197	4	594,000	(f,i)
	Ce	1.1×10^9	0.0197	4	594,000	(i)
	Sm	1.1×10^9	0.0197	4	594,000	(i)
	Ba	1.2×10^8	0.0197	4	556,600	(i)
ThO ₂ , UO ₂ ^(d)	Ag	5.7×10^{-4}	0.0104	3	174,200	(f)
	Cs	$1.1 \times 10^{-10(b)}$	0.164	4	77,800	(h)
	Rb	$1.1 \times 10^{-10(b)}$	0.164	4	77,800 ^(c)	(h)
	Sr	7.6×10^8	0.0197	4	594,000	(f)
	Eu	7.6×10^8	0.0197	4	594,000	(f,i)
	Ce	7.6×10^8	0.0197	4	594,000	(i)
	Sm	7.6×10^8	0.0197	4	594,000	(i)
	Ba	8.4×10^7	0.0197	4	556,600	(i)
UC ₂	all ^(e)	(e)	(e)	(e)	(e)	(f,i)

(a) Myers (1981d) provided values specifically for $UC_{0.4}O_{1.6}$; see "Discussion".

(b) Myers (1981d) recommended a value of $1.6 \times 10^{-9}\ s^{-1}$.

(c) General Atomic (1977b) recommended a value of $22,820\ J\ mol^{-1}$.

(d) Values for UO₂ are assumed to be the same as those for ThO₂.

(e) No retention of metallic FP by UC₂ or ThC₂ is assumed.

References:

(f) Myers (1981d).

(g) Acharya (1984).

(h) FDDM/F.

(i) General Atomic (1977b).

Assumptions

1. Carbide fuels do not retain metallic fission products (Myers, 1981d).
2. The diffusion coefficient for each metallic FP in UO_2 kernels is the same as that in ThO_2 kernels (Myers, 1981d).
3. The diffusion coefficient of any metallic FP in UC_xO_y is derived from that in UO_2 by multiplication by the factor $[1 + (2 - y)/2]^2$, to incorporate the assumption that no retention in the UC_2 portion of the UC_xO_y fuel occurs (Myers, 1981d).
4. The kernel material is homogeneous (FDDM/F).
5. The burnup dependence for all metallic FP except for that for Ag is assumed to be the same as that for Cs (i.e., $n = 4$).
6. The diffusion coefficients of Eu, Ce, and Sm in oxide and UCO kernels are the same as that of Sr.
7. The diffusion coefficient of Rb can be related to that of Cs using a simple analytical expression; likewise Ba can be related to Sr (see "Discussion" below).
8. The dominant process in metallic FP release from the kernel is, in fact, diffusion (Myers, 1988).¹
9. Distinction between surface and bulk diffusion is not needed (i.e., a single diffusion coefficient is sufficient) (Myers, 1988).¹
10. Vaporization of the FP from the surface of the kernel does not govern the rate of FP transport into the buffer (Myers, 1988).¹
11. Thermodynamic considerations (e.g., equilibrium between the kernel and the surrounding coating layers) are not important (Myers, 1988).¹
12. The same transport mechanisms are predominant at AC temperatures as at NOC temperatures, thus the models and data relevant to NOC simulations are also relevant to AC.

Uncertainties

FDDM/F reports the standard deviation in the natural logarithm of the diffusion coefficients as follows. The standard deviations represent diffusion in both UCO and ThO_2 as diffusion is assumed to be comparable in both. For Cs:

$$\sigma(\ln D_{\text{Cs}}) = 2.6 \quad , \quad (5.24)$$

with the same value assumed to apply to Rb. For Sr:

¹The relevance of these assumptions to the model as presented is discussed or inferred by Myers (1988). This is not to say that Myers (1988) supports or justifies the use of these assumptions; in fact, the opposite is sometimes the case.

$$\sigma (\ln D_{Sr}) = 5.7 \quad , \quad (5.25)$$

with the same value assumed to apply to Ba, Eu, Ce, and Sm. For Ag:

$$\sigma (\ln D_{Ag}) = 1.6 \quad . \quad (5.26)$$

General Atomic (1977b) also provides equations for the standard deviation of $\ln D'$, but in the more generalized temperature-dependent form:

$$\sigma (\ln D') = \left[a + b \left(\frac{10^4}{T} \right) + c \left(\frac{10^4}{T} \right)^2 \right]^{1/2} \quad , \quad (5.27)$$

for constants a , b , and c . The values for a given by General Atomic (1977b) do not correspond with Eqs. (5.2.4) through (5.2.6). B. F. Myers (1993) comments that the use of these temperature-dependent uncertainties is a refinement not justified by the accuracy of the uncertainty estimate.

MODEL CHRONOLOGY

General Atomic (1977b) provides the most comprehensive collection of parameters for metallic FP diffusion in kernels up to that time. However, the model equations presented in 1977 were of the standard form for the diffusion coefficient, without any burnup dependence. Myers (1981d) developed the model equations presented above which incorporate the burnup-dependent term. No significant development of the diffusion model equations or enhancement of the experimental database since 1981 is apparent.

It is not apparent why the value of C_1 for Cs was changed by a factor of 10 from Myers (1981d) to Acharya (1984, 1987) and FDDM/F. The value of Q for Rb was modified from that in General Atomic (1977b) to agree with the value for Cs (refer to Table 5.2.1).

DISCUSSION

The conservative assumption that carbide fuels do not retain metallic FP is related to their low oxygen potential; metals are not bound up as oxides as in UO_2 and are therefore capable of rapid diffusion and release at high temperatures.

CEGA (1990) summarizes the current database as it relates to DDN 11.46. "The present data base is derived primarily from measurement on particles irradiated in accelerated test capsules. There are some FRG data for Cs, Sr, and Ag in oxide kernels of intact particles which were irradiated under near real-time conditions as well as limited laboratory data on Cs release from ThO_2 kernels." The release characteristics could potentially vary for slow and fast burnup rates due to the time required to establish equilibrium in FP profiles between the kernel and surrounding layers.

The current model assumes simple diffusive transport from the point of FP atom recoil to the surface of the kernel and continuous transport across the kernel/buffer interface. The "effective homogeneous diffusion coefficient" as defined in FDDM/F is that average diffusion coefficient which, when used in computer codes for FP transport, will predict the same fractional release from the fuel kernel as that observed experimentally. This approach does not consider details of transport mechanisms or the possibility of inhomogeneities in kernel composition.

Most of the model parameters used for diffusion in UCO kernels as listed in Table 5.2.1 represent extrapolation for $UC_{0.4}O_{1.6}$ kernels (Myers, 1981d). Parameters for $UC_{0.3}O_{1.7}$ kernels probably require an adjustment as indicated in the "Assumptions" section above.

The lack of data for diffusion of Eu, Ce, and Sm require the assumption of comparable behavior of these isotopes with that of Sr (General Atomic, 1977b). Comparison of the data for the diffusion coefficient of Ba in oxide kernels to that of Sr provides the ratio (General Atomic, 1977b):

$$D'_{Ba} = 0.11 e^{4450/T} D'_{Sr} , \quad (5.28)$$

which was used to obtain the parameters for Ba in Table 5.2.1. No data were available for Rb diffusion in oxide kernels, thus a comparison of bond strengths between rubidium and cesium oxides provided the ratio (General Atomic, 1977b):

$$D'_{Rb} = e^{6615/T} D'_{Cs} , \quad (5.29)$$

which was used to give the parameter for Rb mentioned in the footnote of Table 5.2.1.

Myers (1981d) discusses some of the assumptions used in developing the model for metallic diffusion as presented above. The form used in Eq. (5.2.3) was found to fit the Cs release data well and was found to also be applicable to Ag and Pu transport. However, an integer value of n in Eq. (5.2.3) is used, whereas the data is more representative of non-integer values of n . In fact, Becker et al. (1983) comment that a 1978 analysis by B. F. Myers indicated that n varies from 6 to 7 for carbide kernels, in contrast to the present model assumption that carbide kernels do not retain metallic FP.

Myers (1988) discusses some weaknesses in the model: "The fraction of a fission product released from the kernel differs significantly for exposed kernels and for intact particles as demonstrated in the R2-K13 experiment. This difference has heretofore not been recognized ... As a consequence of the system interior to the SiC being closed in intact particles, the processes in the kernel and contiguous material, which operate oppositely, come into balance, i.e., an equilibrium or quasi-equilibrium is established so that the quantity of fission product released from the kernel is determined by thermodynamic considerations and not kinetic ones as assumed in the current models." In other words, use of diffusion coefficients derived from release data from exposed kernels may not be directly applicable to modelling of transport in and release from kernels in intact particles.

Myers (1988) also points out that desorption from the kernel surface has only been analyzed for plutonium release from oxide and carbide kernels, and in this case has been

found to be significant. For AC, Myers (1988) suggests that "... in view of information developed more recently, the interpretation of the tests [of Cs release from bare ThO₂ kernels] can be regarded as questionable."

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

According to Myers (1981d) the parameters for UCO in Table 5.2.1 are for UC_{0.4}O_{1.6} rather than the reference UC_{0.3}O_{1.7}. If so, one should determine whether an adjustment in the parameters according to Assumption 3 might be justified. For example, such an adjustment would give a value for Cs of $C_1 = 1.45 \times 10^{-10} \text{ s}^{-1}$ rather than the value of $1.6 \times 10^{-10} \text{ s}^{-1}$ in Table 5.2.1. However, such a change of 10% does not appear significant relative to the overall uncertainty.

Myers (1988) suggests several issues which should be considered for further model development. Unanalyzed data from both the US and FRG programs should be considered in model revision (e.g., data for Cs, Ag, Sr, Ce, and Eu), which might reduce the model uncertainties significantly (see, e.g., Myers, 1985e). Better understanding of kernel transport might be obtained by detailed consideration of kernel transport as a function of neutron flux and/or fluence and consideration of the effect of vaporization from the kernel surface on transport in and release from the kernel. The issue of differential kernel release for intact and failed particles should be considered; i.e., thermodynamic vs kinetic release factors (Myers, 1985e). Myers (1981e) provides the best starting point for a detailed analysis such as this. Other data from the scientific literature might aid such an analysis, although the lower burnups typical of non-MHTGR fuels may limit the applicability of this data.

DATABASE USED IN MODEL DEVELOPMENT

Myers (1981e) represents the most comprehensive compilation of the database relevant to kernel diffusion of metallic FP as of 1981, and should be referenced for the background data to these models. The number of relevant graphs of the diffusion coefficient data for the various isotopes is too large to include here. Myers (1985e) provides additional relevant data, including some for UCO kernels.

5.3 PARTITION COEFFICIENTS BETWEEN KERNEL AND COATINGS

function	The issue of partition coefficients at interfaces is presently not considered by the reference models. Partition coefficients reflect a preferential distribution of FP species in one material over an adjacent material.
present status	Present assumptions of partition coefficient values equal to one eliminate the need for explicit consideration of this model for the transport of metallic FPs within the particle. Although seldom discussed, modelers should be

aware of this assumption as data exist which raise questions about its accuracy.

model uncertainty Data for evaluation of partition coefficients is limited, but numerical studies have used values ranging from 1 to 10. Myers (1988) states that partition coefficients "are poorly known and nowadays, are not taken into account ... The error introduced by neglecting them is unknown."

references Myers (1981a); Becker et al. (1983); Goodin (1983)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The partition coefficient, ϕ , is defined to be the ratio of the FP concentration at the outer boundary of a kernel or particle coating to the concentration at the inner boundary of an outer, adjacent coating (Myers, 1981a). For the transport of metallic FPs through the particle, the standard assumption is that:

$$\phi = 1 \quad , \quad (5.3.1)$$

ϕ = partition coefficient (dimensionless).

Range of validity

Considerations of partition coefficient values have apparently not been discussed since the early 1980s; therefore, the model must be applied to all reactor conditions. Experimental data are too limited to permit determination of an experimental range of validity.

Assumptions

Differences in the sorptive and solubility properties of kernel and coating layers do not introduce a discontinuity in FP concentration across any interfaces within the particle.

Uncertainty

Goodin (1983) reports a reasonable range of ϕ from 0.3 to 3.0. Myers (1981a) and others report assuming a variation in ϕ from 1 to 3. Myers (1988) states that "the error introduced by [assuming $\phi = 1$] is unknown."

MODEL CHRONOLOGY

No mention of this model is made in FDDM/F, and current references to the partition coefficient with respect to in-particle transport are not common. More discussion of in-particle partition coefficients is apparent during the early 1980s. Interest in values of the partition coefficients from the kernel through the coating layers was expressed as early as the 1960s by Walther (1968).

DISCUSSION

In principle, partition coefficients are important for FP transport across an interface (diffusion, sorption, and solubility effects). Partition coefficients within the particle are typically discussed with respect to metallic FPs. Compared to the metallic FPs, inert gases such as Kr and Xe exhibit negligible sorptive and solubility properties, although this may not be as true for iodine (§6.6). The concept of partition coefficients is discussed again in §6.7 with respect to the fuel compact/graphite interface, where differences in metallic FP sorptivity are known to introduce discontinuities into the concentration profile.

Simulations

An analytical discussion of partition coefficients was presented in some detail by Walther (1968) and incorporated into a computer code to calculate the diffusive transport and release of FPs from coated particles. This early analysis was limited by the lack of experimental data for FP transport phenomena.

In the early 1980s some metallic FP diffusion calculations used values of ϕ between 1 and 3. Myers (1981a) specified that ϕ values of either 3 or 1 were used in the diffusion code IPRE to represent the buffer-PyC or the PyC-SiC interfaces and stated that these values were consistent with experimental data (Stöver et al., 1976; Fukuda et al., 1977). Becker et al. (1983) also used the IPRE code to simulate Ag transport within the particle and assumed a ϕ value of 3 at the inner surface of the SiC layer.

Goodin (1983) used the DIFSHL code to simulate Cs and Ag transport in the particle. For the inner surface of the SiC layer, Goodin states the "value of ϕ is not known but is assumed, as is often done, to be one" and then justifies the assumption as follows. "Varying the value of ϕ over a reasonable range (i.e., 0.3 to 3.0) may result in a change in the derived values for diffusion coefficients by as much as a factor of three. The following points should be emphasized ... The large observed variation in measured or calculated diffusion coefficients ... indicate that determination of an absolute value for a diffusion coefficient within a factor of three is consistent with the experimental uncertainty."

Acharya (1984) employed the COPAR code for particle FP release calculations. "Due to lack of data, the partition coefficients are assumed to be unity, thus assuring that concentrations are continuous at the interface between two layers." No further discussion of these in-particle partition coefficients is apparent after this 1984 work, thus it seems apparent that the standard model employed to date assumes that $\phi = 1$.

Experimental information

Myers (1981a) mentioned two sources of experimental data on partition coefficients within the particle. For the PyC-SiC interface, reference is made to Fukuda et al. (1977). For the buffer-PyC interface, reference is made to Stöver et al. (1976). Figures 5.3.1(a) and 5.3.1(b) are taken from Stöver et al. and show discontinuous concentration profiles within BISO particles for Cs between the buffer and LTI-PyC and HTI-PyC layers, respectively. The concentration profiles appear to vary by factors of three to ten at the interface. The data presented by Fukuda et al. (1977) vary widely, possibly due to the poor spatial resolution of their etching method.

Information on partition coefficients can be obtained from microprobe data of FP concentrations across the particle such as those in Figures 5.3.2 through 5.3.4 (Schenk et al., 1989). These microprobe experiments were obtained by AERE using FRG particles from capsule irradiation tests HFR-K3/1 and HFR-K3/3. The concentrations of several FPs are apparently not continuous across the inner SiC interface. The buildup of Pd at the inner surface of the SiC is most obvious, although similar tendencies are apparent for Ba and Ru. A discontinuity is also apparent in the concentration profile for Cs across the buffer-IPyC interface in Fig. 5.3.4 and possibly in Fig. 5.3.2, with a partition coefficient on the order of 10. This discontinuity is qualitatively and quantitatively similar to those in Figs. 5.3.1(a) and 5.3.1(b). Schenk and Nabielek (1991) schematically portray this microprobe data in terms of the fraction of ^{137}Cs , ^{90}Sr , and ^{110m}Ag in kernel and each coating layer; strontium also shows evidence of preferential residence in PyC rather than SiC, but silver content is more continuous across the interfaces. This evidence suggests that surface and/or interface effects do play some part in metallic FP transport through the particle.

Summary

Myers (1988) summarizes the present state of understanding of and interest in partition coefficients. "Partition coefficients are a function of material, temperature, element and irradiation damage. They are poorly known and nowadays, are not taken into account; this desuetude would surely surprise early workers in fission product transport. The error introduced by neglecting them is unknown. However, in interpreting experiments on the release of fission products from intact particles or particles with two or three coatings intact, the distributions between contiguous coatings are important in correctly deducing diffusion coefficients for transport in them.

"The transport of fission products from one coating to another is by desorption from one surface and adsorption on the facing surface. The desorption step ... may govern the release from the surface in those particles where the distribution is not established. Thus as the temperature is raised, as in accident simulation tests, the transport processes may become too rapid to permit the establishment of a distribution and desorption may come to govern release of the fission products from the coating layer. There are no studies of the desorption of fission products from particle coating materials and one is presently stuck with the ubiquitous, possibly fictional diffusion coefficient to describe the release."

Fig. 5.3.1.a. Measured profile of BISO-LTI coated particle annealed 2 h at 1300°C (post irradiation); line calculated with ANDI (from Stöver et al., 1976).

Fig. 5.3.1.b. Measured profile of BISO-HTI coated particle annealed 97.5 h at 1407°C (post irradiation); line calculated with ANDILOK (from Stöver et al., 1976).

Fig. 5.3.2. Microprobe profiles of fission product elements through coatings of particles: Cs, I, Pd profiles in a particle from sphere HFR-K3/1 after 1600°C test (from Schenk et al., 1990).

Fig. 5.3.3. Microprobe profiles of fission product elements through coatings of particles: Ba, Ru, Ag profiles in a particle with 78% Cs loss from sphere HFR-K3/3 after 1800°C test (from Schenk et al., 1990).

Fig. 5.3.4. Microprobe profiles of fission product elements through coatings of particles: Cs, I, Pd profiles from sphere HFR-K3/3 after 1800°C test (from Schenk et al., 1990).

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The database presented above should be considered with respect to the accuracy of the assumption that $\phi = 1$. If the assumption that $\phi = 1$ is not generally valid, then the relevance for and impact on diffusive models of FP transport within the particle should be considered. Of particular significance is the possibility that calculated diffusion coefficients for coating layers may have an additional source of inherent uncertainty that is rarely recognized.

DATABASE USED IN MODEL DEVELOPMENT

The database provided by Stöver et al. (1976) and Schenk et al. (1989) was presented above in Figures 5.3.1 through 5.3.4. The data reported by Fukuda et al. (1977) show significant variations between five samples and are therefore not presented here.

5.4 METALLIC FISSION PRODUCT TRANSPORT IN THE BUFFER LAYER

function	This model provides an analytical format for diffusive transport consistent with the other coating layers but with no effective FP retention by the buffer by recommending a constant, large diffusion coefficient.
present status	The buffer layer is presently assumed to exert no influence on the transport of fission products (i.e., transport throughout the buffer is either instantaneous upon release from the kernel or the diffusion coefficients are assumed to be very large). Although an oversimplification, the effects of the buffer on FP transport and release are insignificant relative to the effects of the other coating layers.
model uncertainty	"The uncertainty associated with the transport in and release from the buffer of fission products is very large but is not significant for core calculations" (Myers, 1988).
references	Myers (1985e, 1988); Acharya (1984)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Transport throughout the buffer layer from the kernel is considered to be instantaneous. In effect, the buffer is not considered in transport considerations, and only the void volume it contributes to FP storage is considered significant in relation to particle performance models.

In practice, for compatibility with code usage, the buffer's presence is taken into account but the diffusion coefficient for all metallic FP is assumed to be so large that no

effective retention by the buffer occurs. The standard diffusion coefficient equation is employed:

$$D = D_o \exp\left(-\frac{Q}{RT}\right), \quad (5.4.1)$$

- D = effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$),
 D_o = pre-exponential factor ($\text{m}^2 \text{s}^{-1}$),
 Q = activation energy (J mol^{-1}),
 T = temperature (K),
 R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

Acharya (1984) recommends values of $D_o = 10^{-10} \text{ m}^2 \text{s}^{-1}$ and $Q = 0$ for the fission products ^{137}Cs , $^{110\text{m}}\text{Ag}$, and ^{90}Sr . In effect, the model equation for the diffusion coefficients of metallic FP becomes:

$$D = D_o = 1.0 \times 10^{-10} \text{ m}^2 \text{s}^{-1}. \quad (5.4.2)$$

Range of validity

The model is considered valid over all temperatures and all conditions. Experimentally, transport within the buffer layer has not been studied in detail, and the actual range of validity of the model cannot be commented upon.

Assumptions

1. No significant sorption or other trapping effects occur within the buffer.
2. The porous buffer structure has no effect on mass transfer.
3. Densification of the buffer under irradiation has no significant effect on FP retention.

MODEL CHRONOLOGY

No background to the model is presented in the references. Acharya (1984) states that the assumption of rapid diffusion through the buffer layer "is justified on the basis of past experience" but does not discuss this further. FDDM/F only states, without comment, that upon kernel release the FP are instantly and homogeneously distributed throughout the buffer. Based on this very limited information, no chronology can be presented for this model.

DISCUSSION

The diffusion coefficient given by Eq. (5.4.2) is significantly larger than the diffusion coefficients expected for the other particle coating layers at typical temperatures, up to approximately 2000°C. The effect of the buffer layer on FP retention by the particle as

predicted by this model is relatively unimportant below those extreme temperatures. In practical terms, the model would be expected to be more physically realistic at AC temperatures, with mass transport accelerated and the significance of any sorptive effects reduced.

With respect to the physical integrity of the buffer layer, Myers (1988) states: "If the buffer densifies without fracture so that the density is greater than 1.5 g/cm^3 , then fission product gases as well as metals are retained as demonstrated by experiments ... no model exists to predict the behavior of the buffer under irradiation." Experimental data on buffer retentivity can be obtained from Myers (1985e).

Logically, some effect of the buffer layer on metallic release would be expected. Fission gases would be expected to encounter little resistance to mass transport across a porous layer, but metallic transport frequently occurs by surface diffusion. Likewise, recoil of metallic FP into the buffer layer would require bulk diffusion of the FP to the surfaces of the buffer material prior to release.

An observation made by Stöver et al. (1976) provides more detailed information on Cs transport across the buffer. "... we investigated the mobility of cesium within the buffer layer. Some examples are shown in Fig. [5.4.1]. Here are presented profiles in propene-derived [LTI] coatings of particles which were irradiated in the FRJ-2 Juelich. The post-irradiation profile has a maximum near the boundary between buffer and LTI-layer. This profile can be flattened by a short-time anneal at 1000°C . Afterwards cesium is nearly homogeneously distributed in kernel and buffer layer. We found that a considerable fraction of the cesium returned from the buffer to the kernel. From this we conclude that some portion of the Cs in the buffer is mobile like a gas. Another part is less mobile. The distribution between the two phases depends on irradiation temperature. The driving force for diffusion into the outer layer is mainly determined by the mobile cesium fraction within the buffer." These results suggest sorption-like behavior.

The microprobe data presented previously in Figs. 5.3.2 through 5.3.4 of §5.3 also provides some information on the distribution of FP across the buffer after annealing at 1600°C (HFR-K3/1) and 1800°C (HFR-K3/3) for hundreds of hours. The profiles of Cs, Ba, and I appear to be approximately constant across the buffer for the HFR-K3/3 particles in Figs. 5.3.3 and 5.3.4. Figure 5.3.2 shows a discontinuity in Cs and I profiles within the buffer. If the location of the buffer/LTI-PyC interface is correctly portrayed, then one might conclude that the FP profiles are in fact not constant across the buffer layer after heating at 1600°C but are constant after heating at 1800°C . Additional microprobe data such as this could provide detailed information on the accuracy of this model.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

With the buffer expected to play at most a minor role in FP release from the particle, significant effort in modelling of transport in the buffer layer is not justified. Considerations of densification and cracking of the buffer layer and sorption of metallic FP might be considered in further analysis, and microprobe data such as that presented in §5.3 might also prove informative. A corollary issue is that any FP retention by the buffer could effectively increase the FP inventory available for release during accidents.

Fig. 5.4.1. Mobility of cesium in buffer layers of LTI-particles (from Stöver et al., 1976).

DATABASE USED IN MODEL DEVELOPMENT

Myers (1985e) presents data and compares metallic FP release from laser-drilled particles with exposed kernels and with exposed buffer layers. Figure 5.4.1 provides some data obtained during the 1970s. Microprobe data of FP concentration profiles across the particles was presented in §5.3.

5.5 METALLIC FISSION PRODUCT TRANSPORT IN THE PyC LAYERS

function	This model provides a diffusion coefficient with only temperature-dependence for transport through intact PyC layers. Failed PyC layers are assumed to provide no FP retention capability.
present status	With SiC the main barrier to FP transport, models for metallic FP transport are not significant unless the SiC layers are defective or have become permeable. Determinations of diffusion coefficients often rely on BISO particle data, and dependencies on burnup and surface concentration have not been accounted for by the model equations.
model uncertainty	Although extensive data exist for a variety of metallic FP, the variation of diffusion coefficients with burnup can introduce significant uncertainties (Myers, 1988). These uncertainties may be due in part to the structural evolution of the PyC during irradiation, with increased porosity and permeability. As an example, Myers (1988) states the uncertainty in the diffusion of Cs at 850°C is a factor of 23.
references	General Atomic (1977b); Myers et al. (1974, 1979); Amian et al. (1982)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

Transport of metallic FP through the OPyC layer is defined by the traditional diffusion equation, with diffusion coefficients given by (Acharya, 1987):

$$D = D_0 \exp\left(-\frac{Q}{RT}\right), \quad (5.5.1)$$

- D = effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$),
 D_0 = pre-exponential factor ($\text{m}^2 \text{s}^{-1}$),
 Q = activation energy (J mol^{-1}),
 T = temperature (K),

R = ideal gas constant (8.314 J mol⁻¹ K⁻¹).

Values for D_0 and Q are given in Table 5.5.1. Although the diffusion coefficients for the IPyC layer are the same in unirradiated particles, the IPyC layer is assumed to fail during irradiation (Goodin et al., 1985) with no FP retention capability.

Range of validity

The model is assumed to apply over all reactor conditions as long as the OPyC layer remains intact.

The experimental parameters for the diffusion of Ba, Eu, Ce, Sm, and Rb are discussed in General Atomic (1977b). Diffusion data for Ba were obtained for temperatures from

Table 5.5.1. Parameters for calculation of metallic FP diffusion coefficients and uncertainties in PyC layers, Eqs. (5.5.1) and (5.5.2)

Fission product	D_0 (m ² s ⁻¹)	Q (J mol ⁻¹)	$a^{(a)}$	$b^{(a)}$	$c^{(a)}$	Reference
Cs	$5.00 \times 10^{-5(b)}$	318,000 ^(b)	2.26	-0.349	0.0306	Myers et al. (1979)
Ag	5.30×10^{-9}	154,000	1.00	(c)	(c)	Amian et al. (1982)
Ba	2.10×10^{-7}	181,000	1.40	-0.211	0.0167	General Atomic (1977b)
Eu	1.3×10^{-10}	68,000	1.52	(c)	(c)	General Atomic (1977b)
Sm	"	"	"	(c)	(c)	General Atomic (1977b)
Ce	"	"	"	(c)	(c)	General Atomic (1977b)
Rb	5.5×10^{-4}	334,000	2.37	-0.282	0.025	General Atomic (1977b)
Sr	2.30×10^{-6}	197,000	2.71	-0.50	0.04	Myers et al. (1974)

- (a) All values for calculating uncertainties are taken from FDDM/F; different values of a , b , and c are reported in General Atomic (1977b).
 (b) Amian et al. (1982) recommend values of $D_0 = 1.88 \times 10^{-6}$ m² s⁻¹ and $Q = 254,000$ J mol⁻¹.
 (c) Values only listed for a , none for b or c .

1000 to 1700°C and source concentrations of 10^{-2} to 10^{-5} g-Ba/(g-carbon), although data from the larger source concentrations were not used in derivation of the reference diffusion coefficient. Diffusion data for Eu were obtained for temperatures from 800 to 1250°C and source concentrations of 1.9×10^{-3} and 6.0×10^{-7} g-Eu/(g-carbon), although data from the larger source concentrations were not used in derivation of the reference diffusion coefficient. The reference diffusion coefficient for Eu was derived from only two data, at 1000 and 1250°C. Only a single datum is reported for Ce diffusion in PyC at 1150°C in LTI PyC. As of 1977, no diffusion data for Sm or Rb were available. The data for Ba and Eu were obtained during the late 1960s and early 1970s and were therefore probably obtained using BISO particles and either LTI or HTI PyC.¹

The data for Sr diffusion is discussed in Myers et al. (1974), and the reference diffusion coefficient was obtained using data for both LTI and HTI PyC. The experimental range of irradiation and annealing temperatures and kernel burnup can be determined from Table 5.5.2 (from Myers et al., 1974).

The data for Cs diffusion is discussed in Myers et al. (1979) and was obtained from BISO particles with LTI PyC coatings. The experimental range of irradiation conditions and annealing temperatures can be determined from Tables 5.5.3 and 5.5.4 (from Myers et al., 1979).

For Ag diffusion data, the experimental parameters mentioned in general by Amian et al. (1982) are fast fluences $\leq 0.7 \times 10^{25}$ n m⁻² ($E > 0.1$ MeV), kernel burnups of either 7 to 11% FIMA or 30% FIMA, and annealing temperatures of 1050 to 1250°C. Detailed source data for Ag are not discussed.

Assumptions

1. Data derived from source concentrations significantly higher than those expected in irradiated particles should not be used in deriving diffusion coefficients.
2. For europium, two data points for low source concentrations provide an accurate diffusion coefficient.
3. The diffusive behavior of samarium and cerium should approximate that of europium.
4. The relative diffusive behavior of rubidium to cesium is the same as that of strontium to barium.
5. Data from irradiated and unirradiated transport experiments are comparable and can be used interchangeably in deriving diffusion coefficients.
6. The diffusion coefficients are constant from beginning to end of irradiation.
7. Temperature is the only significant variable affecting diffusive transport at AC temperatures.
8. The oxidative character of the environment (kernel, CO gas, etc.) is not considered in evaluating diffusion through the PyC layer.

¹B. F. Myers (1993) comments that data from HTI-PyC BISO particles were not used for model derivation. The reference diffusion data were obtained during the period when HTI PyC was under consideration for use.

Table 5.5.2. Diffusion coefficients for strontium in pyrocarbon (from Myers et al., 1974)

Postirradiation Anneal Measurements Using BISO-Coated Particles						
Coating Type	Coating Thickness (μm)	Kernel Type	Irradiation Temp. ($^{\circ}\text{C}$)	FIMA (%)	Anneal Temp. ($^{\circ}\text{C}$)	D (cm^2/sec)
LTI	57	(Th,U) C_2	890	2.3	1200	3.0×10^{-8}
LTI	58	(Th,U) C_2	975	1.3	1400	3.0×10^{-8}
LTI	58	(Th,U) C_2	975	1.3	1550	9.0×10^{-9}
LTI	--	ThO_2	≤ 800	3	1400	4.0×10^{-9}
HTI	68	(Th,U) C_2	685	5.7	1400	2.7×10^{-9}
HTI	68	(Th,U) C_2	685	5.7	1500	5.2×10^{-8}
HTI	68	(Th,U) C_2	685	5.7	1650	1.3×10^{-7}
HTI	98	(Th,U) C_2	950	1.5	1400	4.4×10^{-9}
HTI	98	(Th,U) C_2	950	1.5	1550	5.3×10^{-8}
HTI	68	(Th,U) C_2	900	2.3	1200	6.1×10^{-10}
HTI	68	(Th,U) C_2	900	2.3	1400	2.0×10^{-8}
HTI	68	(Th,U) C_2	900	2.3	1550	4.8×10^{-8}
HTI	--	ThO_2	≤ 800	3	1400	9.0×10^{-10}

Diffusion in Unirradiated (Wafer) Samples (Coating Type = HTI)

Anneal Temp. ($^{\circ}\text{C}$)	D (cm^2/sec) (non-loaded)	D (cm^2/sec) (pre-loaded)
1000	--	8.5×10^{-11}
1100	8.0×10^{-10}	1.5×10^{-9}
1200	3.7×10^{-9}	--
1300	1.0×10^{-8}	7.8×10^{-9}
1400	2.3×10^{-8}	--
1500	4.4×10^{-8}	4.4×10^{-8}
1700	--	3.5×10^{-7}

Table 5.5.3. Data from GA measurements of cesium migration in LTI pyrocarbon coatings using BISO-type particles
(from Myers et al., (1979))

Sample Ident.	Irrad. Temp. (°C)	% FIMA	Fast Fluence (10^{25} n/m ²)	Irrad. Time (d)	Kernel Type	Coating Thick. (a) (μm)	Coating Density (a) (Mg/m ³)	Anneal Temp. (°C)	D (m ² /s)	$10^4/T$ (K ⁻¹)
3363-117	1310	5.7	2.1	87	(Th,U)C ₂	39	2.03	1200	9.0(-17)	6.79
								1750	5.8(-13)	4.94
								1850	5.7(-13)	4.71
4000-632	890	23	6.4	174	(Th,U)C ₂	57	2.01	1200	4.2(-16)	6.79
								1400	3.6(-13)	5.98
								1550	3.2(-13)	5.49
								1650	1.5(-12)	5.20
								1750	8.9(-12)	4.94
4000-660	975	13	2.5	174	(Th,U)C ₂	58	1.66	1400	1.65(-15)	5.98
								1550	3.9(-14)	5.49
								1650	1.0(-13)	5.20
								1750	2.4(-13)	4.94
4000-323	1350	3.5	6.5	270	ThC ₂	67	1.84	1500	4.3(-15)	5.64
								1650	2.65(-14)	5.20
								1750	2.1(-13)	4.94
								1500	5.7(-15)	5.64
4000-334	1050	10	8.0	93	ThC ₂	61	1.90	1650	1.9(-14)	5.20
								1750	6.7(-14)	4.94
								1500	7.5(-14)	5.64
4000-339	750	10.5	8.0	93	ThO ₂	81	1.78	1650	1.3(-14)	5.20
								1750	8.4(-13)	4.94
								1500	3.4(-14)	5.64
4000-339	1050	10.7	8.0	93	ThO ₂	81	1.78	1750	1.05(-13)	4.94
								1500	1.15(-15)	5.64
4413-75	1325	7	7.0	232	ThO ₂	85	1.89	1650	3.7(-14)	5.20
								1500	1.1(-14)	5.64
4503-53	999	8.26	1.4		(Th,U)O ₂	124		1650	1.7(-14)	5.20
								1500	7.4(-15)	5.64
4503-53	1100	10.6	0.9		(Th,U)O ₂	124		1650	1.5(-14)	5.20
								1500	9.4(-15)	5.64
4503-53	971	19.4	1.4		(Th,U)O ₂	124		1650	1.45(-14)	5.20
								1380	6.6(-16)	6.05
4503-53	1500	1.4			ThO ₂					

(a) Preirradiation values.

Table 5.5.4. Data from ORNL measurements of cesium migration in LTI pyrocarbon coatings using BISO-type particles
(from Myers et al., 1979)

Sample Ident.	Irrad. Temp. (°C)	% FIMA	Flux (n/m ² ·s)	Irrad. Time (d)	Kernel Type	Coating Thick. (a) (μm)	Coating Density (a) (Mg/m ³)	Anneal Temp. (°C)	D (m ² /s)	10 ⁴ /T (K ⁻¹)
A-1	<700	11	4(17)	~58	UO ₂	64 ^(b)	2.01	1250	2.3(-16)	6.57
A-2	↓	↓	↓	↓	↓	↓	↓	↓	5.05(-16)	↓
A-3	↓	↓	↓	↓	↓	↓	↓	↓	3.7(-16)	↓
A-4	↓	↓	↓	↓	↓	↓	↓	↓	2.1(-16)	↓
A-5	↓	↓	↓	↓	↓	↓	↓	1400	7.8(-15)	5.98
A-6	↓	↓	↓	↓	↓	↓	↓	↓	1.6(-14)	↓
A-7	↓	↓	↓	↓	↓	↓	↓	↓	9.1(-15)	↓
A-8	↓	↓	↓	↓	↓	↓	↓	↓	3.6(-15)	↓
A-9	↓	↓	↓	↓	↓	↓	↓	↓	1.1(-14)	↓
A-10	↓	↓	↓	↓	↓	↓	↓	↓	1.9(-14)	↓
A-11	↓	↓	↓	↓	↓	↓	↓	↓	1.2(-14)	↓
A-12	↓	↓	↓	↓	↓	↓	↓	↓	1.5(-14)	↓
A-13	↓	↓	↓	↓	↓	↓	↓	1500	6.6(-14)	5.64
A-14	↓	↓	↓	↓	↓	↓	↓	↓	7.3(-14)	↓
A-15	↓	↓	↓	↓	↓	↓	↓	↓	5.9(-14)	↓
A-16	↓	↓	↓	↓	↓	↓	↓	↓	7.0(-14)	↓
A-17	↓	↓	↓	↓	↓	↓	↓	↓	8.2(-14)	↓
A-18	↓	↓	↓	↓	↓	↓	↓	↓	1.1(-13)	↓
A-19	↓	↓	↓	↓	↓	↓	↓	↓	8.0(-14)	↓
A-20	↓	↓	↓	↓	↓	↓	↓	↓	8.1(-14)	↓
A-21	↓	↓	↓	↓	↓	↓	↓	1600	2.6(-13)	5.34
A-22	↓	↓	↓	↓	↓	↓	↓	↓	2.1(-13)	↓
A-23	↓	↓	↓	↓	↓	↓	↓	↓	2.1(-13)	↓
A-24	↓	↓	↓	↓	↓	↓	↓	↓	1.5(-13)	↓
A-25	↓	↓	↓	↓	↓	↓	↓	↓	2.6(-13)	↓
A-26	↓	↓	↓	↓	↓	↓	↓	↓	2.0(-13)	↓
A-27	↓	↓	↓	↓	↓	↓	↓	↓	2.7(-13)	↓
A-28	↓	↓	↓	↓	↓	↓	↓	↓	1.3(-13)	↓
A-29	↓	22	↓	↓	↓	↓	↓	1250	7.1(-16)	6.57

Table 5.5.4. (continued)

Sample Ident.	Irrad. Temp. (°C)	% FIMA	Flux (n/m ² ·s)	Irrad. Time (d)	Kernel Type	Coating Thick. (a) (μm)	Coating Density (a) (Mg/m ³)	Anneal Temp. (°C)	D (m ² /s)	10 ⁴ /T (K ⁻¹)
A-30	<700	22	4 (17)	~58	UO ₂	64 ^(b)	2.01	1250	1.3(-15)	6.57
A-31	↓	↓	↓	↓	↓	↓	↓	1250	1.0(-15)	6.57
A-32	↓	↓	↓	↓	↓	↓	↓	1400	1.2(-14)	5.98
A-33	↓	↓	↓	↓	↓	↓	↓	↓	7.5(-15)	↓
A-34	↓	↓	↓	↓	↓	↓	↓	↓	1.2(-14)	↓
A-35	↓	↓	↓	↓	↓	↓	↓	↓	7.4(-15)	↓
A-36	↓	↓	↓	↓	↓	↓	↓	1600	1.8(-13)	5.34
B-1	<800	13	3.5 (17)	~68	↓	57	1.85	↓	3.8(-14)	↓
								↓	2.3(-14)	↓
C-1	650	3.5	4.0 (25) ^(c)	~66	ThO ₂	75	2.00	1400	2.3(-15)	5.98
C-2	↓	↓	↓	↓	↓	↓	↓	↓	1.9(-15)	↓
C-3	↓	↓	↓	↓	↓	↓	↓	↓	2.5(-15)	↓
C-4	↓	↓	↓	↓	↓	↓	↓	↓	3.3(-15)	↓
C-5	↓	↓	↓	↓	↓	↓	↓	1600	2.2(-14)	5.34
C-6	↓	↓	↓	↓	↓	↓	↓	1600	2.1(-14)	5.34
D-1	<800	13	3.5 (17)	~68	UC ₂	52	1.83	1400	2.65(-15)	5.98
D-2	↓	↓	↓	↓	↓	↓	↓	↓	2.1(-15)	↓
D-3	↓	↓	↓	↓	↓	↓	↓	↓	1.5(-15)	↓
D-4	↓	↓	↓	↓	↓	↓	↓	1600	3.4(-14)	5.34
D-5	↓	↓	↓	↓	↓	↓	↓	1600	4.0(-14)	5.34

(a) Preirradiation values.

(b) Thickness of high-density isotropic outer layer.

(c) Fast neutron fluence (E > 29 fJ).

9. The IPyC layer is assumed to fail during irradiation, with no retention of FP.

Uncertainty

An expression for the uncertainty in the values of the diffusion coefficients is given by FDDM/F as the standard deviation, σ , of $\ln D$:

$$\sigma (\ln D) = a + b \left(\frac{10^4}{T} \right) + c \left(\frac{10^4}{T} \right)^2, \quad (5.5.2)$$

a, b, c = constants.

The values for a, b , and c recommended by FDDM/F are given in Table 5.5.1. These values differ from those recommended in General Atomic (1977b).

MODEL CHRONOLOGY

General Atomic (1977b) is the best source for discussion of the diffusion coefficients in PyC layers for most of the metallic FP. The only reported addition to the diffusion model equations after the 1970s was that for Ag by Amian et al. (1982).

DISCUSSION

Fission product transport in pyrocarbon layers occurs via diffusion along grain boundaries, in pores, or along pore surfaces (Myers, 1988). Myers (1988) comments on the significant uncertainty arising from the dependence of diffusion coefficient on burnup and the possibility that this dependence relates to increasing porosity of the OPyC layer. General Atomic (1977b) specifically mentions the variation in the bulk diffusion coefficient as a function of FP surface concentration. The impact of this variable on diffusion data is rarely discussed or considered in MHTGR transport calculations.

The effect of LTI vs HTI PyC on diffusion data is represented by Fig. 5.5.1 from Stöver et al. (1976), which suggests that careful attention should be paid to any models derived from data using HTI-PyC BISO particles, if any.

In practice, FP release based on the assumption of 3% maximum OPyC failure during irradiation (§2.5) will dominate any diffusive release through intact OPyC layers. Diffusive release from the OPyC layer is significant for fuel with a significant fraction of defective or failed SiC layers; e.g., SiC degradation and FP diffusion through OPyC during accident conditions and heating tests.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

If gradual deterioration of the PyC layers can be expected over time (e.g., increased permeability under irradiation), then such effects may vary the effective diffusion coefficient

Fig. 5.5.1. Arrhenius plot of cesium diffusion in LTI and HTI pyrocarbon (from Stöver et al., 1976).

during the lifetime of the fuel. A better understanding of this effect, if it exists, would be useful.

The surface-concentration effect on measured diffusion coefficients may be an important parameter in evaluating diffusion data for PyC layers. Based on the comments by Myers (1988) that the diffusion coefficients are burnup-dependent, one must wonder if this dependence on burnup might be related to the increasing surface concentration of the metallic FP over the lifetime of the fuel.

Some data for large source concentrations are available. If sufficient data exist, the available diffusion data might be evaluated to determine the feasibility of an expression for the diffusion coefficient which varies as a function of burnup/source concentration over the lifetime of the fuel.¹

Microprobe data on particles which have been irradiated but not subjected to postirradiation heating would provide information on the assumption that the IPyC layer provides no resistance to metallic FP transport.

DATABASE USED IN MODEL DEVELOPMENT

The database for Sr diffusion in PyC was presented in Table 5.5.2. The data points are plotted in Fig. 5.5.2 (from Myers et al., 1974). The database for Cs diffusion was presented in Tables 5.5.3 and 5.5.4. The data points are plotted in Fig. 5.5.3 (from Myers et al., 1979). The database for Ag diffusion is not presented by Amian et al. (1982). The data points for Ba diffusion in PyC are plotted in Fig. 5.5.4 (from General Atomic, 1977b). The database used in deriving the diffusion coefficient for Eu consists of "two data ... for the lower source concentration: 6.0×10^{-13} [$\text{m}^2 \text{s}^{-1}$] at 1523 K and 2.1×10^{-13} [$\text{m}^2 \text{s}^{-1}$] at 1273 K" (General Atomic, 1977b). The available database for Ce diffusion is given by General Atomic (1977b): "Apparently, only one diffusion coefficient value for cerium in pyrocarbon is available. This value, $\sim 3.2 \times 10^{-14}$ m^2/s , was obtained in a postirradiation anneal test at 1423 K on a pyrocarbon (LTI type) coated UC_2 particle irradiated to 13% FIMA." General Atomic (1977b) refers to two source references for additional details of the data for Ba, Eu, and Ce diffusion: Gulf General Atomic (*HTGR Base Program Quarterly Progress Report for the Period Ending May 31, 1968*, USAEC Report GA-8662, June 28, 1968); and M. T. Morgan, H. J. deNordwall, and R. L. Towns (*Release of Fission Products from Pyrocarbon-Coated HTGR Fuel Particles During Postirradiation Anneals*, USAEC Report ORNL-TM-4539, December 1974).

¹B. F. Myers (1993) comments that a burnup-dependent diffusion coefficient for metallic FP in PyC was derived in the past, but the reference for this has not been determined.

Fig. 5.5.2. Diffusion coefficients for strontium in pyrocarbon (from Myers et al., 1974).

Fig. 5.5.3. Diffusion coefficients for cesium in LTI pyrocarbon (from Myers et al., 1979).

Fig. 5.5.4. Diffusion coefficients for barium in pyrocarbon (from General Atomic, 1977b; references available therein).

5.6 METALLIC FISSION PRODUCT TRANSPORT IN THE SiC LAYER

function	This model provides a diffusion coefficient with only temperature-dependence for transport through intact SiC layers of Cs, Sr, and Ag. Failed SiC layers are assumed to provide no FP retention capability. ¹
present status	Until recently the reference model was the Goodin-Nabielek (GN) model (§2.4.4), which assumed no metallic FP transport in SiC (except for Ag) prior to SiC failure, followed by complete loss of SiC retention. Recently a diffusion model has again been recommended for Cs, Sr, and Ag transport through SiC, while other metallic FP are assumed to have insignificant diffusion prior to SiC failure. This diffusion model is presented here as the reference model in conjunction with the models for evaluation of SiC failure presented in §2.4.
model uncertainty	The transport of metallic FP in SiC is affected by the structure and the chemical behavior of the SiC (Myers, 1988). The SiC structure is dependent on the coating process parameters, on the irradiation and thermal history, and on the structural deterioration at high temperatures. These variables introduce significant uncertainty into experimental diffusion coefficient determinations and into models of transport through SiC, and this uncertainty needs to be reduced to less than an order of magnitude between predicted and measured metallic FP release (CEGA, 1990).
references	Verfondern et al. (1993); Myers (1984c, 1988); Martin (1993a); Goodin (1983)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

Transport of Cs, Sr, and Ag in the SiC layer is defined by the traditional diffusion equation, with diffusion coefficients given by:

¹Apparently the release of silver remains governed by its diffusion coefficient in SiC even after SiC failure. Although the reference documents do not discuss this matter explicitly, it may not be significant as the fractional Ag release is typically greater than estimates of fractional failure.

$$D = \sum_i D_{o,i} \exp\left(-\frac{Q_i}{RT}\right), \quad (5.6.1)$$

D = diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
 $D_{o,i}$ = pre-exponential factor ($\text{m}^2 \text{s}^{-1}$)
 Q_i = activation energy (J mol^{-1})
 T = temperature (K),
 R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

The diffusion coefficients for Cs and Sr include two terms in the summation, while that for Ag contains only one term. Values for D_o and Q are given in Table 5.6.1.

The diffusion coefficients in intact SiC for all metallic FP except Cs, Sr, and Ag are assumed to be zero; upon SiC failure (as determined in §2.4), the transport of all metallic FP (except Ag) through the SiC layer becomes instantaneous.

Range of validity

The diffusion model is assumed to be valid throughout the operating temperature range of the MHTGR. The SiC failure models are assumed valid until the SiC "fails" as defined by the model equations of §2.4 (see "Range of validity" for specific models in that section). The problem with the SiC failure model under accident conditions (GN model) is that it is derived solely on data from German fuel. Results from a recent heating test on U.S. UCO fuel suggests that this model may not be valid in describing the FP release from U.S. fuel (Martin, 1993a).

Table 5.6.1. Parameters for calculation of metallic FP diffusion coefficients in SiC, Eq. (5.6.1)^(a)

Fission product	$D_{a,1}$ ($\text{m}^2 \text{s}^{-1}$)	Q_1 (kJ mol^{-1})	$D_{a,2}$ ($\text{m}^2 \text{s}^{-1}$)	Q_2 (kJ mol^{-1})
Cs	6.7×10^{-14}	106	1.1×10^{-4}	437
Sr	1.2×10^{-9}	205	1.8×10^{-6}	791
Ag	3.6×10^{-9}	215	-	-
Ba, Eu, Ce, Sm, Rb ^(b)	0.0	0.0	-	-

(a) Reference: Verfondern et al. (1993).

(b) No diffusion through intact SiC is assumed.

The specification of an experimental range of validity for the reference diffusion coefficients requires analysis of the source data and conditions under which the diffusion coefficients were determined, with emphasis on temperatures, irradiation or nonirradiation conditions, annealing, etc. The database is extensive, especially for Cs, and a review of the existing data would be a study in itself. Myers (1984c) analyzes the experimental data for Cs diffusion upon which his derived diffusion coefficients are based, and should be referred to for a summary of the experimental conditions. Source data through 1984 for the metallic FP are presented by Myers (1984d). Additional source references can be obtained from Goodin (1983).

Assumptions

1. Unlike Cs and Sr, the diffusive transport and release of Ag from SiC does not change with the failure of the SiC layer.
2. The SiC failure models of §2.4 are accurate. Specifically, the GN model is applicable to U.S. fuel.
3. Temperature is the only significant variable affecting diffusive transport in SiC, at both normal and accident conditions.
4. The diffusion coefficients do not vary significantly with irradiation conditions such as neutron fluence and irradiation temperature.
5. The diffusion coefficients do not vary significantly with varying source concentrations of the FP on the SiC surface.
6. Any FP solubility within the SiC is insignificant.
7. The diffusion coefficients do not vary with kernel material; specifically, the oxygen potential within the particle does not affect transport into the SiC layer.
8. The reference diffusion coefficient for Cs in SiC is assumed to be that derived by Myers (1984c) from the data for laminar SiC structures. This diffusion coefficient is assumed to accurately represent the retentiveness of (columnar) SiC in U.S. fuel for Cs.

Uncertainty

FDDM/F presents an uncertainty equation analogous to that used previously for diffusion in the PyC layers [Eq. (5.5.2)], but provides uncertainty parameters for only Ag diffusion:

$$\sigma (\ln D) = a + b \left(\frac{10^4}{T} \right) + c \left(\frac{10^4}{T} \right)^2 \quad (5.6.2)$$

$$\begin{aligned} a &= 1.51, \\ b &= 0.0900, \\ c &= 0.00666. \end{aligned}$$

FDDM/E provides uncertainty values with respect to some of the pre-exponential factors and activation energies listed in Table 5.6.1. However, the source of these uncertainty values are not referenced and therefore are not presented here.

Recent results from heating of U.S. UCO fuel particles indicate an uncertainty of metallic FP release significantly $>10\times$ relative to the reference models (Martin, 1993a). Significant uncertainty in the GN SiC failure model results from its derivation from German-fuel-specific data rather than U.S. fuel data.

MODEL CHRONOLOGY

Only silver transport has been consistently treated using the diffusive model. Although transport of the other metallic FP can also be assumed to occur by diffusion, an alternative model defines fractions of particles whose SiC layer is permeable to the metallic FP (Nabielek et al., 1982), analogous to the approach used in §2.4 for SiC failure probabilities. This controversy is most pronounced for cesium transport, with the diffusive model represented by the work of Myers (1984c) and the failure model represented by the GN model (Goodin et al., 1985; Goodin, 1989), in which "Cs release is a direct indicator of SiC failure."

The published diffusion coefficients vary from study to study. These considerations suggest the model for metallic FP transport in SiC remains in a state of evolution, with the current reference diffusion coefficients subject to change at the next model analysis or the next experimental determination of diffusion coefficients. For example, although FDDM/F recommends a model of no transport until SiC failure for all metals except Ag, it also recommends a diffusion coefficient for Cs (Christ, 1985) in those situations where a nonzero diffusion coefficient is required for calculations and suggests using this diffusion coefficient for all metallic FP except Ag.

DISCUSSION

Diffusion data

Values for D_0 and Q as given in FDDM/F and elsewhere are presented in Table 5.6.2 for the common metallic FP species. The recommended model diffusion coefficient for Cs is that presented by Myers (1984c) for diffusion through SiC structures characterized as laminar.

Much of the existing data for diffusion of metallic FP in SiC is summarized in several figures. Figure 5.6.1 is taken from Amian et al. (1983) and represents a literature review of published values for diffusion coefficients (references to the data can be obtained from Amian et al., 1983). Figures 5.6.2 and 5.6.3 are taken from Goodin (1983) and show the HTGR data for diffusion of Cs and Ag (references can be obtained from Goodin, 1983). Myers (1984c) analyzed the data portrayed in Fig. 5.6.2 and extracted those data which were consistent to obtain Cs diffusion coefficients in both columnar and laminar SiC structures. A study by Verfondern et al. (1989) on Cs release from postirradiation heating of FRG fuel spheres determined effective diffusion coefficients for Cs in SiC which were comparable to Myers' (1984c) diffusion coefficient for laminar SiC structures (see Fig. 5.6.4). An

independent study by R. C. Martin (1990) of the same data arrived at the same conclusion. On this basis Myers' diffusion coefficient for laminar SiC structure is recommended for design calculations.

Myers (1986) discusses a HRB model attributed to Christ (1985) which explicitly incorporates a fast-fluence-dependent diffusion coefficient for Cs in SiC for calculations of

Table 5.6.2. Parameters for calculation of metallic FP diffusion coefficients in SiC, as presented in FDDM/F and in other sources, Eq. (5.6.1)

Fission product	D_0 ($\text{m}^2 \text{s}^{-1}$)	Q (J mol^{-1})	Reference
Ag	5.3×10^{-9}	154,000	FDDM/F
Cs ^(a)	0.0	-	FDDM/F, Goodin et al. (1985)
Sr ^(a)	0.0	0.0	FDDM/F
Ba, Eu, Ce, Sm, Rb ^(a)	0.0	0.0	FDDM/F
Cs (i = 1) ^(b)	6.68×10^{-14}	106,000	Myers (1984c)
Cs (i = 2) ^(b)	1.12×10^{-4}	437,000	Myers (1984c)
Cs (i = 1) ^(c)	6.68×10^{-14}	106,000	Myers (1984c)
Cs (i = 2) ^(c)	2.37×10^{-2}	481,000	Myers (1984c)
Cs	6.68×10^{-14}	106,000	Acharya (1987)
Cs	1.74×10^{-11}	176,000	Myers (1984d)
Cs	3.5×10^{-9}	236,600	Amian et al. (1983)
Ag	4.95×10^{-10}	182,000	Myers (1984d)
Ag	4.5×10^{-9}	217,700	Amian et al. (1983)
Sr	7.90×10^{-10}	210,000	Acharya (1984)
Sr	1.03×10^{-15}	43,000	Myers (1984d)

(a) FDDM/F model assumes no diffusion through intact SiC.

(b) Diffusion coefficient representative of a laminar SiC structure; this diffusion coefficient represents the recommended diffusion coefficient for Cs in SiC.

(c) Diffusion coefficient representative of a columnar SiC structure.

Fig. 5.6.1. Literature review on diffusion data in SiC single crystals compared to results on pyrolytically deposited SiC coatings (from Amian et al., 1983).

Fig. 5.6.2. Comparison of diffusion coefficient data for ^{137}Cs in SiC (from Goodin, 1983).

Fig. 5.6.3. Comparison of diffusion coefficient data for $^{110\text{m}}\text{Ag}$ in SiC (from Goodin, 1983).

Fig. 5.6.4. Comparison between optimized diffusion coefficients (symbols) and the recommendation (solid line) as the result from the investigation presented by Verfondern et al. (1989) (from Verfondern et al., 1989).

in-reactor release (Fig. 5.6.5). Christ's expression for the diffusion coefficient of Cs in SiC is given by:

$$D = D_0 \exp\left(\frac{\phi}{\phi_0}\right) \exp\left(-\frac{Q}{RT}\right), \quad (5.6.4)$$

$$\begin{aligned} D_0 &= 5.5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}, \\ Q &= 125,500 \text{ J mol}^{-1}, \\ \phi_0 &= 5 \times 10^{25} \text{ n m}^{-2} (E > 0.1 \text{ MeV}), \\ \phi &= \text{neutron fluence (n m}^{-2}\text{)}. \end{aligned}$$

This diffusion coefficient was incorporated into a two-term diffusion coefficient [as in Eq. (5.6.1)] for use as the FRG reference model for cesium transport in SiC (Verfondern et al., 1993).

The diffusive model is limited by the significant variation in experimental diffusion coefficients as a function of SiC deposition and irradiation conditions and the very low diffusion coefficients measured for high-quality SiC over most of the temperature range experienced by the fuel. Several factors introduce uncertainty in comparisons of diffusion data from different experiments: the variation in SiC microstructure from experiment to experiment due to different deposition conditions, the effect of irradiation on diffusion in irradiated vs nonirradiated samples, and the microstructural evolution of the SiC under irradiation and at high temperatures. An example of this uncertainty is provided by Fig. 5.6.2, in which the in-reactor diffusion coefficients are significantly lower than those for out-of-reactor heating at the same temperatures.

Barthold (1993) points out that the potential presence of α -SiC within the β -SiC structure could have significant effects on the diffusion of FP species, with diffusion coefficients varying by orders of magnitude for SiC deposited at different temperatures. This concern is consistent with the microscopic observations of Lauf and Braski (1981) of localized heavily-faulted regions within the β -SiC with α -like characteristics.

Other variables may come into play that the diffusion model does not take into account. An earlier model for Ag transport proposed by Homan et al. (1978) suggested that a critical concentration of Ag on the SiC surface was required before a breakthrough transport mechanism was activated. In a study by van Opdorp (1971) of aluminum diffusion into SiC, striking but unexplainable differences were seen in the diffusion profiles if the Al was introduced from a gas-phase source or from diffusion across a solid interface. In §5.5 evidence was presented that diffusion coefficients in PyC will vary according to the source concentration. Surface effects are rarely considered in analyzing diffusion data.

Diffusion vs SiC failure

This experimental variability provides strong motivation to the proponents of the SiC failure model. One sometimes encounters their argument that each particle in a FRG fuel sphere would release the same fraction of Cs inventory if the diffusion model was valid (Goodin, 1987). This argument is strongly challenged by R. C. Martin (1990). However,

Fig. 5.6.5. Temperature and fluence dependence of the HRB Model and temperature dependence of the FDDM Model for diffusion of cesium through SiC layers (from Myers, 1986).

even the proponents of the failure model recognize the deficiencies of their model and periodically suggest modifications which represent a compromise between the two modelling approaches in the hope of obtaining better agreement between model and experiment. Specific comments in this regard are provided by Goodin (1987) and J. L. Martin et al. (1988). Specifically, the Martin-Goodin-Nabielek model (J. L. Martin et al., 1988) hypothesized that Cs transport in SiC can be represented by two significantly different diffusion coefficients, with a failure-like mechanism during heating which initiates transport characterized by the larger diffusion coefficient.

Myers (1988) cuts to the heart of the failure model. "While the current [failure] model is based on the assumption of fission product-SiC attack [see §2.4.3] at lower temperatures as the only effect leading to transport of fission products through SiC, there is very little demonstrable justification for this. It should be noted that evidence for chemical attack of the SiC in many cases consists in a raggedness of the inner boundary of the SiC layer as seen in metallographic mounts and by no means is proof of enhanced transport of fission products through the SiC layer; thus the underlying assumption of the current model which attributes to chemical attack the onus of SiC 'failure' is, for practical purposes, pure hypothesis."

Myers (1988) goes on to summarize the failings of the GN model assumptions. "Recent results from Seibersdorf demonstrate that [the claim that Cs does not diffuse through SiC] is incorrect and they support a recent review of data in which diffusion in SiC is treated as a real phenomenon. Extensive studies on (1) the physical characterization and (2) the measurement of transport have been conducted at KFA. The characterization has not led to an understanding of transport in SiC which is not surprising given the lack of a theoretical framework in which to relate transport and structure. Surely of comparable importance with static physical properties would be the changes induced in the SiC by irradiation and annealing; about these changes there is presently little knowledge." The variation between in-reactor and out-of-reactor data for Cs diffusion (Fig. 5.6.2) is relevant to these comments.

Recently Röllig (1991) demonstrated that the range of ^{137}Cs release from particles in FRG fuel sphere R2-K13/1 after heating at 1600°C could be reproduced by assuming a log-normal distribution of diffusion coefficients for Cs in SiC. The concept of a particle-to-particle distribution of diffusion coefficients partially resolves some of the perceived weaknesses of a diffusive approach to release while better simulating the effects of manufacturing- and irradiation-induced variations in SiC microstructure on FP diffusion.

Fission product inventory in SiC

Myers et al. (1986) present some interesting data of measured FP inventories in SiC at the end of irradiation. Figures 5.6.6 and 5.6.7 present evidence that the FP inventories within the SiC layer may vary as a function of the accumulated fast neutron fluence. Initial particle release profiles during AC-like heatup (Figure 5.6.8; from Myers, 1986) also show evidence that the initial Ag release is a function of the fast neutron fluence, and an analytical model is proposed to predict this initial Ag release as a function of the fluence. Additional details are presented by Myers (1986) and Myers et al. (1986) which provide useful information for microstructural considerations of FP transport through SiC.

Fig. 5.6.6. The dependence of the cesium content of the SiC layer on fast neutron fluence for different irradiation times (from Myers et al., 1986).

Fig. 5.6.7. The dependence of the cesium content of the SiC layer, normalized to equivalent SiC neutron damage, on the fast neutron fluence (from Myers et al., 1986).

Fig. 5.6.8. Initial release of silver and cesium in KFA heating experiments at 1600°C (from Myers, 1986).

Update

To avoid comparing apples and oranges, diffusion coefficients need to be measured for comparable particles manufactured by consistent methods rather than comparing results from different batches with unknown structural etc. variations between them and irradiated and heated under varying conditions.

The recent results on heating unbonded U.S. TRISO HEU UCO particles irradiated in capsules HRB-17 and HRB-18 illustrates this point (Morris et al., 1992). Out of 80 particles heated to 1600°C for 100 h, four particles showed significant but highly variable Cs release (2%, 6%, 35%, and 60% for each particle). Europium loss was also significant for these particles. The recommended diffusion coefficient for Cs in Table 5.6.1 underestimates the average Cs loss of the 80 particles (1.2%) by several orders of magnitude (Martin, 1993a). In comparison, Myers' (1984c) diffusion coefficient for columnar SiC overestimates the average Cs release by less than a factor of six.

With this the only AC data for modern U.S. UCO fuels, Martin (1993a) recommended Myers' columnar SiC diffusion coefficient for design calculations until new heating data is obtained, despite its adverse effect on safety margins for FP release during accidents. These heating results are consistent, however, with the SiC grain structure in recent U.S. fuel: large columnar grains across the SiC layer. The German SiC layers are not laminar but they are characterized by smaller grains and a more polycrystalline structure, which may explain the correlation of their Cs retentiveness with Myers' diffusion coefficient for laminar SiC structures.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Röllig's (1991) approach of using a distribution of particle-to-particle diffusion coefficients for transport in SiC is the most promising approach to more accurately reproducing the particle-to-particle distribution of FP release. This approach is conceptually consistent in relating variations in SiC microstructure before and after irradiation and heating to FP transport. Martin (1993a, 1993b) discusses the concept of time-dependent diffusion coefficients during irradiation and heating such as that suggested by Christ's (1985) fast-fluence-dependent diffusion coefficient, and suggests other approaches for refining the existing models for metallic FP transport in SiC.

The recent FRG AVR data provide the first extensive database using a standardized particle manufacturing process. The recent heating data obtained by Morris et al. (1992) disprove the hypothesis that the U.S. program can assume its SiC product will perform as well as the German product despite significant structural differences. Until new heating tests are conducted on modern U.S. fuel with the latest variations in SiC deposition conditions, only a very conservative and pessimistic model can be considered to reliably predict metallic FP transport through SiC. Such a model is represented by Myers' (1984c) diffusion coefficient for SiC with columnar grain structures.

Until FP release data is obtained from the latest fuel variant, model refinement can consider the existing data as a function of experimental conditions and irradiation parameters similar to that of Myers (1984c). The FP inventory data in SiC presented by

Myers et al. (1986) should be considered as well as suggestions made by R. C. Martin (1990) of possible irradiation and heating effects on the SiC structure and FP transport. In-reactor vs out-of-reactor diffusion data in the temperature range of 1250 to 1500°C should be compared with respect to neutron damage and annealing effects and any related effects on the thermal stability of the SiC layer. Likewise, the irradiation history of the particles should be considered in comparing the higher-temperature diffusion data ($\geq 1500^\circ\text{C}$).

The issue of surface effects on diffusion is rarely considered. Not only might the surface concentration of FP quantitatively affect the calculated diffusion coefficients, but a larger unknown arises when considering the possibility of oxygen or CO reaction with the SiC to form a surface layer of SiO_2 , a process very favorable thermodynamically. Not only is this process of SiO_2 formation well studied for silicon substrates, but the nature of such layers as diffusion barriers for metallic atom transport are known and information has been obtained for phenomena such as Cs pileup at the interface of SiO_2 layers on silicon. Surface oxidation is known to strongly affect FP behavior for graphite and primary circuit alloys, and analogous effects for FP transport through SiC have apparently not been previously considered in diffusion modelling. A statement by Price (1977) is relevant: "In many cases, the diffusion profiles [in semiconductor-grade SiC] deviated from Fick's Law, indicating different diffusion coefficients near the surface or in the low-concentration tails. Effective diffusion coefficients also were strongly influenced by the presence of a second dopant."

DATABASE USED IN MODEL DEVELOPMENT

Some of the database relevant to the existing diffusion model is represented by Figs. 5.6.2 and 5.6.3. Many of the other figures provide data which could be considered in model revision. Additional detail on the data and relevant experimental conditions can be obtained from the previously-mentioned references and from additional references mentioned therein.

5.7 UPDATE

The following references have been suggested for additional relevant information.

Brown, P., and R. L. Faircloth, "Metal Fission Product Behavior in High Temperature Reactors- UO_2 Coated Particle Fuel," *J. Nucl. Mater.*, 59 (1976) 29-41.

Minato, K., T. Ogawa, S. Kashimura, and K. Fukuda, "Fission Product Palladium-Silicon Carbide Interaction in HTGR Fuel Particles," *J. Nucl. Mater.*, 172 (1990) 184-196.

The recent observation that NPR UCO kernels vary in stoichiometry from UO_2 to UC_2 requires consideration of the effect of stoichiometry distribution on the kernel diffusion coefficients of metallic FP. The observation of percent-level "gold spots" in the SiC layers of NPR particles (i.e., inclusions of silicon "soot" within the SiC deposited during the coating process) is not believed to seriously impact NOC fuel performance, but no mention of the

potential AC effects has been made. Free silicon will vaporize at AC temperatures, and the relative diffusion of metallic FP through gold spot inclusions has not been discussed.

The heating tests mentioned in §5.6 on U.S. UCO HEU fuel from HRB-17/18 piggyback samples were augmented by an additional 1000 h heating test at 1600°C on 25 particles. The measured cesium release was an order of magnitude higher than the release from German particles in fuel sphere R2-K13/1 with a similar time-at-temperature heating profile.

A reasonable conclusion from the above is that the U.S. MHTGR program does not know how the latest fuel design will perform at accident temperatures near 1600°C and that important reference AC models are not valid for predicting fuel performance.

When a reference U.S. fuel design is used to obtain reproducible heating test results and IMGA data on individual particles, the approach used by Röllig (1991) should be applied to determine a representative distribution of diffusion coefficients of metallic FP in SiC for use in model revision.

6. FISSION PRODUCT TRANSPORT FROM PARTICLE TO COOLANT

6.1 INTRODUCTION

Transport mechanisms

Fission product transport from particle to coolant involves both diffusion through and sorption on the graphitic structures. Diffusion represents transport through the bulk or along the surface of the material structure, while sorption represents the gas-phase equilibrium with the surface concentration of the diffusing species. Diffusion in graphite has been studied in detail, and more complicated models (based on diffusion plus trapping) have been found to apply than the standard Fickian diffusion model. Diffusion in the compact matrix material has not been studied experimentally.

The transport of fission gas is known to be very rapid from particle release to entrainment by the coolant. One estimate (Myers et al., 1977) suggests a time of one second from gas escape into the compact/graphite gap to gas entrance into the main coolant stream. Holdup of fission gas by the compact and graphite structure is sufficiently insignificant that little modelling effort is devoted to this regime of gas transport. However, transport of metallic FP through the compact and graphite structure is quite important as significant retention on the graphitic structures is known to occur via sorption. As the graphitic structures act as a secondary barrier to metallic FP release to the coolant and thus reduce the mobile source term available during accidents, most of this chapter is devoted to the transport of metallic species through the fuel compact and graphite.

A model is presented for metallic FP transport across the compact/graphite interface which uses sorption isotherms to calculate an effective partition coefficient across the interface analogous to the partition coefficients discussed in §5.3. An evaporation-like model is also presented for metallic FP release from the surface of the graphite into the coolant, which combines mass transfer considerations with the sorption isotherm at the surface.

Sorption isotherms

Sorption involves the attraction and holding of atoms and molecules (the sorbate) by the surface of a solid body (the sorbent) with which they are in contact. Sorption can represent both adsorption (adhesion to the surface of the solid) and absorption into the solid. MHTGR design is concerned with sorption of FP atoms at the surfaces of the compact matrix material (§6.5), the graphite structure (§6.6), and the metallic alloys within the primary circuit (§8.4). Sorption can occur by either a relatively weak physical attraction between the surface and the sorbate, or by the stronger chemisorption which involves chemical reaction between the sorbate and the sorbent. Sorption of inert fission gases is of little concern because of their unreactive behavior. Sorption of metallic FP and of iodine are greatest interest in MHTGR design.

The capacity of a sorbate for FP sorption is typically characterized by the sorption isotherm, which gives the relationship between the external pressure of the species and its concentration within the sorbate. The standard approach to FP sorption considers the separate contributions to sorbate concentration by the high- and low-sorbate concentration regimes, as represented by the Freundlich and Henrian isotherms, respectively (Myers, 1981c). In general, the same governing equations apply to sorption in the fuel compact and in the structural graphite.

These isotherms represent the expected behavior of fission products in their elemental form. The potential existence of some fission products as chemical compounds and the resulting effect on sorption is often uncertain. The application of isotherms derived from equilibrium data to transient conditions is also open to question.

Fuel compact and graphite materials

The fuel compact has the shape of a small solid cylinder and contains a mixture of fuel particles and small pieces of H-451 graphite (called "shim" particles) embedded in a carbonaceous matrix consisting of petroleum pitch and graphite powder (EG&G, 1992). During fabrication, the compact is heated to high temperatures to carbonize the matrix. The fuel compact contains significant porosity. As a historical note, the fuel compact was usually referred to as a fuel rod until recent years (see, e.g., GA Technologies, 1986).

The core graphite employed in the U.S. design for MHTGRs is H-451 graphite, produced from petroleum coke filler and pitch binder and highly graphitized by baking at temperatures approaching 3000°C (EG&G, 1992). This manufacturing process produces a graphite structure with a combination of large and small pores. H-451 replaced H-327 graphite during the 1970s as the HTGR structural graphite because of its better strength, heat transfer, and dimensional change characteristics. As a historical note, the internal graphite structure was often referred to as the "graphite web" in the transport of FP (see, e.g., Myers et al., 1977).

Normal vs accident conditions

For each of the models presented in this chapter, only a single model is used to simulate both normal and accident conditions. The effect of temperature is explicitly included in those models for which temperature effects are significant. The temperature dependencies of sorption isotherms are explicitly expressed in the governing equations; therefore, the treatment of sorption under accident conditions is identical to that under normal operating conditions, provided the sorption isotherms are valid throughout the temperature range experienced by the fuel. The equations for sorption on graphite were modified in recent years to include a fast-fluence-dependent term as well as a temperature-dependent term which takes into account annealing effects at higher temperatures, effectively bridging the gap between NOC and AC.

6.2 FISSION GAS TRANSPORT IN THE FUEL COMPACT AND GRAPHITE

function	This model provides a simplified model for rapid release of fission gases without any functional dependencies specified.
present status	Although the transport model is conservative in postulating instantaneous gas release from the fuel compact and graphite, the consequences of this conservatism should not be significant.
model uncertainty	For the fuel compact, the consequence of the transport model "is negligible and the uncertainty is therefore unimportant" (Myers, 1988). The same conclusion can be applied to the model for transport through the graphite.
references	Myers et al. (1977); Myers (1988); EG&G (1992)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The fission gases are instantaneously transported through the fuel compact matrix material upon release from the fuel particles (Myers, 1988). Likewise, release to the primary circuit is not delayed by the graphite (EG&G, 1992). Therefore, release of gaseous fission products from the particle is synonymous with release into the coolant without any time delay. This model can be expressed as:

$$f = 1 \quad \text{at } t = 0, \quad (6.2.1)$$

- f = the fractional fission gas release from the core graphite with respect to that released from the particle at $t = 0$,
 t = time after fission gas release from the particle to the compact matrix material (arbitrary units).

Range of validity

This model is assumed to apply under all temperatures and operating conditions experienced by the reactor.

Assumptions

1. Neither the fuel compact material nor the graphite structure pose any effective resistance to gas transport.
2. No trapping of gas occurs within the compact or graphite.

3. Sorption of fission gas on the graphite and carbonaceous structures does not occur or is not significant at MHTGR temperatures.

Uncertainty

The uncertainty has not been quantified but is considered to be unimportant (Myers, 1988). Myers et al. (1977) report an estimate by Mysels and Rovner that the time delay between gas release to the compact/graphite interface and release to the coolant is approximately one second ("in the absence of adsorption").

MODEL CHRONOLOGY

FDDM/F mentions this model in relation to gas release from the fuel compact, but does not mention this model in relation to release from the graphite. The model as stated above has not changed since its presentation by Schwartz et al. (1974). Myers et al. (1977) reported an approximate quantification to the holdup time of fission gases by the graphite structure.

DISCUSSION

The porosity of the fuel compact matrix material can approach 50% (EG&G, 1992). This large porosity would be expected to expedite rapid release of inert gases. Although the porosity of the graphite would be marginal in comparison, apparently any delay in gas transport by the graphite is not expected to be significant. This assumption was stated explicitly by Schwartz et al. (1974): the noble gases "are conservatively assumed to become gasborne immediately upon being released from the fuel particles."

Myers et al. (1977) perhaps provide the most detailed discussion of this model (refer to §6.1, "Fuel compact and graphite materials", regarding the terminology used). "The fission product gases which are released from the fuel rods are transported through the graphite web by two mechanisms: (1) transverse flow of the helium coolant and (2) diffusion. The time delay in this transport governs the decay of fission gas nuclides during passage through the graphite web.

"Transverse flow is the process in which helium coolant flows through the graphite web surrounding the upper part of the fuel rod stack, into and along the gap between the fuel rods and graphite, and back through the graphite web surrounding the lower part of the fuel rod stack to the main helium coolant stream. The fission gases in the gap and the graphite are entrained by the helium undergoing transverse flow and are swept into the main helium coolant stream. In unpublished work at GA, Mysels and Rovner have estimated the possible effects of transverse flow on the transport of fission products through the graphite web. They concluded that in the absence of adsorption, the gaseous fission products entrained by the helium in the gap will be delivered to the circulating mainstream in times of the order of 1 s." They then report the estimate for diffusive delay time to be between 250 and 300 s, indicating that transverse helium flow will dominate fission gas transport to the coolant.

Sorption of fission gas by the carbonaceous structures should not occur at reactor operating temperatures.

Although models of the release of gaseous fission products from heavy metal contamination do not predict instantaneous release, such a difference may not be significant as the gas atoms produced during fission of the contaminant should implant into the carbonaceous matrix, and thus require solid-state diffusion back to the surface of the porosity prior to gas-phase release.

For more detailed discussion of gas transport mechanisms through graphitic structures, one can refer to Röllig (1977) although the difference in structural graphite used in their analysis should be kept in mind.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

As this model is not expected to be significant in terms of overall gas release from the core, further consideration of this model is not warranted unless additional information suggests a reexamination is justified. One potential area for investigation is confirmation that transverse flow along the compact/graphite interface is the dominant pathway for fission gas release to the coolant.

DATABASE USED IN MODEL DEVELOPMENT

No experimental data upon which to base this model were mentioned in the references, thus any database relevant to this model is unknown at this time. In lieu of experimental data, the calculations mentioned by Myers et al. (1977) might be considered as supporting evidence for the model.

6.3 METALLIC FISSION PRODUCT TRANSPORT IN THE FUEL COMPACT

function	This model provides a simple approximation for rapid distribution of FP metals within the compact without any functional dependencies specified.
present status	Although the model is very simple and conservative, the consequences are not expected to be significant because the transport of metallic FP in the compact is not the rate-limiting step for release from the core.
model uncertainty	No data exist for transport of metallic FP in the fuel compact matrix material, thus the model uncertainty is large. However, "the effects are regarded as negligible" (Myers, 1988).
references	Alberstein et al. (1975); Myers (1988); EG&G (1992)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

Any quantity of metallic FP entering the compact matrix material is assumed to instantaneously distribute itself homogeneously throughout the matrix material (Myers, 1988). This model can be expressed as:

$$C(x) = \bar{C} \quad \text{at } t = 0, \quad (6.3.1)$$

- $C(x)$ = metallic FP concentration at position x within the fuel compact (arbitrary units),
 $\bar{C}$ = average metallic FP concentration throughout the compact matrix material (arbitrary units),
 t = time after metallic FP release from the particle to the compact matrix material (arbitrary units).

The subsequent release from the fuel compact is governed by sorption effects (§6.5) (EG&G, 1992).

Range of validity

This model is considered valid for both normal and accident conditions, and under all reactor operating conditions. Apparently no data exist (EG&G, 1992) with which to limit this assumed range of validity.

Assumptions

1. Mass transfer and diffusion of metallic FP within the fuel compact are not rate-limiting.
2. The dispersion of metallic FP throughout the fuel compact has no significant dependence on temperature, fast fluence, or any other variable.

Uncertainty

The uncertainty of this model has not been estimated but should be insignificant relative to overall FP release from the core.

MODEL CHRONOLOGY

FDDM/F presents this model in comparable form. The references listed above only briefly discuss this model. The model as stated above has not changed since its presentation by Alberstein et al. (1975).

DISCUSSION

The statement by Alberstein et al. (1975) also summarizes the state of the model at the present time. "Diffusion of metallic fission products in the porous fuel rod matrix material is presently assumed to be sufficiently rapid that the fission product atoms would be, in the absence of thermal diffusion, spread uniformly throughout the fuel rod. Hence, any holdup of metallic fission products due to diffusion in a concentration gradient is conservatively neglected. Thermal diffusion could, however, produce a nonuniform distribution of fission products in the fuel rod, although no experimental evidence of this phenomenon exists at this time."

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Refinement of this model would require some kinetic considerations of the rate of dispersal of the metallic FP throughout the fuel compact as they are released from the particle. This effect would only be significant in initial transient releases to the graphite, thus refinement of this model is not a high priority.

DATABASE USED IN MODEL DEVELOPMENT

No data is available for metallic FP transport in the fuel compact (Myers, 1988; EG&G, 1992), thus no database presently exists upon which to evaluate this model.

6.4 METALLIC FISSION PRODUCT DIFFUSION IN GRAPHITE

function	This model provides diffusion coefficients for FP metals in graphite as a function of temperature and fractional graphite oxidation.
present status	The diffusion coefficients are based on data from the early to middle 1970s and do not take into account all the important variables which impact diffusion in graphite. The model itself (Fickian diffusion) is an oversimplification of the actual transport mechanisms, which are known to include both diffusion and trapping (Myers, 1988).
model uncertainty	Because of the lack of model dependency on such variables as neutron fluence, oxidation of the graphite, helium pressure, and FP source concentration, and because of the use of the simplified model, the uncertainty is considered to be "much larger than a factor of 10" and "the uncertainty associated with Ag diffusion in graphite is enormous, being estimated to be a factor of 2000" (Myers, 1988).

references FDDM/F; General Atomic (1977b); Myers et al. (1974, 1979);
Myers (1983a, 1988)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The standard Fick's law diffusion coefficient is typically used to model the diffusion of metallic FP in H-451 graphite:

$$D = D_o \exp\left(-\frac{Q}{RT}\right) , \quad (6.4.1)$$

D = effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$),

D_o = pre-exponential factor ($\text{m}^2 \text{s}^{-1}$),

Q = activation energy (J mol^{-1}),

T = temperature (K),

R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

A recent refinement of the model incorporates the effects of graphite oxidation on diffusion (FDDM/F):

$$D = D_o \left[1 + d_o (1 - e^{-B}) \right] e^{-Q/RT} , \quad (6.4.2)$$

B = weight percent burnoff (i.e., extent of graphite oxidation),

d_o = constant (dimensionless),

all other terms as defined above.

Values for the parameters D_o , Q , and d_o for diffusion in H-451 graphite are given in Table 6.4.1.

Range of validity

Although no limitations of the model are mentioned in FDDM/F, in fact the source references clearly state limitations on the range of validity of these reference diffusion coefficients. For Cs, the reference parameters are valid at surface concentrations less than $0.2 (\mu\text{mol Cs})/(\text{g graphite})$, and the model is valid at steady-state but not for the approach to steady-state. For Sr, the reference parameters are valid only for surface concentrations $\leq 0.7 (\mu\text{mol Sr})/(\text{g graphite})$.

Table 6.4.1. Parameters for calculation of metallic fission product diffusion coefficients in graphite and the uncertainties, Eqs. (6.4.2) and (6.4.3)

Element	D_0 ($\text{m}^2 \text{s}^{-1}$)	Q (J mol^{-1})	a	b	c	$d_0^{(a)}$	Ref. ^(b)
Sr	1.66×10^{-2}	268,000	2.10	-0.545	0.0396	3.0	(d)
Ce	1.66×10^{-2}	268,000	4.60	0.0	0.0	3.0	(e)
Eu	1.66×10^{-2}	268,000	4.60	0.0	0.0	3.0	(e)
Sm	1.66×10^{-2}	268,000	4.60	0.0	0.0	3.0	(e)
Cs	1.72×10^{-6}	148,900	2.49	-0.243	139.0	3.0	(f)
Rb ^(c)	1.72×10^{-5}	148,900	4.60	0.0	0.0	3.0	(e)
Ba	1.54×10^{-4}	243,000	5.00	0.0	0.0	3.0	(e)
Ag	1.38×10^{-2}	226,000	4.61	0.0	0.0	3.0	(g)

- (a) Value for d_0 based on data from strontium (FDDM/F).
- (b) All uncertainty parameters taken from FDDM/F.
- (c) The diffusion of Rb is assumed to be ten times faster than that of Cs.
- (d) Myers et al. (1974).
- (e) General Atomic (1977b).
- (f) Myers et al. (1979).
- (g) FDDM/F.

Assumptions

- None of the following experimental variables significantly affect the diffusion of metallic FP in graphite: the concentration of the diffusing FP, irradiation effects and annealing of the graphite, the ambient helium pressure, or any mixed isotope effect due to the presence of other FP.
- The value of d_0 determined from Sr data is applicable to the other metallic FP.
- Parameters for the diffusion of Sr in graphite can also be used to describe the diffusion of Ce, Eu, and Sm.
- The diffusion of Rb is assumed to be ten times faster than that of Cs.

Uncertainty

An expression for the uncertainty in the values of the diffusion coefficients is given by FDDM/F as the standard deviation, σ , of $\ln D$:

$$\sigma(\ln D) = a + b \left(\frac{10^4}{T} \right) + c \left(\frac{10^4}{T} \right)^2, \quad (6.4.3)$$

T = temperature (K),
 a = constant (dimensionless),
 b = constant (K),
 c = constant (K²).

Values for a , b , and c are reproduced from FDDM/F in Table 6.4.1.

MODEL CHRONOLOGY

Equation (6.4.2) is apparently from an internal GA memorandum which has not been reviewed by this writer.

DISCUSSION

Design Data Need 11.57

Several comments in CEGA (1990) specific to DDN 11.57 are pertinent here, with emphasis added by this writer. "The validity of the methods for predicting fission metal release during normal operation have been assessed by applying them to predict the observed metal release in operating HTGRs ... and in irradiation capsules and in-pile loops ... Most of the available data are for the Cs isotopes with a small amount of Ag and Sr data. In general, the releases of fission metals were underpredicted by factors of several and, in some cases, by more than an order of magnitude. The cause of the underpredictions is ambiguous because the SiC defect fractions and the particle failure fractions are typically not well known; however, there is strong circumstantial evidence suggesting that the transport across the fuel compact/fuel element gap and the transport in the graphite web are not properly modelled ... The validity of the methods for predicting fission metal release during core conduction cooldown transients have not been assessed systematically."

DDN 11.57 then goes on to suggest an approach to correct these deficiencies. "An experimental data base is needed to validate the integrated models and core-survey codes used to predict fission metal release from the core ... Particular attention must be given to the effects of irradiation and environment on the transport of fission metals in core graphite."

Barthold (1993) also points out the strong effect that the uncertainty in the calculated temperature profile across the graphite can have on, for example, Cs-137 release, and that existing codes model the graphite web as a slab rather than in two dimensions.

Myers' analysis

The best recent discussion of this model is provided by Myers (1988) and will be quoted here. "The transport of fission product metals in polycrystalline graphite depends on the type and nature of the graphite, the structure of the graphite, the temperature, concentration of diffusant, extent of irradiation damage, state of oxidation, ambient pressure of gas (He) and any interaction of different diffusants. Given H-451 graphite, the important variables are the temperature, irradiation damage, oxidation state and the pressure for HTGR conditions. The present model does not account for all these important variables and is based mainly on older reactor data for which the dependence of the diffusion on these variables is not explicit, except for temperature. Significant experiments have been conducted since the model was formulated and the parameters evaluated. The uncertainty for the diffusion of Cs and Sr is a factor of 10 based on a statistical analysis of the older reactor data; however, this uncertainty poorly represents the actual state of affairs since the range of the variables implicit in the reactor data is smaller than that of interest except, again, for the temperature. Furthermore, the older reactor data represent averages over the ranges of some variables. The presently used model does not take into account the effects of irradiation damage and pressure for which some data exist. The incorporation of these effects would, in general, reduce the calculated release of Cs and Sr from the graphite except, perhaps, for neutron fluence less than half the maximum value accumulated in the fuel element in its reactor lifetime. There is a vague perception circulating that incorporating these effects would only exacerbate the problem of underprediction of Cs release in core calculations.

"More fundamentally, the model, based on Fickian diffusion, couples the loading of the graphite and diffusion through it. Careful experiments demonstrate that the Fickian model does not apply to H-451 graphite (and also not to A-3 matrix graphite). These experiments demonstrate that a diffusion trapping model more accurately predicts the concentration-distance profiles observed. In diffusion trapping models, the loading and diffusion are decoupled. Superficial examination of observed and calculated profiles for R2-K13 data indicate that, for Cs, the measured and calculated profiles have the same shape but that the calculated profile is a factor of about 5 lower in concentration. The diffusion trapping model, applied to the R2-K13 data, would result in agreement of the measured and calculated profiles; whether the adjustment of parameters needed to do so would be acceptable would be another matter to be resolved. The diffusion-trapping model tends to the Fickian model as temperature declines; at 800°C the models are the same for H-451 graphite but above 900°C, the models become quite different.

"Considering the omission of fluence and pressure effects and the use of an inaccurate model in treating diffusion of fission products in graphite, one sees that the uncertainty is much larger than a factor of 10. Correcting these deficiencies will remove this large increment in uncertainty and probably reduce the uncertainty below the factor of 10 ... A detailed review of the available data, models and core calculations is necessary to begin to reduce this uncertainty; PIE and analysis of capsule A of the HFR-B1 experiment will also help considerably."

Alternative models

Some of the alternative diffusion models which can be considered besides Fickian diffusion are:

1. diffusion-trapping model,
2. two-path coupled diffusion model,
3. diffusion-sorption models,
4. grain-boundary diffusion model.

Myers (1983a) and Myers et al. (1979) discuss these transport models in more detail. Application of the diffusion-trapping model to Cs diffusion is discussed in Hill et al. (1983). Figure 6.4.1 suggests this model provides better agreement with experiment than does the Fickian diffusion model.

General model information

Figure 6.4.2 is also taken from Hill et al. (1983) and indicates the effect of ambient helium pressure on the diffusion of Cs in graphite. Figure 6.4.3 (from Myers et al., 1974) shows the dependence of the Sr diffusion coefficient in graphite on the Sr concentration. Myers et al. (1974) also discuss evidence of the significance of the mixed isotope effect. This evidence tends to contradict several of the assumptions on which the reference Fickian model is based.

Some limited information on the diffusivity of Ag in graphite is provided by Myers (1981e). Whether this information was used to derive the reference diffusion coefficient for Ag is uncertain. Acharya (1987) attempted to reproduce experimental concentration profiles for Ag in graphite with only limited success, and concluded that the diffusion coefficient for Ag in graphite "appears to be at fault". However, he provides few details of his calculations.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Statements that Cs release from the core can be significantly underpredicted raise concerns about the reference models for metallic FP transport in graphite. Underpredictions of release run counter to the philosophy of conservatism in predicting FP release.

To resolve this underprediction and refine the existing models, one should refer to Myers' (1988) comments quoted above for considerations in transport modelling in graphite. The suggestions related to reconsideration of the available data and application of non-Fickian models for diffusive transport appear more realistic than the present simple diffusion model.

DATABASE USED IN MODEL DEVELOPMENT

Figure 6.4.4 shows the range of experimental diffusion coefficients used to derive the reference diffusion coefficient for Sr in graphite, and Fig. 6.4.5 shows the same for Cs.

Fig. 6.4.1. Comparison of model cesium profiles with experimental profile (82-VEA) (from Hill et al., 1983).

Fig. 6.4.2. Dependence of the cesium diffusion profile on pressure (from Hill et al., 1983).

Fig. 6.4.3. Variation of the diffusion coefficient with concentration of strontium in A.G.L.9 graphite at 1000°C [from Myers et al., 1974; data taken from Sandalls and Walford, *J. Nucl. Mater.*, 62 (1976) 265-272].

Fig. 6.4.4. Strontium diffusion coefficients in graphite (from Myers et al., 1974; references available therein).

Fig. 6.4.5. Diffusion coefficients for cesium in graphite (from Myers et al., 1979; references available therein).

Detailed information on the experimental data for Sr can be obtained from Myers et al. (1974) and that for Cs from Myers et al. (1979). The range of experimental data for Ba diffusion is shown in Fig. 6.4.6 (from General Atomic, 1977b). Comparison of the relative diffusivity of Ce and Sr is given by Fig. 6.4.7. However, as a conservative approximation the diffusivities of Ce, Eu, and Sm are assumed to be the same as that of Sr; the logic of this choice is discussed in General Atomic (1977b).

6.5 METALLIC FISSION PRODUCT SORPTION IN THE FUEL COMPACT

function	This model uses sorption isotherms to calculate the partial pressure of FP metals in the gas phase from their concentration in the compact matrix material as a function of temperature.
present status	The sorption isotherms for the common metallic FP are considered adequate except for Sr and Ag, which suffer from a lack of data. The greatest unknown in the model equations may be the effects of oxidation on the sorptivity of the compact matrix material.
model uncertainty	"The sorption isotherms for Cs, Sr and Rb on fuel compact matrix material have uncertainties which are large only for Sr ... For Ag, the uncertainties are very large and there are no reliable data" (Myers, 1988). Lack of data on the mixed isotope effect for multi-species sorption and on the reduced sorptivity of oxidized graphitic materials introduces additional uncertainty.
references	Myers et al. (1974, 1979); FDDM/F; General Atomic (1977b); Myers (1981c)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The FP concentration sorbed on the compact matrix material is in equilibrium with the partial vapor pressure, P , of that FP species. The partial vapor pressure is assumed to consist of contributions from both the Freundlich (P_F) and Henrian (P_H) isotherms (Myers, 1981c):

$$P = P_F + P_H \quad , \quad (6.5.1)$$

Fig. 6.4.7. Comparison of diffusion coefficients for cerium and strontium in graphite (from General Atomic, 1977b; references available therein).

$$\ln P_F = \left(A + \frac{B}{T} \right) + \left(D + \frac{E}{T} \right) \ln C , \quad (6.5.2)$$

$$\ln P_H = \left(A + \frac{B}{T} \right) + \left(D - 1 + \frac{E}{T} \right) \ln C_i + \ln C , \quad (6.5.3)$$

$$\ln C_i = d_1 - d_2 T , \quad (6.5.4)$$

P_F	=	Freundlich isotherm vapor pressure (Pa),
P_H	=	Henrian isotherm vapor pressure (Pa),
T	=	temperature (K),
C	=	concentration of sorbate species (mmol kg ⁻¹ of fuel compact material),
C_i	=	transition concentration between the two sorption isotherms (mmol kg ⁻¹),
A, D, d_1	=	constants (dimensionless),
B, E	=	constants (K),
d_2	=	constant (K ⁻¹).

The constants are obtained by fitting Eq. (6.5.2) to experimental data obtained within the Freundlich regime, and by fitting Eq. (6.5.3) to data obtained within the Henrian regime. Constants appropriate for several FP species are provided in Table 6.5.1 for sorption on the fuel compact matrix material.

Range of validity

The range of validity of the model is assumed to encompass both NOC and AC. In fact, the experimental range of validity only covers NOC (i.e., equilibrium nontransient conditions). The application of the sorption isotherms to AC depends on the relaxation time to equilibrium, which is an open question. The experimental data for Sr were obtained for Sr concentrations above 30 $\mu\text{mol g}^{-1}$ and temperatures above 1027°C. For Cs, sorptivity was measured from 700 to 1300°C and the effects of irradiation on sorptivity were measured up to fluences of $4 \times 10^{25} \text{ n m}^{-2}$.

Assumptions

1. The sorption isotherm for Sr can be used to represent the sorption of all other common metallic FP except Cs, Ag, and Rb.
2. The effect of irradiation on the sorption of Cs is representative of the effect of irradiation on the sorption of the other metallic FP.
3. Considerations of the effects of neutron irradiation, oxidation of the fuel compact matrix material, and the mixed isotope effect should not significantly affect the reference sorption isotherms.

Table 6.5.1. Parameters for calculation of metallic fission product sorption in the fuel compact matrix material and uncertainties, Eqs. (6.5.1) through (6.5.6)

Element	A	B	D	E	d ₁	d ₂	$\sigma (\ln P_i)$		Reference	Data ^(a)
							P _F	P _H		
Cs	19.33	-4.729×10^4	1.518	4338	3.397	6.15×10^{-4}	0.65	0.87	(f)	Yes
Ag	19.3	-4.73×10^4	1.51	4340	3.40	6.15×10^{-4}	(b)	2.65	(g)	No
Rb	22.1	-4.47×10^4	4.53	68.0	3.40	6.15×10^{-4}	0.92	1.23	(h)	Graphite only
Sr	54.3 ^(c)	-1.49×10^5	-8.52	2.85×10^4	3.13	0.0	2.14	2.14	(i)	Yes
Ba, Ce, Eu, Sm	54.3 ^(c)	-1.49×10^5	-8.52	2.85×10^4	3.13	0.0	(d)	(d)	(h)	No
others ^(e)	54.3 ^(c)	-1.49×10^5	-8.52	2.85×10^4	3.13	0.0	(d)	(d)	(h)	No

(a) Indicates whether experimental data exists for sorption of the FP within the fuel compact.

(b) No value given by FDDM/F.

(c) Value recommended by FDDM/F; Myers et al. (1974) recommend a value of 42.8.

(d) The isotherm equations represent approximate upper limits for vapor pressure; the actual uncertainties are unknown.

(e) Zr, Nb, Mo, Tc, Pm, Nd, Pr, Y, Pd, Sn, La, Ru, Rh.

(f) Myers et al. (1979).

(g) FDDM/F.

(h) General Atomic (1977b).

(i) Myers et al. (1974).

4. The model can be applied to the transient conditions encountered during accident conditions.
5. The relative sorptivities of Rb and Cs in graphite can be used to approximate Rb sorptivity on the compact matrix material based on the experimental sorptivity of Cs on the matrix material.
6. For Sr, the transition to Henrian sorption behavior is assumed to occur at Sr concentrations below $22.8 \mu\text{mol (g matrix material)}^{-1}$ and the transition concentration is assumed to be independent of temperature (Myers et al, 1974).

Uncertainty

The uncertainty is given in terms of the standard deviation of the natural logarithm of the vapor pressure P_i , for $i = F$ (Freundlich regime) or $i = H$ (Henrian regime). Because the dependence of the uncertainty on the temperature is less significant than the dependence on the concentration, the temperature dependence is disregarded in the following formulation for the uncertainty (FDDM/F):

$$\sigma(\ln P_i) = \sqrt{d_{1i} + d_{2i} \ln C + d_{3i} (\ln C)^2}, \quad i = F, H, \quad (6.5.5)$$

$\sigma(\ln P_i)$ = standard deviation of $\ln P_i$, for $i = F, H$,
 C = concentration of sorbate species (mmol kg^{-1} of fuel compact material),
 d_{1i}, d_{2i}, d_{3i} = constants, for $i = F, H$ (dimensionless).

In fact, FDDM/F only provides nonzero values for d_{1i} , thus Eq. (6.5.5) reduces to:

$$\sigma(\ln P_i) = \sqrt{d_{1i}}, \quad i = F, H, \quad (6.5.6)$$

with no effective dependence on either concentration or temperature (perhaps due to limited data for the concentration dependence of the sorption isotherm). The value of the uncertainty for each metallic FP in Freundlich and Henrian regimes is given in Table 6.5.1, as recommended by FDDM/F. FDDM/F also states that the upper and lower bounds for the vapor pressure at one standard deviation can be calculated from:

$$\ln P_u = \ln P + \sqrt{\sigma^2(\ln P_F) + \sigma^2(\ln P_H)}, \quad (6.5.7)$$

$$\ln P_l = \ln P - \sqrt{\sigma^2(\ln P_F) + \sigma^2(\ln P_H)}, \quad (6.5.8)$$

P_u, P_l = upper and lower bounds for the vapor pressure P , respectively, Eq. (6.5.1), all other terms as defined previously.

MODEL CHRONOLOGY

The model parameters were derived from experimental data of Sr and Cs sorption in fuel compacts during the 1970s. No revision of the compact sorption model has occurred since then.

DISCUSSION

Model derivation

For background to the theory of sorption, one can refer to Myers et al. (1974). For implementation of the model equations into a computational format, one should refer to the description of the TRAFIC code by P. D. Smith (1978). In the model, the term C_t represents the transition concentration above which the Freundlich isotherm accurately portrays the sorption data, and below which the Henrian isotherm is appropriate to describe the data. Although the model is assumed to be applicable to transient AC simulations, the only available data is based on steady-state equilibria between the vapor phase and the solid surface.

Based on the experimental data for Cs sorption, no significant effect of fast neutron fluence on the sorption properties of the compact matrix material is apparent. This lack of irradiation effects probably results from the porous and disordered nature of the material at the start of irradiation, in contrast to the effects on the structural graphite (§6.6). Experimental data only exist for Cs and Sr sorption on fuel compact matrix material. No data exist for Rb sorption on the compact material, so the Rb sorption isotherm was derived from the data for Cs by analogy with their relative sorptivities on graphite.

A relevant point for AC modelling is made by General Atomic (1977b): "Under temperature transient conditions, the mobility of certain fission product metallic elements, which are normally immobile, must be considered. These elements are cerium, europium, samarium, zirconium ... There are no sorption data for these elements, and they are assumed to have the same sorption isotherms as strontium." This statement indicates a potential weakness in application of data representative of NOC to model AC behavior.

Model analysis

Myers (1988) summarizes the existing model and database for metallic FP sorption on the fuel compact matrix material. The large uncertainties for Sr exist because there are "no measurements in the Henrian region, the region of primary interest ... Measurements have shown that the sorptivity of Cs on matrix material is insensitive to the effects of neutron fluence; the assumption of a similar independence for Sr sorptivity also contributes to the larger uncertainty in the Sr case. For Ag, the uncertainties are very large and there are no reliable data. This uncertainty represents the second most important contribution to the overall uncertainty of Ag release from the core. Data to be obtained during the PIE of cell A of HFR-B1 and of the encapsulated samples in the forthcoming HRB-21 irradiation capsule will be the only source of information on the sorptivity of Ag on matrix material ...

The effect of oxidation on the sorptivity of the matrix material is unknown and will not be measured unless experiments beyond HRB-21 are completed. It is likely that the effect of oxidation on matrix material is small."

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Apparently no data relevant to this model have been obtained since the 1970s. Improvement of this model would be difficult without new data (such as that expected from HRB-21). One consideration relevant to model refinement would be whether oxidation of the compact matrix material would have significant effects on sorptivity of metallic FP.

DATABASE USED IN MODEL DEVELOPMENT

The experimental data for Sr sorption are presented in Fig. 6.5.1, taken from Myers et al. (1974). The experimental data for Cs sorption on irradiated and unirradiated fuel compact matrix material are presented in Fig. 6.5.2, taken from Myers et al. (1979). Refer to these references for additional experimental details.

6.6 METALLIC FISSION PRODUCT SORPTION IN GRAPHITE

function	This model uses sorption isotherms to calculate the partial pressure of FP metals in the gas phase from their concentration in graphite (or vice versa) as a function of temperature and fast neutron fluence.
present status	The current sorption isotherms are derived from data for both irradiated and unirradiated graphite and are acceptable for modelling purposes. A significant unknown is the effect of oxidation on the sorption isotherms, with an expected decrease in sorptivity (Myers, 1988).
model uncertainty	For graphite, the uncertainties associated with the sorption isotherms for Cs and Sr are relatively small, but the uncertainty for Ag is large due to lack of data. The uncertainty associated with the oxidation of graphite and its effect on sorption may be significant (Myers, 1988). Lack of data on the mixed isotope effect for multi-species sorption introduces additional uncertainty.
references	Myers et al. (1979); General Atomic (1977b); Myers (1981c)

Fig. 6.5.1. Isotherms for strontium on fuel compact matrix and graphite at 1500 K (from Myers et al., 1974).

Fig. 6.5.2. Comparison of sorption data for cesium sorption on irradiated and unirradiated fuel compact matrix material (M-205) (from Myers et al., 1979).

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

For unirradiated graphite, the same model equations apply to metallic FP sorption on graphite as apply to sorption on the fuel compact matrix material (§6.5). The partial vapor pressure, P , of gaseous FP species in equilibrium with the sorbed concentration is given by Myers (1981c):

$$P = P_F + P_H , \quad (6.6.1)$$

$$\ln P_F = \left(A + \frac{B}{T} \right) + \left(D + \frac{E}{T} \right) \ln C , \quad (6.6.2)$$

$$\ln P_H = \left(A + \frac{B}{T} \right) + \left(D - 1 + \frac{E}{T} \right) \ln C_t + \ln C , \quad (6.6.3)$$

$$\ln C_t = d_1 - d_2 T , \quad (6.6.4)$$

P_F	=	Freundlich isotherm vapor pressure (Pa),
P_H	=	Henrian isotherm vapor pressure (Pa),
T	=	temperature (K),
C	=	concentration of sorbed species [mmol (kg-graphite) ⁻¹],
C_t	=	transition concentration between the two isotherms (mmol kg ⁻¹),
A, D, d_1	=	constants (dimensionless),
B, E	=	constants (K),
d_2	=	constant (K ⁻¹).

The constants appropriate for several FP species are provided in Table 6.6.1 for sorption on unirradiated graphite and at the beginning of irradiation.

The sorptivity of the graphite will increase with exposure to fast neutron irradiation. Equations (6.6.1) to (6.6.4) remain valid, but a modified value of C must be used in these equations to represent the increased FP concentration on the graphite (General Atomic, 1977b; Myers et al., 1979):

$$C_F = \frac{C_{irr}}{1 + \gamma_F \cdot \gamma \cdot e^{a_F} \cdot C_{irr}^{b_F}} , \quad (6.6.5)$$

Table 6.6.1. Parameters for calculation of metallic fission product sorption on graphite and uncertainties, Eqs. (6.6.1) through (6.6.4)

Element	A	B	D	E	d_1	d_2	$\sigma^2 (\ln P_i)$		Reference	Data ^(a)
							P_F	P_H		
Cs	24.00	-35,730	-1.561	6,123	2.035	1.786×10^{-3}	0.79 ^(u) 1.48 ⁽ⁱ⁾	1.12 ^(u) 1.48 ⁽ⁱ⁾	(e)	H-451
Ag	24.0	-35,700	-1.56	6,120	2.04	1.79×10^{-3}	(b)	7.00	(f)	No
Ag	0.56	-1,571	-1.56				(b)	(b)	(g)	No
Rb	24.39	-30,949	0.938	2,664	2.04	1.79×10^{-3}	1.48	1.48	(h)	TS-688
Ba	19.37	-47,313	0.426	3,728	-2.12	0.0	1.48	1.48	(h)	H-451
Sr	19.38	-40,090	-0.324	4,088	-2.12	0.0	1.48	1.48	(h)	H-451
Ce, Eu, Sm	19.38	-40,090	-0.324	4,088	-2.12	0.0	(c)	(c)	(h)	No
Others ^(d)	19.38	-40,090	-0.324	4,088	-2.12	0.0	(c)	(c)	(h)	No

- (a) Indicates whether experimental data exists for sorption of the FP in graphite, and the type of graphite.
 (b) Value not given.
 (c) The isotherm equations represent approximate upper limits for vapor pressure; the actual uncertainties are unknown.
 (d) Zr, Nb, Mo, Tc, Pm, Nd, Pr, Y, Pd, Sn, La, Ru, Rh.
 (e) Myers et al. (1979).
 (f) FDDM/F.
 (g) Acharya (1987).
 (h) General Atomic (1977b).
 (i) Irradiated.
 (u) Unirradiated.

$$C_H = \frac{C_{irr}}{1 + \gamma_H \cdot f \cdot \left(\frac{10^4}{T}\right)^{\alpha_H} \cdot \exp\left[-\beta_H \left(\frac{10^4}{T}\right)\right]}, \quad (6.6.6)$$

$$\gamma_i = \frac{\delta_i}{1 + e^{\epsilon(T-1423)}}, \quad i = F, H, \quad (6.6.7)$$

$$\alpha_F = \left(\frac{\zeta}{T}\right) - \left(\frac{\theta}{T^2}\right), \quad (6.6.8)$$

$$\beta_F = \kappa - \left(\frac{\lambda}{T}\right) + \left(\frac{\mu}{T^2}\right), \quad (6.6.9)$$

- C_i = sorbate concentration appropriate to the isotherm i , with $i = F$ for the Freundlich regime and $i = H$ for the Henrian regime (mmol per kg of graphite),
 C_{irr} = concentration of sorbate on the irradiated graphite (mmol per kg of graphite),
 γ = fast neutron fluence [n m^{-2} , ($E > 29 \text{ fJ}$)_{HTGR}],
 T = temperature (K),
 γ_i = annealing factor (dimensionless),
 $\alpha_H, \delta_i, \kappa$ = constants, for $i = F, H$ (dimensionless),
 β_H, ζ, λ = constants (K),
 θ, μ = constants (K^2),
 ϵ = constant (K^{-1}).

Values of the model parameters for irradiated graphite are given in Table 6.6.2. The values calculated for C_F and C_H above are applied to Eqs. (6.6.2) and (6.6.3), respectively, to determine the total equilibrium vapor pressure of the FP species.

Range of validity

The model is applied to both NOC and AC situations. However, the experimental data cover only equilibrium conditions, with no data available to interpret transient conditions. In addition, no data is available to provide information on the effect of oxidizing conditions on the sorption isotherms. Experimentally, sorption of Cs on unirradiated H-451 graphite has been measured for temperatures from 700 to 1100°C and concentrations from approximately 0.3 to 7 mmol Cs per kg graphite. Data for Cs sorption on irradiated H-451 graphite has been obtained for neutron fluences up to $3.4 \times 10^{25} \text{ n m}^{-2}$ at temperatures from

Table 6.6.2. Parameters for calculation of metallic fission product sorption on irradiated graphite, Eqs. (6.6.5) through (6.6.9)

Element	Henrian regime			Freundlich regime							Ref.	Data ^(a)
	α_H	β_H	δ_H	ϵ	δ_F	ζ	θ	κ	λ	μ		
Cs	17	2.584	1.025×10^{-31}	0.04394	6.55×10^{-29}	21,830	9.87×10^6	3.663	11,400 ^(b)	$-4.937 \times 10^{6(c)}$	(e)	H-451
Ag	17	2.58	1.03×10^{-31}	0.0439	6.55×10^{-29}	21,800	9.87×10^6	3.66	11,100	4.94×10^6	(f)	No
Rb	17	2.58	1.025×10^{-31}	0.0439	6.55×10^{-29}	21,830	9.87×10^6	3.663	11,140	4.937×10^6	(g)	No
Sr	13	1.745	1.434×10^{-31}	0.0439	5.133×10^{-28}	13,890	6.094×10^6	-0.976	-3,273	-4.358×10^6	(g)	H-451
Ba, Ce, Eu, Sm	13	1.745	1.434×10^{-31}	0.0439	5.133×10^{-28}	13,890	6.094×10^6	-0.976	-3,273	-4.358×10^6	(g)	No
others ^(d)	13	1.745	1.434×10^{-31}	0.0439	5.133×10^{-28}	13,890	6.094×10^6	-0.976	-3,273	-4.358×10^6	(g)	No

(a) Indicates whether experimental data exists for sorption of the FP in irradiated graphite, and the type of graphite.

(b) Value may be in error: FDDM/F suggests a value of 11,100 and General Atomic (1977b) suggests a value of 11,140.

(c) Value may be in error: FDDM/F and General Atomic (1977b) suggest a value of $+4.94 \times 10^6$.

(d) Zr, Nb, Mo, Tc, Pm, Nd, Pr, Y, Pd, Sn, La, Ru, Rh.

(e) Myers et al. (1979).

(f) FDDM/F.

(g) General Atomic (1977b).

700 to 1300°C and concentrations from 0.1 to 10 mmol kg⁻¹. Data for Sr sorption on unirradiated H-451 graphite were obtained for temperatures from 800 to 1600°C and Sr concentrations of approximately 0.15 to nearly 100 mmol kg⁻¹. Data for Sr sorption on irradiated H-451 graphite were obtained for temperatures from 1100 to 1600°C and concentrations from approximately 1.3 to 50 mmol kg⁻¹.

Assumptions

1. The sorption of Ag and Rb is similar to that of Cs, while the sorption of Ba, Ce, Eu, Sm, and other metallic FP is similar to that of Sr.
2. The model obtained under conditions corresponding to NOC can also be applied as an AC model.
3. Effects due to oxidation or the presence of mixed isotopes are insignificant.
4. No chemical reaction of the FP or other nonsorptive phenomena are significant.

Uncertainty

The uncertainty equations and comments in §6.5 for sorption on the fuel compact material are also applicable to sorption on graphite. The values for uncertainty given in FDDM/F for sorption on graphite are constants, without dependence on either temperature or concentration. Although the uncertainty is expressed as the standard deviation, σ , values for σ^2 are reported in Table 6.6.1 for consistency between FDDM/F and Myers et al. (1979).

MODEL CHRONOLOGY

The model for metallic FP sorption on irradiated and unirradiated graphite was developed in the 1970s and presented by General Atomic (1977b). The current model has not been revised from that presented by General Atomic and used by Myers et al. (1979).

DISCUSSION

Model derivation

Myers et al. (1985c) discuss the "annealing" model for sorptivity represented by Eqs. (6.6.5) through (6.6.9), in which the "irradiation damage in graphite is removed by annealing at temperatures above 1350 K." According to FDDM/F, the value of 1423 in Eq. (6.6.7) represents the "temperature [K] at which half the sorptivity increase resulting from irradiation has been nullified by annealing."

Although FDDM/F applies the model parameters for Cs to the sorption of Ag, Acharya (1987) recommended other values for the model parameters for Ag on unirradiated graphite as indicated in Table 6.6.1. The derivation of model parameters for Ag and the assumptions used in the derivation are unknown. FDDM/F apparently assumes that sorption of Ag is similar to sorption of Cs.

Design Data Needs

CEGA (1990) comments on the existing data relevant to this model in DDN 11.48. "The correlations for Cs, Sr, and Pu sorptivities on graphite are derived largely from measurements on unirradiated graphites, but there are limited data for Cs and Sr on irradiated graphite and irradiated fuel compact matrix material. The available data indicate that the transport of Cs, Sr, and Ag in graphite is strongly affected by neutron irradiation. There are limited laboratory data that indicate the vapor pressure of Cs over graphite increases in the presence of coolant impurities and as a consequence of partial graphite oxidation. Ag transport through graphite may be reduced by elevated system pressures."

In DDN 11.57 the underprediction of experimental Cs release is commented upon, and "there is strong circumstantial evidence suggesting that the transport across the fuel compact/fuel element gap and the transport in the graphite web are not properly modelled." However, DDN 11.57 does not comment whether the effects of sorptivity on transport may be a concern here.

General comments

Myers (1988) summarizes the current state of the models for metallic FP sorption on graphite. "The sorption of fission products on graphite is dependent on the type and structure of the graphite, the temperature, extent of irradiation damage (mainly for highly graphitized graphites), state of oxidation and the partial pressure of the sorbate (an expected decrease in sorptivity), the current sorption isotherms for Cs and Sr account for the dependencies; the associated uncertainties are relatively small and unlikely to be reduced. However, the uncertainty associated with oxidation and in fact with knowledge of the state of oxidation of the core graphite increases the total uncertainty to an unknown but presumably significant extent. Experiments in capsule HRB-21 are designed to obtain information on the effect of oxidation on sorptivity ... The uncertainty in the sorptivity of Ag is quite large for lack of data. The uncertainty is expected to be reduced significantly ... when the HRB-21 sorptivity experiments are completed. Additional data on the effect of neutron fluence on sorptivity are anticipated following completion of HRB-21 and HFR-B1 ..."

Additional evidence that sorption isotherms may not be the only consideration in FP release from graphite is provided in a recent Foreign Trip Report by B. F. Myers (1991), in which he comments on KFA work on iodine sorption in graphite. In reacting graphite powder with iodine vapor, after a time the activity of the iodine sorbed on the graphite began to decrease although the iodine partial pressure was held constant. This change in sorbate concentration was attributed to reaction of the iodine with the metallic impurities in the graphite to form volatile metallic iodides. The initial sorption on the graphite was reported to be 700 to 1000 nmol of iodine per kg of graphite. Use of very pure graphite reduced the sorptivity to the range of 1 to 2 nmol per kg of graphite, nearly three orders of magnitude difference from that of impure graphite. The potential of this nonsorptive release mechanism could be significant if verified by additional experiments.

The proceedings of the conference edited by Hoinkis (1983) contains much information on the phenomena relevant to FP behavior in graphite and should be referred to for additional information.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

If relevant data could be obtained, the significance of oxidation of the graphite on sorption isotherms should be determined. The results from the HRB-21 and HFR-B1 experiments should be evaluated for their relevance to this model, as suggested by Myers (1988). Additional information on the release of metallic iodides due to graphite impurities should be obtained if possible. Whether equilibrium sorption models can be accurately applied to model transient conditions should be evaluated.

The conclusion of DDN 11.57 that transport from fuel compact through graphite may not be accurately modelled is a cause for concern. The impact of these uncertainties on release estimates should be evaluated to determine whether significant effort in improved understanding of these phenomena is needed.

DATABASE USED IN MODEL DEVELOPMENT

Myers et al. (1974) presented data for Sr sorption on nonreference graphites, mostly H-327. General Atomic (1977b) presented additional data for Sr sorption on irradiated and unirradiated H-451 graphite. Figure 6.6.1 compared the data for Sr sorption on H-451 graphite with the isotherms for H-327 graphite. Figure 6.6.2 shows the Sr sorption data on irradiated H-451 graphite, and Fig. 6.6.3 compares the sorption isotherms of Sr and Ba on unirradiated H-451 graphite. Myers et al. (1979) analyzed the sorption data for Cs on irradiated and unirradiated H-451 graphite. Figure 6.6.4 shows the Cs sorption data for unirradiated H-451 graphite, Fig. 6.6.5 shows the data for irradiated H-451 graphite, and Fig. 6.6.6 compares the sorptivities for irradiated and unirradiated graphite, showing the significant increase of sorptivity with irradiation. Details of the experiments and the data shown in Figs. 6.6.1 through 6.6.6 can be found in General Atomic (1977b) and Myers et al. (1979).

Fig. 6.6.1. Comparison of strontium data for H-451 graphite with isotherms for H-327 graphite (from General Atomic, 1977b).

Fig. 6.6.2. Data and least-squares fit for strontium sorption on irradiated H-451 graphite (from General Atomic, 1977b).

Fig. 6.6.3. Comparison of strontium and barium isotherms for sorption on H-451 graphite (unirradiated) (from General Atomic, 1977b).

Fig. 6.6.4. Sorption isotherms for cesium on unirradiated H-451 graphite (from Myers et al., 1979).

Fig. 6.6.5. Sorption isotherms for cesium on H-451 graphite irradiated to a fluence of $3.4 \times 10^{25} \text{ n m}^{-2}$ at 980°C (from Myers et al., 1979).

Fig. 6.6.6. Comparison of sorptivities for irradiated and unirradiated H-451 graphite (C_i , C_u = sorbate concentrations for irradiated and unirradiated graphites, respectively; fluence = $3.4 \times 10^{25} \text{ n m}^{-2}$) (from Myers et al., 1979).

6.7 METALLIC FISSION PRODUCT TRANSPORT ACROSS THE COMPACT/GRAPHITE INTERFACE

function	Given the metallic FP concentration at the compact surface, this model uses the sorption isotherms for compact and graphite to calculate the FP concentration at the graphite surface.
present status	The existing model is based on the sorption isotherms for the fuel compact and graphite and has been shown to provide reasonable estimates of transport across the interface (Myers et al., 1985c), although CEGA (1990) is less confident. The model is limited by the accuracy of the sorption isotherms used for calculations.
model uncertainty	This model incorporates the uncertainties in the compact and graphite sorption isotherms (§6.5 and 6.6) and includes additional uncertainties arising from the temperature drop across the interface from surface effects of sorption by graphite (Myers et al., 1985c) and from the possibility of transverse flow along the fuel compact surface (Myers, 1988).
references	Alberstein et al. (1975); Myers et al. (1985c); General Atomic (1976d)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

Given a known temperature and concentration of metallic FP at the fuel compact surface, one can calculate the equilibrium vapor pressure of the FP at the compact surface. Equations (6.5.1) to (6.5.4) of §6.5 are used for this calculation and will not be repeated here.

Knowing the equilibrium pressure at the compact/graphite interface and the temperature distribution across the interface, the FP concentration at the graphite surface, C , can be calculated from the isotherm equations for sorption on graphite (§6.6). The following equation can be derived from Eqs. (6.6.1) to (6.6.3), but the exact solution in terms of the concentration may require numerical evaluation:

$$P = e^x (C^y + C_i^{y-1} C) \quad , \quad (6.7.1)$$

$$x = A + \frac{B}{T} \quad , \quad (6.7.2)$$

$$y = D + \frac{E}{T} , \quad (6.7.3)$$

with the transition concentration, C_t , given by:

$$\ln C_t = d_1 - d_2 T , \quad (6.7.4)$$

- P = equilibrium FP vapor pressure at the compact/graphite interface (Pa),
 C = FP concentration at the graphite surface region [mmol (kg-graphite)⁻¹],
 C_t = transition concentration between the two isotherms [mmol (kg-graphite)⁻¹],
 T = temperature at the graphite surface (K),
 A, D, d_1 = constants (dimensionless),
 B, E = constants (K),
 d_2 = constant (K⁻¹).

The constants required for these calculations are listed in §6.5 and §6.6, Tables 6.5.1, 6.6.1, and 6.6.2. P. D. Smith (1978) describes the numerical solution of Eq. (6.7.1) within the TRAFIC code.

An approximate analytical solution, accurate when the sorbate concentration differs significantly from the transition concentration, can be calculated by the following sequence of calculations (Alberstein et al., 1975).

1. Calculate the transition concentration using Eq. (6.7.4).
2. Calculate the transition pressure, P_t , corresponding to C_t :

$$\ln P_t = \left(A + \frac{B}{T} \right) + \left(D + \frac{E}{T} \right) \ln C_t . \quad (6.7.5)$$

3. Freundlich regime: If $P > P_t$ (or alternatively $C > C_t$), the FP concentration on the graphite surface is approximated from Eq. (6.6.2):

$$\ln C = \left[D + \frac{E}{T} \right]^{-1} \left[\ln P - \left(A + \frac{B}{T} \right) \right] . \quad (6.7.6)$$

4. Henrian regime: If $P < P_t$ (or $C < C_t$), the FP concentration on the graphite surface is approximated from Eq. (6.6.3):

$$\ln C = \ln P_H - \left(A + \frac{B}{T} \right) + \left(D - 1 + \frac{E}{T} \right) \ln C_t . \quad (6.7.7)$$

During irradiation, the concentration calculated using Eqs. (6.7.1), (6.7.5), or (6.7.6) must be modified to represent the concentration sorbed on irradiated graphite. For this,

Eq. (6.6.5) is used if the pressure is in the Freundlich sorption regime or Eq. (6.6.6) is used if in the Henrian regime (§6.6).

The resulting concentration distribution between compact and graphite is often defined in terms of a temperature-dependent ratio called the partition coefficient, ϕ :

$$\phi = \frac{\text{concentration of FP on fuel compact surface}}{\text{concentration of FP on graphite surface}} \quad (6.7.8)$$

Calculations of FP distributions normally determine ϕ from the sorption isotherms rather than using a specified value of ϕ under given isothermal conditions. Any specified value of ϕ needs to take into account the temperature drop across the compact/graphite gap and the relative volumes of the contiguous compact and graphite regions (Myers et al., 1979).

The graphite surface concentration is subsequently used as a source term to the diffusion equations for calculation of FP transport through the graphite block (Alberstein et al., 1975), in conjunction with the diffusion parameters listed in §6.4.

Range of validity

The range of experimental and model validity is based on the sorption isotherms used in calculations. Reference should be made to the statements in §6.5 and §6.6.

Assumptions

Most of the following assumptions are taken from Alberstein et al. (1975).

1. The concentration of metallic FP is uniform throughout the compact (§6.3).
2. Transport of FP atoms within the compact matrix material is rapid with respect to diffusion in graphite.
3. The FP vapor pressure is uniform across the compact/graphite gap.
4. The vapor pressure is accurately represented by the sorption isotherms for the fuel compact material, using compact surface concentration and temperature as input.
5. The concentration at the graphite surface is accurately represented by the sorption isotherms for graphite, using the equilibrium vapor pressure and the graphite surface temperature as input.
6. Transport across the interface is not limited by kinetic considerations (e.g., by atomic evaporation from the compact surface).
7. The temperature profile across the compact/graphite interface can be reasonably approximated.
8. The change of gap width during irradiation is not significant with respect to the transport processes (i.e., kinetic effects in gas-phase transport are not significant).

Uncertainty

The uncertainty of this model has not been quantified. Refer to "model uncertainty" above for a qualitative discussion.

MODEL CHRONOLOGY

No model specific to this interface transport is presented in FDDM/F, as this model is subsumed by the combined sorption models for compact and graphite. This model was presented by Alberstein et al. (1975) and updated by P. D. Smith (1978) as discussed above.

DISCUSSION

Barthold (1993) points out that the assumptions stated above are consistent with the assumption that the temperature distribution in the compact is axisymmetric. However, very large radial gradients exist in the reactor which change with time, and the effect of asymmetries in temperature distributions on transport across the gap should be assessed.

CEGA (1990) comments on this model in the discussion of DDN 11.57. "The validity of the methods for predicting fission metal release during normal operation have been assessed by applying them to predict the observed metal release in operating HTGRs ... and in irradiation capsules and in-pile loops ... In general, the releases of fission metals were underpredicted by factors of several and, in some cases, by more than an order of magnitude. The cause of the underpredictions is ambiguous ... however, there is strong circumstantial evidence suggesting that the transport across the fuel compact/fuel element gap and the transport in the graphite web are not properly modelled." CEGA (1990) does not discuss further the suspected problems in the compact/graphite interface transport model.

Transverse flow

Myers (1988) mentions the possibility of transverse flow along the interface in perturbing the steady-state FP distribution across the gap which this model represents, and indicates that studies of this flow have been conducted. Alberstein et al. (1975) also mention this possibility as a potential release pathway, although they consider this transport pathway to be of secondary importance, and state: "Transverse flow refers to convection of the metallic fission product in the helium which circulates through the graphite web and the fuel rod - graphite gap. This transport mechanism is significant only for the very volatile species at high concentrations in the graphite." Neither Myers nor Alberstein et al. discuss this further, and references for the studies referred to by Myers (1988) have not been located.

Early studies

Figure 6.7.1, taken from Alberstein et al. (1975), shows the typical variation in sorption isotherms between fuel compact and graphite. The compact tends to be significantly more

Fig. 6.7.1. Strontium sorption isotherms for fuel compact matrix material and H-327 graphite at 1000°C (from Alberstein et al., 1975).

sorptive of metallic FP. As a result, for a given equilibrium vapor pressure across the gap the compact surface concentration will tend to be significantly larger than that of the graphite, and the partition coefficient defined by Eq. (6.7.8) will be greater than one.

As of 1976, only one set of measurements of Cs sorption on reference (M-205) fuel compact matrix material was reported (General Atomic, 1976d). This data was used to calculate approximate partition coefficients with H-327 graphite, as listed in Table 6.7.1. For these calculations, an assumption was made that the partition coefficient is independent of sorbate concentration and temperature. No reference or additional information was provided by General Atomic (1976d) for this data.

Capsule R2-K13: Myers et al.

Detailed data on fission product distributions between the fuel compact and the H-451 graphite body was obtained from irradiation capsule R2-K13 (Myers et al., 1985c), from which partition coefficients were calculated for Cs, Ag, and Mn isotopes. The experimental partition coefficients for ^{134}Cs and ^{137}Cs were then compared to calculated coefficients based on the model for graphite sorption presented in §6.6 (Myers et al., 1979). Calculations were performed using the models for both irradiated and unirradiated graphite. The comparison of the data to the models is shown in Fig. 6.7.2. The "irradiation-nonannealing" calculation in Fig. 6.7.2 did not employ the annealing coefficient of Eq. 6.6.7. Nominal irradiation temperatures were 1200°C for cell 2 and 1000°C for cell 3, with the fast fluence approximately $7.6 \times 10^{25} \text{ n m}^{-2} (E > 29 \text{ fJ})_{\text{HTGR}}$.

The agreement between model and experiment is quite good when the effects of irradiation are considered in the model. The horizontal bars of Fig. 6.7.2 represent the uncertainty in the temperature at the compact/graphite interface. A variation of 40 K in the temperature drop would change the partition coefficient by approximately a factor of two (Myers et al., 1985c). Figure 6.7.3 shows the effect of this uncertainty in temperature drop on the calculated partition coefficients. Comparison of Figs. 6.7.1 and 6.7.2 indicates comparable values of partition coefficients for unirradiated graphites in the two experiments.

These experimental partition coefficients and data upon which they are based are presented below in the "Database" section. Several practical comments and observations are provided by Myers et al. (1985c):

1. The observed Cs concentration within the compact matrix material is well within the Henrian regime of vapor pressures.
2. The graphite sorptivity is known to be much greater at the surface, to a depth of perhaps several hundred micrometers (Myers et al., 1985c), attributed to the machining of the surface and the presence of graphite dust with large surface areas. This enhanced sorptivity results in a steep initial FP concentration profile at the surface, which then declines more gradually into the bulk (Myers, 1983a).

Table 6.7.1. Analysis of sorption ratio data for cesium: sorption ratios relative to H-327 graphite (from General Atomic, 1976d)

Material	Binder ^(a)	T(°C)	Matrix Concentration (μmole/g)	φ	Measurement Means ^(b)
M-205	P. pitch	1200	Isotherm	18	MS
M-205	P. pitch	1200	26	10	Anneal
FSV ^(c)	C. pitch	1200	21	15	Anneal
FSV ^(c)	C. pitch	1200	33	12	Anneal
FSV ^(c)	C. pitch	1200	38	14	Anneal
M-155	C. pitch	1200	24	17	Anneal
M-156	C. pitch	1200	23	16	Anneal
M-266	P. pitch	1200	27	10	Anneal
M-259	P. pitch	1200	39	11	Anneal
A-240	P. pitch	1200	46	12	Anneal
B-018	P. pitch	1200	10	21	Anneal
M-224	C. pitch	1200	30	13	Anneal
Calcined petroleum coke	C. pitch	1202	0.98	20,10	FTE
Calcined petroleum coke	C. pitch	963	3.8	10,20	FTE
Calcined petroleum coke	C. pitch	1057	3.8	5,10	FTE
Calcined petroleum coke	C. pitch	954	0.02	14,11	FTE-P

(a) P. pitch = petroleum pitch; C. pitch = coal tar pitch.

(b) MS = mass spectrometer; FTE = Peach Bottom fuel test element diffusion sample; FTE-P = Peach Bottom fuel test element particle sample.

(c) FSV = Fort St. Vrain.

Fig. 6.7.2. Comparison of calculated and measured partition coefficients for ^{134}Cs and ^{137}Cs in cells 2 and 3 of capsule R2-K13 (from Myers et al., 1985c).

Model: ——— { IA = ϕ curve for $\Delta T = 0$ for irradiated-annealing H-451 graphite
 i = ϕ curve for $\Delta T = 40\text{K}$ for irradiated-annealing H-451 graphite
 o = ϕ curve for $\Delta T = 90\text{K}$ for irradiated-annealing H-451 graphite

i = inner location (between fuel rod holes)
 o = outer location (between fuel rod hole and outer graphite surface)

Measure-ments: ——— ϕ for Cs137 with temperature uncertainty range
 ——— ϕ for Cs134 with temperature uncertainty range
 ——— ϕ for Cs137 using unreliable extrapolations
 ——— ϕ for Cs134 using unreliable extrapolations

Fig. 6.7.3. The effect of the fuel compact-graphite temperature drop on the comparison of partition coefficients for ^{134}Cs and ^{137}Cs in cells 2 and 3 of capsule R2-K13 (from Myers et al., 1985c).

Capsule R2-K13: Acharya

Acharya (1987) used the COPAR code for FP release from particles in conjunction with the TRAMP code to calculate the fractional release of ^{137}Cs and $^{110\text{m}}\text{Ag}$ from cells 2 and 3 of the R2-K13 capsule. The calculations also provided concentration profiles across the fuel compact and graphite body, from which approximate partition coefficients at the compact/graphite interfaces could be determined. The results are shown and compared to the measured concentration profiles in Figs. 6.7.4 through 6.7.7. The partition coefficient is determined by the ratio of the FP concentration on either side of the discontinuity at the interface. For ^{137}Cs , Acharya concludes for cell 2 (Fig. 6.7.4) that the "measured and calculated partition coefficients are almost equal ...," although this statement appears to be more accurate for cell 3 (Fig. 6.7.5).

Agreement with experiment was poorer for $^{110\text{m}}\text{Ag}$ partition coefficients. Figure 6.7.6 shows that, for cell 2, the "measured and predicted partition coefficients are significantly different. The measured profile in the graphite displays a steep concentration gradient indicating that the transport in graphite was not properly modeled. The diffusion coefficient for silver in graphite appears to be at fault in this case ... [however,] the material property data base for silver, i.e., diffusion coefficients and sorption isotherms were based on a meager data base." For cell 3 (Fig. 6.7.7) the "measured and predicted partition coefficients are significantly different indicating problems with the sorption isotherms used in the analysis." Unfortunately, Acharya (1987) does not discuss the modeling of the fuel compact, but from the reference to FDDM/E one must assume that models similar to those of §6.5 were employed for sorption on the compact. Although the isotherm for sorption on graphite is presented, no terms for the effects of irradiation are discussed and thus may not have been included in the analysis.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Myers et al. (1985c) have shown the model results to be reasonable, therefore further model development should focus on the sorption isotherms used as input to the model, as discussed in §6.5 and §6.6. As one example, the mixed isotope effect might be considered for inclusion in the model. The negative commentary on this model by CEGA (1990) is troubling; but as details are not provided, the source of the uncertainty cannot be evaluated.

Acharya's (1987) results for Ag are not very good, indicating the sorption model used may not be accurate. According to Myers (1983a) the diffusion of Sr, Ba, and Eu in graphite are adequately described by classical Fickian diffusion but that the diffusion of Ag was better described by a diffusion-sorption model in AGL5 graphite. As the same model is used for diffusion of all metallic FP in graphite (§6.4), a different model for Ag diffusion in graphite and fuel compact might be considered in light of the poor predictions of Figs. 6.7.6 and 6.7.7.

Myers (1988) states that data exist related to transverse flow within the compact/graphite gap. If the source of this data is determined, this release pathway could be evaluated to determine whether or not it is significant.

Fig. 6.7.4. Capsule R2-K13 cell 2 analysis: ^{137}Cs concentration profile (from Acharya, 1987).

Fig. 6.7.5. Capsule R2-K13 cell 3 analysis: ^{137}Cs concentration profile (from Acharya, 1987).

Fig. 6.7.6. Capsule R2-K13 cell 2 analysis: ^{110m}Ag concentration profile (from Acharya, 1987).

Fig. 6.7.7. Capsule R2-K13 cell 3 analysis: ^{110m}Ag concentration profile (from Acharya, 1987).

Barthold (1993) recommends that the effect of asymmetries in thermal gradients on FP transport across the gap should be evaluated.

The potential effects of oxidation on sorption, diffusion, and transport across the interface have apparently received little attention. Some consideration might be justified in the event of water ingress during AC and the subsequent effects on FP transport.

DATABASE USED IN MODEL DEVELOPMENT

The database appropriate to the sorption of metallic fission products in the fuel compact and graphite (§6.5 and 6.6) is also appropriate to this section and should be referred to.

The experimental partition coefficients obtained from the R2-K13 capsule for Cs were presented in Fig. 6.7.2. These partition coefficients for ^{134}Cs and ^{137}Cs , plus those of $^{110\text{m}}\text{Ag}$ and ^{54}Mn , are tabulated in Table 6.7.2. The measured concentration profiles from which the partition coefficients were determined are shown in Figs. 6.7.8 through 6.7.11. The references to inside and outside profiles refer to the spatial relationship of the compact/graphite interface to the external surface of the graphite fuel body, as can be seen from the diagram depicting the locations of graphite samples for FP concentration determinations (Fig. 6.7.12). Table 6.7.3 gives the raw data for these FP concentrations in graphite, and Table 6.7.4 gives the corresponding data for the fuel compact matrix material.

6.8 METALLIC FISSION PRODUCT TRANSPORT ACROSS THE GRAPHITE/COOLANT INTERFACE

function	This model calculates the metallic FP mass flux from the graphite to the coolant given the FP concentration gradient across the graphite/coolant boundary layer, the convective mass transfer coefficient, and the temperature.
present status	The model is based on existing equations for mass transport across a solid/gas interface and assumes the distribution between surface and gas is based on the sorption isotherms for graphite. The actual distribution of the FP between surface and gas (i.e., equilibrium or nonequilibrium) remains a question (Myers, 1988).
model uncertainty	The uncertainty of the existing model is based on the uncertainty of the graphite sorption isotherms (see §6.6). Additional uncertainty exists if the FP are not released to the coolant via single-atom transport mechanisms (i.e., molecular transport, dust effects, etc. as discussed in §8).
references	P. D. Smith (1978); Alberstein et al. (1975); Acharya (1987); Myers (1988)

Table 6.7.2. Measured and predicted partition coefficients (ϕ) at the fuel compact - graphite boundary for cell 2 and cell 3 of capsule R2-K13 (from Myers et al., 1985c)

$$\phi = \frac{\text{Concentration in fuel rod at surface}}{\text{Concentration in graphite at surface}}$$

Isotope	Cell 2			Cell 3		
	Measured ϕ			Measured ϕ		
	Inner	Outer	Mean	Inner	Outer	Mean
Cs-134	1.15	0.52	0.84	0.30 ^(a)	0.74	0.52
Cs-137	1.5	0.72	1.1	0.62 ^(a)	1.4	1.0
Ag-110m	0.81	0.06	0.44	0.57 ^(a)	1.7 ^(a)	1.1
Mn-54	0.06	0.21	0.14	2.3 ^(a)	(b)	2.3

(a) Unreliable extrapolation.

(b) No measurements close enough to fuel rod boundary.

Fig. 6.7.8. Fuel compact and graphite fission product concentration profiles for cell 2 of capsule R2-K13 (inside profile) (from Myers et al., 1985c).

Fig. 6.7.9. Fuel compact and graphite fission product concentration profiles for cell 2 of capsule R2-K13 (outside profile) (from Myers et al., 1985c).

Fig. 6.7.10. Fuel compact and graphite fission product concentration profiles for cell 3 of capsule R2-K13 (inside profile) (from Myers et al., 1985c).

Fig. 6.7.11. Fuel compact and graphite fission product concentration profiles for cell 3 of capsule R2-K13 (outside profiles) (from Myers et al., 1985c).

Table 6.7.3. Gamma spectrometry and weighing of drilling samples (discs) from graphite bodies position 2-B-1 (cell 2) and 3-B-2 (cell 3) of capsule R2-K13 (from Myers et al., 1985c)

Sample Designation	Weight (g)	Atoms per 1 g sample weight				
		Mn 54	Ru 106	Ag 110m	Cs 134	Cs 137
<u>Cell 2:</u>						
<u>Position 2-B1:</u>						
Disc No. 1, inner	0.201	1.8-13	1.2-13	1.2-14	3.0-14	2.2-15
• 2, •	0.195	6.4-11	-	2.0-14	2.7-14	1.9-15
• 3, •	0.169	5.9-11	-	1.7-14	2.2-14	1.6-15
• 4, •	0.162	-	-	1.1-14	2.0-14	1.5-15
• 5, •	0.158	6.5-11	2.1-13	5.2-13	1.6-14	1.2-15
• 6, •	0.155	6.0-11	3.6-12	2.2-13	1.3-14	9.7-14
• 7, •	0.209	1.9-12	-	5.3-12	8.0-13	5.8-14
Disc No. 1, outer	0.104	-	-	1.2-15	7.3-14	5.5-15
• 2, •	0.188	-	-	1.1-15	7.1-14	5.2-15
• 3, •	0.184	-	-	2.9-14	5.2-14	3.9-15
• 4, •	0.180	-	-	6.8-13	4.3-14	3.2-15
• 5, •	0.189	6.1-11	-	7.2-12	3.0-14	2.2-15
• 6, •	0.271	4.2-11	-	-	1.2-14	9.2-14
<u>Cell 3:</u>						
<u>Position 3-B2:</u>						
Disc No. 1, inner	0.122	1.7-12	-	1.6-13	1.2-15	8.2-15
• 2, •	0.175	4.6-11	-	-	3.4-14	2.4-15
• 3, •	0.173	3.1-11	-	-	2.4-14	1.7-15
• 4, •	0.160	3.7-11	4.2-12	-	1.9-14	1.3-15
• 5, •	0.166	-	-	-	1.5-14	1.0-15
• 6, •	0.188	3.4-11	-	-	9.7-13	6.4-14
• 7, •	0.218	5.1-11	-	4.4-11	4.1-13	2.7-14
Disc No. 1, outer	0.146	-	-	5.8-12	8.8-14	6.1-15
• 2, •	0.148	4.8-11	-	-	6.1-14	4.3-15
• 3, •	0.167	-	-	-	4.5-14	3.1-15
• 4, •	0.192	3.1-11	-	-	1.3-14	9.0-14
• 5, •	0.158	-	-	-	2.3-14	1.8-15
• 6, •	0.240	1.3-12	-	-	3.6-13	2.7-14

• Samples probably mixed up
- cannot be evaluated

Table 6.7.4. Results of gamma spectrometric analyses from fuel compact matrix pieces of capsule R2-K13 (from Myers et al., 1985c)

Fuel Body	2		3	
Rod No.	2-B-1		3-B-2	
Sample Weight (g)	0.030		0.019	
Inventories ^(a)	Atoms/ g Graphite	mmol/ kg ^(b)	Atoms/ g Graphite	mmol/ kg ^(b)
Mn-54	6.0E+12 ^(c)	1.0E-5	7.4E+12	1.2E-5
Zr-95	8.8E+12	1.5E-5	1.2E+13	2.0E-5
Ru-106	3.7E+13	6.1E-5	4.1E+13	6.8E-5
Ag-110m	7.3E+13	1.2E-4	1.7E+13	2.8E-5
Cs-134	4.0E+14	6.6E-4	7.4E+14	1.2E-3
Cs-137	4.0E+15	6.6E-3	1.0E+16	1.7E-2
Eu-154	2.5E+14	4.2E-5	5.3E+13	8.8E-5

(a) Inventories calculated back to end of irradiation.

(b) This unit is convenient for the discussion of sorptivity in Section 5.6.1.

(c) 6.0E+12 denotes 6.0×10^{12} .

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The transport of metallic FP atoms across the graphite/coolant interface at the coolant hole is given by a mass transport equation which relates the mass flux into the coolant hole to the concentration gradient across the boundary layer and the FP desorption behavior at the graphite surface (Alberstein et al., 1975; P. D. Smith, 1978). The general mass flux equation is given by:

$$J_L = H (C_a - C_-) , \quad (6.8.1)$$

- J_L = mass flux of metallic FP atoms ($\mu\text{mol cm}^{-2} \text{ s}^{-1}$),
- H = convective mass transfer coefficient (cm s^{-1}),
- C_a = FP concentration in the coolant inside the boundary layer ($\mu\text{mol cm}^{-3}$),
- C_- = FP concentration in the coolant free stream ($\mu\text{mol cm}^{-3}$).

Applying the appropriate assumptions, the following equation is obtained:

$$J_L = H \left(\frac{10^6 P}{R T_L} - C_- \right) , \quad (6.8.2)$$

- P = FP vapor pressure in equilibrium with the coolant hole surface concentration (atm),
- R = ideal gas constant ($82.06 \text{ cm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$),
- T_L = graphite wall temperature (K).

The equilibrium vapor pressure, P , is calculated by coupling the appropriate equation for the FP sorption isotherm (§6.6) and the surface concentration resulting from FP diffusion through the graphite (§6.4). Refer to P. D. Smith (1978) for discussion of the numerical approach to obtaining the surface concentration at the coolant hole. The convective mass transfer coefficient, H , is computed from standard empirical correlations, as presented in §8.3 below.

For time-dependent calculations, Eq. (6.8.2) takes the form (Alberstein et al., 1975):

$$J_L(t) = H(t) \left(\frac{10^6 P(t)}{R T_L} - C_-(t) \right) , \quad (6.8.3)$$

$x(t)$ = variable dependence on the time, t , for $x = J_L, H, P$.

The ability of the TRAFIC code to also consider the time-dependence of the coolant temperature, T_L , has not been determined. The formulation for this process in TRAMP is not known, but is likely similar to that of TRAFIC.

Range of validity

1. The model formulation is assumed valid for all reactor conditions.
2. The formulation is valid provided the correct mass transfer coefficient is used for the specified flow conditions.

Assumptions

1. An equilibrium distribution is established between the FP concentration in the graphite and in the coolant (i.e., kinetic considerations of release are not significant).
2. The effects of dust etc. are not significant in enhancing removal of FP atoms from the surface of the graphite over that predicted by equilibrium sorption isotherms (e.g., by sorption of the FP from the graphite surface into the dust itself).
3. Any operative mixed isotope effect will not significantly affect the predictions of the model.
4. Consideration of the effects of graphite oxidation will not significantly affect the predictions of the model.

Uncertainty

The uncertainty of this model has not been quantified. Refer to "model uncertainty" above for a qualitative discussion.

MODEL CHRONOLOGY

As this model is based on standard solid/gas transport considerations, no explicit model for this transport step is specified in FDDM/F. Alberstein et al. (1975) presented this model as used in the TRAFIC code (P. D. Smith, 1978), and this model has apparently been retained to the present without changes. This model represents an improvement over an earlier simpler model (Schwartz et al., 1974) which decoupled the processes of diffusion in and vaporization from the graphite.

DISCUSSION

The transition from Eq. (6.8.1) to Eq. (6.8.2) is obtained by assuming $C_s = 0$, manipulating the ideal gas equation into the form:

$$C_s = \frac{n}{V} = \frac{10^6 P}{R T_L} \quad (6.8.4)$$

C_s = FP concentration inside the boundary layer ($\mu\text{mol cm}^{-3}$),
 n = amount of FP in the boundary layer (mol),
 V = volume of the boundary layer (cm^3),
 P, R, T_L as previously defined.

The factor 10^6 converts the concentration from mol/cm^3 to $\mu\text{mol}/\text{cm}^3$.

The FP atoms which accumulate at the graphite coolant hole surface must cross the coolant boundary layer to enter the coolant stream. Two effects are involved in this transport (Alberstein et al., 1975): desorption of the atoms from the surface and the mass transport characteristics of the boundary layer. Transport from the surface is modelled as a desorption effect, and the assumptions inherent in the use of sorption isotherms for calculation of gas phase pressure come into play. Myers (1988) raises the question of whether the sorption distribution is in fact established, or whether kinetic considerations might come into play which could enhance the FP removal from the surface above that which would be desorbed. Relevant to this issue is the underprediction of Cs release commonly encountered in simulation of release from the core (Myers, 1988). If kinetic effects must be considered in modelling release from graphite, then the mathematical model reported to have been developed by Gaus for such a process might be applicable (Myers, 1988).

Barthold (1993) comments that any equilibrium, if established, between the graphite and boundary layer would be a dynamic equilibrium, and the lack of an established equilibrium would result in enhanced removal from the surface that is not governed by the reference isotherms. He also comments that, rather than a single boundary layer, a series of boundary layers must be traversed by a FP species, and the use of a single boundary layer implies an assumption that only a single layer need be considered for accurate modelling.

Other evidence that non-sorption considerations might be relevant is the release of iodine in the form of volatile metal iodides from impure graphite, as discussed in §6.6. Significant release of metal iodides would alter model predictions of iodine release based on the sorption isotherms, as these iodides would not be expected to exhibit the same behavior as pure iodine. If kinetic or chemical phenomena exist which can enhance the release over that predicted by the sorption isotherms, then the existing release model might not be as conservative as is usually desired. Relevant to this concern is the lack of a model for oxidation effects on FP transport and release from graphite.

One simulation of Cs and Ag release from graphite fuel bodies is provided by Acharya's (1987) simulation of release during the R2-K13 capsule test (discussed in §6.7 with respect to experimental partition coefficients at the compact/graphite interface). Acharya used the COPAR code for release from the particles and the TRAMP code for overall release. The results for Ag will not be discussed, as experimental problems with the mass balance were encountered. For Cs release from cell 2, the "total predicted release is identical to the measured fractional release of about 6×10^{-04} ... [However] this could be fortuitous, simply because numerous assumptions have been made to simplify the analysis process." For cell 3, the "predicted release fraction of 1.7×10^{-06} is low as compared to the measured release of 6×10^{-05} " (by a factor of 35). As uncertainties in predictions of release from the particles enter into the uncertainty in release from the graphite, one cannot make definitive statements regarding such predictions, especially without knowing what "numerous assumptions" were used to obtain such good agreement for cell 2. The results for cell 3 may support Myers' statement regarding common underprediction of Cs release from graphite, in addition to the statement by Acharya (1987) that it is "also possible (likely) that the holdup in the graphite is overpredicted."

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The model's failure to consider the effects of oxidation on graphite sorption is a limitation, especially for accident conditions involving air or water ingress. Oxidation would be expected to increase release to the coolant just as it is expected to decrease sorptivity. Oxidation effects, if significant, need to be included in the model. Such inclusion might take the form of modified sorption isotherms, perhaps related to the existing model for oxidation of graphite, §11.6.4.

The evidence that iodine reacts with metallic impurities in the graphite to be released as metallic iodides should be considered further. Release of such species will not adhere to the sorption isotherm for iodine as is presently assumed. The potential for reaction of iodine with metallic FP species sorbed on the graphite could also modify metallic release characteristics from those predicted by the sorption isotherms for pure metallic species. Future results from these experiments at KFA should be noted.

The assumption that an equilibrium distribution at the interface can be used to accurately model FP transport should be evaluated, as a dynamic equilibrium or non-equilibrium situation could enhance FP release from the surface over that predicted using the reference sorption isotherms.

DATABASE USED IN MODEL DEVELOPMENT

Except for the experiments and simulations noted in the "Discussion" section, the appropriate database has been presented in §6.6 for metallic sorption in graphite.

6.9 UPDATE

The following references have been suggested for information relevant to the Japanese program.

Sawa, K., S. Shiozawa, K. Fukuda, and Y. Ichihashi, "Verification of Fission Product Release Model From High Temperature Engineering Test Reactor Fuel," *J. Nucl. Sci. Technol.*, 29 (1992) 842-850.

Minato, K., T. Ogawa, S. Kashimura, K. Fukuda, M. Shimizu, Y. Tayama, and I. Takahashi, "Metallic impurities-silicon carbide interaction in HTGR fuel particles," *J. Nucl. Mater.*, 175 (1990) 14-19.

Hayashi, K., F. Kobayashi, K. Minato, K. Ikawa, and K. Fukuda, "In-Pile Release Behavior of Metallic Fission Products in Graphite Materials of an HTGR Fuel Assembly," *J. Nucl. Mater.*, 149 (1987) 57-68.

Fukuda, K., T. Ogawa, S. Kashimura, K. Ikawa, K. Iwamoto, K. Yamamoto, T. Itoh, and H. Matsushima, "Release Behavior of Fission Gas from Coated Fuel Particles under Irradiation," *J. Nucl. Sci. Technol.*, 19 (1982) 889-902.

This writer is not aware of the recent generation of additional data relevant to the contents of this chapter except possibly the time-dependent release of metallic FP surface contamination during heating at 1400° and 1600°C of HRB-17/18 piggyback particles. Graphite sorption specimens which were included in HRB-21 piggyback samples should provide relevant data if and when they are analyzed. The HFR-B1 experiment should provide relevant PIE data on FP sorption on and transport in graphite; it is expected that this PIE will be performed in the future.

7. FISSION PRODUCT RELEASE FROM HEAVY-METAL CONTAMINATION

7.1 INTRODUCTION

The term "heavy metal" is used to refer to uranium and thorium atoms. Heavy-metal (HM) contamination has two sources: HM impurities within the graphite and fuel compact matrix material, and HM atoms distributed over particle surfaces and throughout the fuel compact matrix from exposed kernels during fuel compact manufacturing and the subsequent processing steps. The greatest concern is HM contamination from exposed kernels; i.e., from damage to the coatings during coating or fuel compact manufacturing. The models for gaseous FP release from HM contamination under NOC and AC are an extension of the model equations for gas release from exposed kernels (§4). No data exist for release of metallic FP from contamination, thus the same simple model is used as that developed for FP transport through the compact material.

Heavy-metal contamination should not be confused with HM dispersion (discussed in §2.4.5). However, HM contamination is sometimes confused with the presence of defective particles and exposed kernels within the compact, because the quality control technique used to measure HM contamination (i.e., leaching of the compact) cannot distinguish between the presence of HM contamination and that of exposed kernels. However, such a categorization would not justify separate models for gas release from exposed kernels and HM contamination as presented in FDDM/F.

Heavy-metal contamination is often the largest fission gas source term to the coolant because of the rapid gas release (Stansfield et al., 1983); metallic FP from contamination is largely retained by sorption on graphite. Because this contamination resides outside the primary containment structure of the particles (i.e., outside the SiC layer), only the secondary containment effects of the fuel compact matrix and the core graphite can delay release of these FP to the coolant circuit.

7.2 FISSION GAS RELEASE UNDER NORMAL OPERATING CONDITIONS

function	This model calculates the fractional steady-state isotopic gas release from HM contamination as a function of fractional contamination, temperature, and isotope half-life.
present status	Two models exist for steady-state fission gas release from HM contamination: one used in core calculations and another more detailed model which distinguishes release from the amorphous and graphitic components of the matrix material (Myers, 1988). The model used in core calculations and described below is an adaptation of the model used for gas release from exposed kernels.

model uncertainty Although the uncertainty is small ("less than 1.4") for model predictions of gas release at 1100°C, the assumption of the same temperature dependence of gas release as that for exposed kernels introduces greater uncertainty (Myers, 1988). The greatest uncertainty exists for iodine and tellurium release from HM contamination, as no data exists for temperatures below 1200°C.

references FDDM/F; Myers (1985a); EG&G (1992)

Model equations

The model for steady-state fission gas release from uranium or thorium HM contamination during normal operating conditions is given in FDDM/F:

$$\left(\frac{R}{B}\right)_{kjiCT} = \left(\frac{R}{B}\right)_{kji} \cdot f_c \cdot f(T) , \quad (7.2.1)$$

with the functional parameters defined to be:

$$\left(\frac{R}{B}\right)_{kji} = 3 \sqrt{\frac{\xi_k}{\lambda_i}} , \quad (7.2.2)$$

$$f(T) = \frac{(R/B)_T}{(R/B)_o} = \frac{(R/B)_m}{(R/B)_o} + \left(1 - \frac{(R/B)_m}{(R/B)_o}\right) \exp\left(\frac{Q}{RT_o}\right) \exp\left(-\frac{Q}{RT}\right) , \quad (7.2.3)$$

- $(R/B)_{kjiCT}$ = steady-state fractional release for fuel type k , isotope i of element j , due to HM contamination C at temperature T ,
- f_c = fractional HM contamination,
- $(R/B)_T$ = steady-state fractional release at temperature T ,
- $(R/B)_o$ = steady-state fractional release at the reference temperature ($T_o = 1373$ K),
- $(R/B)_m$ = curve-fitting parameter,
- T = temperature (K),
- T_o = reference temperature for steady-state fractional release (1373 K),
- ξ_k = reduced diffusion coefficient for element j in fuel type k (s^{-1}),
- λ_i = radioactive decay constant of isotope i of element j (s^{-1}),
- Q = activation energy for steady-state fission gas release ($J \text{ mol}^{-1}$),
- R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

Combination of the above equations gives the complete model equation:

$$\left(\frac{R}{B}\right)_{kjict} = 3 \cdot f_c \cdot \sqrt{\frac{\xi_k}{\lambda_i}} \cdot \left\{ \frac{(R/B)_m}{(R/B)_o} + \left(1 - \frac{(R/B)_m}{(R/B)_o}\right) \exp\left(\frac{Q}{RT_o}\right) \exp\left(-\frac{Q}{RT}\right) \right\}. \quad (7.2.4)$$

Values for the parameters as suggested by FDDM/F are listed in Table 7.2.1. The format of the above equations is similar to that used in §4.2.2 for steady-state gas release from exposed kernels under NOC.

Range of validity

The validity of the model is assumed to extend over the range of normal operating conditions. The validity of this model under hydrolyzing conditions is limited (see §7.4 below).

Experimentally, data was obtained for the steady-state release of Kr and Xe isotopes from fuel compacts without graphite shim particles (a "one-component" system) with the contaminated compacts inserted into a furnace at 1100°C and irradiated in the TRIGA reactor (Myers, 1985a). The test procedure is described by Myers et al. (1977). According

Table 7.2.1. Parameters for use in the model equation for fractional steady-state fission gas release from heavy-metal contamination (U, Th) under normal operating conditions, Eq. (7.2.4), and the associated uncertainty (from FDDM/F)

Parameter	Units	Krypton		Xenon	
		Value	Uncert. ^(a)	Value	Uncert. ^(a)
ξ_k	s ⁻¹	1.09×10^{-7}	0.30	9.81×10^{-9}	0.30
$(R/B)_m/(R/B)_o$	Dimensionless	0.0730	(b)	0.210	(b)
Q	J mol ⁻¹	53,100	0.20	45,200	0.35
T _o	K	1373	-	1373	-

- The uncertainty is given as the standard deviation in the natural logarithm of the parameter.
- FDDM/F does not explicitly provide a value for the uncertainty of this parameter; it does however provide a value for a parameter "n" which does not appear in this model. The uncertainty in the natural logarithm for "n" is given as 0.19 for Kr and 0.24 for Xe. Perhaps this unknown parameter was mistakenly inserted in place of $(R/B)_m/(R/B)_o$, in which case these values may be valid for inclusion in this table.

to Myers et al. (1977), the samples are irradiated to produce approximately 10^{14} fissions. No additional information on these experiments has been obtained although a reference document not reviewed by this writer should be helpful (D. T. Goodin, 1984b, "Test Report on Transient Release from Matrix Contamination," GA Technologies Document No. 907629).

Assumptions

1. The same activation energies for gas release from exposed kernels can be used to model gas release from HM contamination.
2. The release of iodine and tellurium at temperatures below 1200°C is assumed to be the same as at 1200°C .
3. The effect of multiple components (amorphous and graphitic) within the compact matrix material can be disregarded (i.e., a single activation energy can be used for release from these components).
4. The rate of fission gas release from thorium contamination is similar to that from uranium.

Uncertainty

The uncertainties in the values of the model parameters are presented in FDDM/F as the standard deviation in the natural logarithm of the parameter. These uncertainties are given above in Table 7.2.1. Some question exists as to the uncertainty in $(R/B)_m/(R/B)_o$; refer to footnote (b) of Table 7.2.1.

MODEL CHRONOLOGY

This model is presented in FDDM/F without reference. Although apparently derived as an offshoot of the model used for gas release from exposed kernels and based on the data presented in Goodin (1984b), no detailed discussion of the derivation of the model parameters has been located. Whether the model is discussed in Goodin (1984b) is unknown to this writer. The only references to this model which have been reviewed are the summaries presented in Myers (1985a, 1988) and EG&G (1992).

DISCUSSION

FDDM/F includes this model under the heading of release of FP gas from exposed kernels. Although the model formulations are very similar, technically the release from HM contamination occurs either outside the particles or from the exterior surface of the particles. Therefore, this model is included in a separate section in this compilation devoted exclusively to FP release from HM contamination.

Two models exist for steady-state fission gas release from HM contamination: one used in core calculations which assumes comparable rates of release of fission gas from the amorphous and graphitic components of the matrix material, and another more detailed

model which distinguishes release from the two components (Myers, 1985a). Additional background to the two component release model can be obtained from Röllig (1977).

The most detailed statement on this model which has been located is that presented in Myers (1988) and will be quoted in detail. "From recent measurements of the steady-state fission gas release from U contamination in the matrix material, the values of the diffusion parameter at 1100°C [Eq. (7.2.2)] were determined with a small uncertainty of less than 1.4. The largest uncertainty contributing to the steady-state fission gas release arises from the temperature dependence which is assumed to be the same as for steady-state fission gas release from exposed kernels. Activation energies derived from the detailed model for release from HM contamination (not used in core calculations) have values between 1 and 1.25 times the values assumed for Kr from the exposed kernel data and between 0.6 and 1.6 times those for Xe, depending on the nuclide. The activation energy varies with nuclide as a result of two or more processes contributing to release; this is taken into account in the detailed model. The reduction in uncertainty obtained by using the detailed model and the derived activation energies would probably be not more than a factor 1.5. The greatest uncertainty associated with release from HM contamination is that for release of iodine and tellurium. These fission products are known to be retained in the matrix material at temperatures below 1200°C; but there are no data on these elements below 1200°C and the conservative assumption is made that the release below 1200°C is the same as at 1200°C ... What has been stated above for the release from U contamination is assumed to apply to Th contamination. Since the grains of contamination are small and the fission fragments leave them by recoil, this assumption should introduce no error." This writer is not aware of source documentation which provides the quantification of this detailed model mentioned above.

EG&G (1992) comments that the graphite shim is more retentive of FP than the rest of the fuel compact matrix material. Because these experimental compacts contained no shim particles, actual in-reactor release could be expected to be smaller than that predicted by the model.

Some fraction of the fission gas generated is released during steady-state operation. After reactor shutdown, the remaining short-lived isotopes will decay but the longer-lived isotopes will persist. The existing model does not indicate how much of this inventory would be expected to remain within the fuel compact in relation to processing, waste handling, and treatment.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Myers (1985a) develops a modified model for steady-state gas release from HM contamination in the compact which is more consistent with the transient AC formulation (discussed below in §7.3). Although not incorporated into FDDM/F and not investigated here, this model could be evaluated for its relevance to future model revisions.

The contents of Goodin (1984b) should be reviewed and the database and any relevant comments contained therein should be considered.

DATABASE USED IN MODEL DEVELOPMENT

Myers (1985a) only presents that data from Goodin (1984b) relevant to the transient model. That data is presented in §7.3 below. This writer has not reviewed Goodin (1984b) and therefore can only comment that the database associated with this model should be available in that document and should be relevant for inclusion in this section.

Earlier measurements on simulated contamination are reported in Myers et al. (1977). As these data were obtained for nonreference compact materials and manufacturing processes and were apparently not used in model derivation, the data will not be presented here but can be reviewed in the source document.

Related FRG data for gas release from compacts obtained during the 1970s can be located in Röllig (1977). As these data were not used in the quantitative development of this model, they will not be presented here but can be referenced for additional background.

7.3 FISSION GAS RELEASE UNDER DRY ACCIDENT CONDITIONS

function	This model calculates the transient fractional fission gas release from HM contamination as a function of temperature and isotope.
present status	The model is a derivative of that used for gas release from exposed kernels under accident conditions. The model reproduces well the available data, but is limited by lack of data for krypton release and for iodine and tellurium release at temperatures below 1200°C (Myers, 1988).
model uncertainty	The uncertainties are small except in those cases where data are lacking, as mentioned above. Lack of data for Kr release introduces a factor of 3 uncertainty in predictions of Kr release (Myers, 1988).
references	Myers (1985a, 1988); FDDM/F

Model equations

The model for transient fission gas release from uranium or thorium HM contamination under nonhydrolyzing accident conditions was presented by Myers (1985a) using an approach similar to that used for gas release from exposed kernels under accident conditions but with modified coefficients. Hydrolyzing conditions are considered in §7.4 below. FDDM/F uses this model with only minor changes in the format of the model equations from that of Myers (1985a). The model equations, as given in FDDM/F, are as follows:

$$f(t) = \sum_{i=1}^2 f_{\alpha_i} f_{\beta_i} + S \cdot t, \quad (73.1)$$

$$f_{\alpha_i} = \sqrt{1 - e^{-\alpha_i t}}, \quad i = 1, 2, \quad (73.2)$$

$$f_{\beta_1} = \frac{1 - C}{1 + \delta_1}, \quad (73.3)$$

$$f_{\beta_2} = \frac{C}{1 + \delta_2}, \quad (73.4)$$

$$S = \frac{\gamma_1 (1 - C)}{1 + \frac{\gamma_1 (1 - C)}{1 - f_{\beta_1}}} + \frac{\gamma_2 C}{1 + \frac{\gamma_2 C}{1 - f_{\beta_2}}}, \quad (73.5)$$

$$\alpha_i = [1 + e^{a_i(T - b_i)}]^{-1}, \quad i = 1, 2, \quad (73.6)$$

$$\delta_i = e^{d_i(T - T_{0i})}, \quad i = 1, 2, 3, \quad (73.7)$$

$$C = \frac{\delta_3}{1 + \delta_3}, \quad (73.8)$$

$$\gamma_i = f_i + g_i T, \quad i = 1, 2, \quad (73.9)$$

- $f(t)$ = fractional release of fission gas from HM contamination,
 t = time (h),
 T = temperature (K),
 $S, \alpha_i, \gamma_i, f_i$ = parameters (h^{-1}),
 b_i, T_{0i} = constant (K),
 a_i, d_i = constants (K^{-1}),
 g_i = constant ($\text{K}^{-1} \text{h}^{-1}$),
 $f_{\alpha_i}, f_{\beta_i}, \alpha_i, \delta_i, C$ = parameters (dimensionless).

Values for the above parameters for Xe, I, and Te are given in Table 7.3.1 as presented in FDDM/F. Values for the Kr release parameters are assumed to be the same as those for Xe.

Several of the values differ between FDDM/F and Myers (1985a), for unknown reasons; most of the differences are in the values for Xe. The units given in FDDM/F for the constants a_i and b_i appear to be in error, and the consistency of units in Eq. (7.3.5) is unclear (i.e., combination of dimensional and dimensionless units).

Range of validity

The model was developed for transient fission gas release in the absence of a neutron flux (nonhydrolyzing conditions). The model does not consider accident conditions involving overpower transients. No other specific limitations on the applicability of the model are mentioned.

Experimentally, fuel compacts containing uranium contamination but no graphite shim particles were irradiated at low temperatures (100°C) to approximately 10^{14} fissions (Myers et al., 1977), following by measurement of the transient release of Xe, I, and Te in the temperature range of 1200 to 1600°C in the absence of a neutron flux (Myers, 1985a). No measurements of Kr release were performed. Additional information on the experimental range of validity may be available in Goodin (1984b).

Assumptions

1. The release of Kr is comparable to that of Xe under all relevant accident conditions.
2. The release of Te and I at temperatures below 1200°C is conservatively assumed to equal that at 1200°C.
3. For Te and I, the release at temperatures between 1200 and 1400°C is better modelled using the data taken at 1200 and 1400°C, and excluding the 1600°C data.
4. For Te and I, the release at temperatures between 1400 and 1600°C is better modelled using the data taken at 1400 and 1600°C, and excluding the 1200°C data.
5. The rate of fission gas release from thorium contamination is comparable to that from uranium contamination.

Assumptions 3 and 4 are discussed in Myers (1985a) as well as additional detailed assumptions related to numerical derivation of the model.

Uncertainty

According to FDDM/F the uncertainty for this model has not been established. Reference should be made to the statements in "present status" and "model uncertainty" above.

Table 7.3.1. Parameters for use in the model equations for fission gas release from heavy-metal contamination under accident conditions, Eqs. (7.3.1) through (7.3.9) (from FDDM/F)

Parameter	Units	Xe	Kr ^(a)	I ^(b)	Te
a ₁	(K ⁻¹)	-1.01 × 10 ^{-3(c)}	-1.01 × 10 ⁻³	-2.09 × 10 ⁻³	-3.54 × 10 ⁻³
a ₂	(K ⁻¹)	0.0	0.0	0.0	-7.23 × 10 ⁻³
b ₁	(K)	3940 ^(d)	3940	2400	2360
b ₂	(K)	0.0	0.0	2400	1910
d ₁	(K ⁻¹)	-7.25 × 10 ^{-3(e)}	-7.25 × 10 ⁻³	-9.57 × 10 ⁻³	-5.20 × 10 ^{-3(f)}
d ₂	(K ⁻¹)	0.0	0.0	(g)	-2.53 × 10 ⁻³
d ₃	(K ⁻¹)	(h)	(h)	-4.00 × 10 ⁻²	-4.00 × 10 ⁻²
f ₁	(h ⁻¹)	6.44 × 10 ⁻⁴	6.44 × 10 ⁻⁴	-2.20 × 10 ⁻³	-2.20 × 10 ⁻³
f ₂	(h ⁻¹)	0.0	0.0	5.48 × 10 ⁻⁴	5.60 × 10 ⁻⁴
g ₁	(K ⁻¹ h ⁻¹)	5.00 × 10 ⁻⁷	5.00 × 10 ⁻⁷	2.15 × 10 ⁻⁶	2.15 × 10 ⁻⁶
g ₂	(K ⁻¹ h ⁻¹)	0.0	0.0	0.0	0.0
T _{0₁}	(K)	1670 ⁽ⁱ⁾	1670	1650	2360 ^(j)
T _{0₂}	(K)	0.0	0.0	(g)	2760
T _{0₃}	(K)	(k)	(k)	1570	1770

- (a) Kr release is assumed to duplicate that of Xe.
(b) For temperatures below 1473 K, f(t) is assumed to equal that at 1473 K.
(c) Myers (1985a) suggests a value of 3.85 × 10⁻⁴.
(d) Myers (1985a) suggests a value of 2833.
(e) Myers (1985a) suggests a value of -5.81 × 10⁻³.
(f) Myers (1985a) suggests a value of -2.51.
(g) Here δ₂ is a constant, independent of temperature, and given by (1 + δ₂)⁻¹ = 0.09.
(h) Here C = 0.0 in Eqs. (7.3.3) and (7.3.4).
(i) Myers (1985a) suggests a value of 1627.
(j) Myers (1985a) suggests a value of 1874.
(k) Here C = 0.0 in Eq. (7.3.8).

MODEL CHRONOLOGY

This model was presented by Myers (1985a) and was adapted with insignificant changes in FDDM/F.

DISCUSSION

Comparison of the above equations with those in §4.4 for fission gas release from exposed kernels under nonhydrolyzing accident conditions shows a similar equation format. The main differences are the following:

1. the term f_s in Eq. (4.4.1) is broken up into two terms in Eq. (7.3.1),
2. the term S in Eq. (7.3.5) is more complex and includes the additional parameter γ_i ,
3. the definition for the term δ_i has been modified, and
4. the term C is now a variable, whereas in §4.4 it was a constant.

Except for the differing parameter values for Xe, the only significant difference between FDDM/F and Myers (1985a) is in the representation of the term C . What appears as C in FDDM/F is represented by $(1 - C)$ in Myers (1985a), but the formulation of the equations is unchanged.

The theory and background to the derivation of the model equations and parameters are given in considerable detail in Myers (1985a) with reference to Myers et al. (1978). In addition, Myers (1985a) presents quantitative comparisons and discussions of the one-component vs two-component models for compact structure (see §7.2) with respect to this transient release model. Use of the one-component model is found to be acceptable for Xe, but the data for I at 1200°C and that for Te at 1200 and 1400°C are better reproduced using the two-component model (or "mixing model"). This detailed theory will not be reviewed here. The effort required for such a review can be pursued if additional data becomes available or more refined extrapolation is required into those regimes where data is presently lacking (i.e., Kr release or I and Te release at temperatures below 1200°C). The data and general model derivation will be briefly presented.

Some of the experimental data attributed to Goodin (1984b) is presented in Myers (1985a) and reproduced here. Experimental data was obtained at temperatures of 1200, 1400, and 1600°C for the isotopes ^{133}Xe , ^{131}I , and ^{132}Te . These data are given in Figs. 7.3.1 through 7.3.3 (from Myers, 1985a). Myers determined that the single component model [$i = 1$ in Eqs. (7.3.1) through (7.3.9)] could reasonably reproduce the experimental data at the three temperatures (see Fig. 7.3.1). However, a two-component model was required to reproduce the I and Te data and to provide reasonable interpolation at temperatures intermediate between 1200, 1400, and 1600°C (model results compared to the data in Figures 7.3.2 and 7.3.3).

The release curves for Xe and I (Figures 7.3.1 and 7.3.2) are compared in Fig. 7.3.4. The release behavior of iodine is obviously different from that of Xe at 1200°C, and Myers states "the deviation of the release profile at 1200°C from the expected behavior based on the release profiles at 1400 and 1600°C ... is probably due to the increased interaction of iodine

Fig. 7.3.1. Fractional release of ^{133}Xe from a fuel compact with heavy metal contamination at 1200, 1400, and 1600°C. Symbols represent experimental data and solid curves are calculated (from Myers, 1985a).

Fig. 7.3.2. Fractional release of ^{131}I from a fuel compact with heavy metal contamination at 1200, 1400, and 1600°C. Symbols represent experimental data and solid curves are calculated (from Myers, 1985a).

Fig. 7.3.3. Fractional release of ^{132}Te from a fuel compact with heavy metal contamination at 1200, 1400, and 1600°C. Symbols represent experimental data and solid curves are calculated (from Myers, 1985a).

Fig. 7.3.4. Comparison of fractional release curves for ^{133}Xe and ^{131}I at 1200, 1400, and 1600°C (from Myers, 1985a).

with the fuel [compact] matrix components at temperatures below 1400°C." Likewise, for Te "the expected chemical interaction with the fuel rod components appears to be stronger than in the case of iodine, persisting to at least 1400°C." This observation suggests that the commonly held assumption of the transport behavior of I and Te being comparable to that of Xe may require some qualification, at least with regard to their behavior within the fuel compact.

EG&G (1992) comments that the graphite shim is more retentive of FP than the rest of the fuel compact matrix material. Because these experimental compacts contained no shim particles, actual in-reactor release could be expected to be smaller than that predicted by the model.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Sufficient detail presently exists in the model that the time required for further model development appears unwarranted, with the possible exception of those regimes mentioned above for which data are not available. For completeness, the information in Goodin (1984b) could be reviewed for possible inclusion in this section in the future. Several values of model parameters as recommended in FDDM/F vary from those presented by Myers (1985a), as documented in Table 7.3.1. As the differences are not insignificant, some determination of the logic behind the apparently revised values used in FDDM/F would be helpful.

DATABASE USED IN MODEL DEVELOPMENT

The database for transient release attributed to Goodin (1984b) and presented by Myers (1985a) was reproduced in Figs. 7.3.1 through 7.3.3 for the isotopes ^{133}Xe , ^{131}I , and ^{132}Te respectively.

7.4 FISSION GAS RELEASE UNDER HYDROLYZING CONDITIONS

function	This model calculates the fractional release of fission gas inventory from HM contamination within the fuel compact as a function of the time-dependent hydrolysis of graphite under similar conditions (partial pressure of water vapor, temperature, graphite burnoff and impurity concentration).
present status	A simple model of gas release from HM contamination under hydrolyzing conditions has been presented by Myers (1986), with a recommendation to evaluate this release mechanism further.
model uncertainty	This model requires the rate coefficient for the reaction of water with matrix material. The hydrolysis rate is approximated from data on the

hydrolysis of H-451 graphite. An uncertainty analysis for this approximation has not been performed (FDDM/F).

references Myers (1986, 1988)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

Myers (1986) presents a simple model for evaluating the fractional release of the fission gas which is generated from HM contamination and resides in the fuel compact matrix material. The "fraction of gaseous fission products released during reaction of fuel [compact] matrix material with water is identical to the fraction of the fuel [compact] matrix material reacted." This model can be represented by the equation:

$$f(t) = X_{c,h}(t) = \int R_{c,h}(t) dt , \quad (7.4.1)$$

- $f(t)$ = fractional release of the fission gas inventory within the compact matrix material generated from HM contamination at time t ,
- $X_{c,h}(t)$ = fraction of the fuel compact matrix material reacting with water up to time t ,
- $R_{c,h}(t)$ = rate of hydrolysis of the compact matrix material (mass fraction reacting per unit time),
- t = time (arbitrary units).

In practice, evaluation of $X_c(t)$ requires information on the rate of reaction between water and compact matrix material. Myers (1986) comments that the rate coefficients for this reaction are 5 to 10 times larger than those for the reaction of water with graphite. However, the model presented in §11.4 suggests a rate 20 times that of graphite, and this rate will be recommended here until additional information is available:

$$R_{c,h} = 20 R_{g,h} , \quad (7.4.2)$$

- $R_c(t)$ = rate of hydrolysis of the compact matrix material (mass fraction reacting per unit time),
- $R_{g,h}(t)$ = rate of hydrolysis of H-451 graphite (mass fraction reacting per unit time).

The equation for $R_{g,h}$ is presented in §11.6.3 and will not be repeated here.

Range of validity

The statements presented in §11.4 and §11.6.3 for "Range of validity" are applicable here.

Assumptions

1. Release of fission gas inventory within the compact matrix material is instantaneous upon hydrolysis of that material.
2. The assumptions stated in §11.4 and §11.6.3 are applicable here.

Uncertainty

No estimate of the uncertainty of this model has been made (FDDM/F).

MODEL CHRONOLOGY

No model for the effect of hydrolysis on fission gas release from HM contamination is presented in FDDM/F. Apparently, the only discussion of this release mechanism to date was that by Myers (1986).

DISCUSSION

No comparable model has been presented for oxidizing conditions such as air ingress. If needed, such a model could be derived as a function of graphite oxidation, analogous to this hydrolysis model.

To be precise, one would think this model should explicitly differentiate between the hydrolysis of the fuel compact matrix material and the hydrolysis of the graphite shim, similar to the model presented in §11.5. Although the matrix material will react at a rate approximately twenty times that of H-451 graphite shim particles, §7.3 commented that the graphite shim should be more retentive of gaseous FP than the matrix material. As a first approximation and lacking additional data, a uniform concentration of FP in both shim and matrix material could be assumed; and the mass fraction of each component could be combined with the rate of hydrolysis of each component to give a modified equation analogous to that in §11.5:

$$f = \sum_i X_i R_i t \quad , \quad (7.4.3)$$

X_i = mass fraction of component i ;
 R_i = rate of hydrolysis of component i (mass fraction per unit time),
 t = time (arbitrary units),
 i = m (matrix material) or g (graphite).

According to FDDM/F the mass fraction of matrix material is a constant 0.42 for the MHTGR, while the mass fraction of the graphite shim particles will vary according to the fuel particle loading within the compact.

Myers (1986) suggests that the requisite rate coefficients for reaction of water with fuel and compact matrix material were measured in 1986 but are not openly available. Myers

(1988) comments on the hydrolysis of the compact matrix material as follows: "The uncertainty of the limited data on the hydrolysis of fuel compact matrix material is difficult to estimate. Recent observations in experiment HFR-B1 indicate that for a reactor-relevant, fuel element configuration, the rate of hydrolysis decreases significantly after the exposed matrix material surface becomes saturated with adsorbed H₂O or its dissociation products. Clearly our current modeling of the hydrolysis is incorrect and after completion of the HFR-B1 experiment and analysis, a large reduction in uncertainty can be expected."

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Data analysis of the HFR-B1 experiment is ongoing at present. As those results become available, they should be evaluated as to their relevance for or justification of the above model. This model as stated does not explicitly introduce the initial fission gas inventory within the fuel compact material into the calculations. The appropriate model equations from §7.2 and §7.3 could be incorporated to provide some initial condition for fission gas inventory at the onset of hydrolysis.

DATABASE USED IN MODEL DEVELOPMENT

The database discussions in §11.4 and §11.6.3 are relevant to this section.

7.5 METALLIC FISSION PRODUCT RELEASE FROM HEAVY-METAL CONTAMINATION

function	This model provides a simple approximation for the concentration of metallic FP from HM contamination within the fuel compact, without functional dependencies.
present status	Due to lack of data, the simple model developed previously for metallic FP transport through the fuel compact is also assumed to apply for metallic FP release resulting from HM contamination.
model uncertainty	Without relevant data, the uncertainty of this model cannot be determined, but the level of uncertainty should not be significant with respect to core release predictions.
references	FDDM/F; Myers (1988)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

Because of the lack of data relevant to metallic FP release from the fuel compact due to HM contamination, FDDM/F recommends using the same model of transport through the compact matrix material as is used for metallic FP transport from the particle to the graphite. This model was presented previously in §6.3 and suggests that a source of metallic FP from HM contamination will instantaneously distribute itself homogeneously throughout the matrix material. This model can be represented as:

$$C(x) = \bar{C} , \quad (7.5.1)$$

$C(x)$ = concentration of HM-contamination-generated metallic FP at position x within the fuel compact (arbitrary units),
 $\bar{C}$ = average concentration of metallic FP throughout the compact matrix material (arbitrary units).

The subsequent release from the fuel compact is governed by sorption effects (§6.5).

Range of validity

The model is applicable to all reactor conditions. Data do not exist upon which to base an experimental range of validity.

Assumptions

1. Mass transfer and diffusion of metallic FP within the fuel compact are not rate-limiting.
2. The dispersion of metallic FP throughout the fuel compact has no significant dependence on temperature, fast fluence, or other variable.
3. Metallic FP release due to thorium contamination behaves similarly to that from uranium contamination.

Uncertainty

Lacking experimental data, the uncertainty of this model cannot be determined.

MODEL CHRONOLOGY

According to FDDM/F and Myers (1988), no data exist for this process. No other references for this release mechanism are known, thus any chronology for this model is unknown.

DISCUSSION

According to Myers (1988), the "assumption is made that all the formed fission product metals are released from the fuel compact matrix material" for both uranium and thorium contaminants. This statement appears to imply that metallic FP transport to the outer surface of the fuel compact is instantaneous upon fissioning of the HM contaminant atom, with no role played by sorption within the compact. The model advanced by FDDM/F is more realistic in considering the effects of sorption in release from the compact.

In reality, fission recoil would implant the metallic FP atoms into the compact matrix material, followed by diffusive transport to the surface porosity prior to release. Whether the time required for this diffusion process would be significant relative to the rate of release from the compact has not been evaluated.

Barthold (1993) points out the lack of information or models on the effect of hydrolyzing or oxidizing conditions on metallic FP release under either NOC or AC, neglecting a potentially significant source of enhanced metallic FP release from HM contamination under off-normal conditions.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The comments of §6.3 are relevant here. Refinement of the model would require kinetic considerations of the rate of dispersal of the metallic FP atoms throughout the fuel compact after they are generated by fissioning of the HM contaminant atoms. Diffusive release of atoms implanted into the matrix material might be considered. In terms of the uncertainty of total FP release from the core, refinement of this model is not a high priority relative to other models.

DATABASE USED IN MODEL DEVELOPMENT

Apparently no data exist with which to analyze this release mechanism; therefore, no database relevant to development of this model can be presented.

7.6 UPDATE

No data relevant to the models in this chapter have been recently generated in the MHTGR program to this writer's knowledge. Analysis of the HFR-B1 experiment, specifically the effect of graphite and fuel compact hydrolysis on fission gas release, may be relevant to §7.4.

8. FISSION PRODUCT TRANSPORT WITHIN THE PRIMARY CIRCUIT

8.1 INTRODUCTION

This chapter covers the transport of metallic FP within the coolant and primary circuit after desorption from the graphite surface (§6.8) and subsequent interactions with the primary circuit alloys. The first two models presented (gas phase diffusivity and mass transfer coefficients) also apply to the transport of fission gases within the coolant; but the primary concern for coolant circuit models is the plateout of metallic FP on the primary circuit (PC) alloys, the resulting radiological hazard for reactor maintenance, and the potential radiological source term during AC depressurization or moisture ingress. The models presented in this chapter relate to DDNs 11.50, 11.51, 11.52, and 11.53 of the NP-MHTGR program (CEGA, 1990).

The model equation for the gas phase diffusivity of FP species is presented first, to be used as input into the calculation of mass transfer coefficients. Mechanisms for metallic FP interaction with the PC alloys are then discussed, followed by mechanisms for reentrainment of the FP into the coolant circuit.

8.2 GAS PHASE DIFFUSIVITY

function	This model calculates the gas phase diffusivity of FP atoms as a function of mass, temperature, and coolant pressure.
present status	The simple assumption of atomic gas phase transport via diffusion remains the dominant model, without consideration or analysis of particulate or molecular transport.
model uncertainty	Lack of consideration of the possibility of non-atomic FP transport within the coolant circuit (i.e., molecular or particulate transport) introduces phenomenological uncertainty into this model of diffusive gas-phase transport of individual FP atoms. According to Myers (1988) the chemical state of the circulating fission products has not been analyzed. With respect to the intrinsic uncertainty of the model, General Atomic (1976a) states: "Because of very limited experimental data, the gaseous diffusivity of radionuclides in helium is quite uncertain." This combined uncertainty may not be insignificant.
references	FDDM/F; Becker (1981); Busch (1966)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The latest model equation presented in FDDM/F is given in the form:

$$D_i = \frac{A}{\mu_i^{1/2}} \frac{T^{1.65}}{P}, \quad (8.2.1)$$

$$\mu_i = \frac{M_i M_{He}}{M_i + M_{He}}, \quad (8.2.2)$$

- D_i = diffusion coefficient for FP species i in helium ($\text{m}^2 \text{s}^{-1}$),
 T = temperature of coolant (K),
 P = total pressure of coolant (MPa),
 μ_i = reduced mass of the FP/helium system for fission product i (g),
 M_j = atomic weight of species j , where $j = i$ or $j = He$ (g mol^{-1}),
 A = constant, of value $8.45 \times 10^{-10} \text{ MPa m}^2 \text{ K}^{-1.65} \text{ s}^{-1}$.

An internal GA memorandum by B. F. Myers is mentioned as the source reference for this model. Gas phase atomic diffusivity is directly dependent on temperature and gas pressure; therefore, the NOC formulation is also applicable to AC.

Range of validity

The model is applied over all reactor conditions. Reference experimental data was obtained by Busch (1966) using in-pile diffusion tubes with coolant flow rates of $4.34 \text{ cm}^3 \text{s}^{-1}$, coolant pressures of 350 psia, probe temperatures of approximately 510, 330, and 170°C, and ^{137}Cs partial pressures of approximately $6 \times 10^{-13} \text{ atm}$ (lower pressures for other FP experiments).

Assumptions

The assumptions which are used to derive the model equation have not been reviewed in detail. Reference should be made to Busch (1966) and to the source reference of Reid et al. (1977, and earlier editions), which has not been reviewed by this writer.

Uncertainties

No quantification of the uncertainty of this model has been presented. Qualitative uncertainty concerns were discussed above.

MODEL CHRONOLOGY

Equation (8.2.1) is a simplified form of the classical equation for binary gas phase diffusion, with the constant A apparently derived from reference Cs gas-phase diffusivity data obtained by Busch (1966). The formulation of the model equation has not changed significantly since presented in the 1970s, only the value of the constant has changed slightly ($\approx 6\%$) from that presented by Hudritsch et al. (1977) and Becker (1981). The reason for this change is unknown, although the previously-mentioned GA internal memo has not been reviewed by this writer.

DISCUSSION

An expression was presented by Becker (1981) for the diffusion coefficient of gaseous species in helium, which was attributed to FDDM/C (1979):

$$D_i = D_o \left(\frac{T_i}{T_o} \right)^{1.65} \left(\frac{P_o}{P_i} \right) \left(\frac{\frac{1}{M_i} + \frac{1}{M_{He}}}{\frac{1}{M_o} + \frac{1}{M_{He}}} \right)^{1/2}, \quad (8.2.3)$$

- i, o = subscripts denoting i th species and a reference species under reference conditions, respectively,
 D = diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$),
 T = coolant temperature (K),
 P = total pressure (atm),
 M = molecular weight (g mol^{-1}).

The notation T_i and P_i is confusing and should refer to the coolant temperature and total pressure, therefore the removal of the subscript i from these variables is recommended. The reference conditions chosen are for ^{137}Cs diffusing in helium, which provide the following reference values:

$$\begin{aligned} D_o &= 0.1682 \text{ cm}^2 \text{s}^{-1}, \\ T_o &= 1000 \text{ K}, \\ P_o &= 23.83 \text{ atm}, \\ M_o &= 137 \text{ g mol}^{-1}. \end{aligned}$$

Use of the above values in Eq. (8.2.3) and conversion to units consistent with Eq. (8.2.1) gives the result:

$$D_i = \frac{8.98 \times 10^{-10}}{\mu_i^{1/2}} \frac{T^{1.65}}{P} \frac{\text{m}^2}{\text{s}}, \quad (8.2.4)$$

which varies approximately 6% from Eq. (8.2.1). Hudritsch et al. (1977) present an equation which provides a result identical to that of Eq. (8.2.4).

Becker indicates Cs is used as the reference for transport and plateout calculations involving Cs, I, and Sr. For plateout of Ag, Becker (1981) used Ag as the reference species, with data derived from Dragon plateout experiments.

Earlier formulations of this model equation were comparable except for inclusion of the reduced mass term within the value for D_0 , see e.g., P. D. Smith (1978). More details of the theoretical origin of these model equations can be obtained from Bird et al. (1960) or Reid et al. (1977).

A statement by Myers (1988) is relevant to this model for gas-phase transport. "Currently fission products are assumed to be transported in the form of gas phase atoms by the circulating He coolant. This assumption could be incorrect in two ways: the fission products could circulate as molecular species or as sorbates on particulate matter. ... There are essentially no measurements on the chemical state of the circulating fission products ..."

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The potential for particulate transport of FP is discussed in §8.7 below. An observation relevant to the transport of iodine in the coolant circuit was mentioned by Myers (1991) in relation to the reaction of iodine with metallic impurities in the graphite: "... iodine released from the particles and the core, in the case of the prismatic HTR, will enter the primary circuit as metallic iodides and be distributed accordingly ... The possibility of iodine being released from the core as metallic iodides has not been considered in safety calculations in the U.S." The significance of these non-atomistic transport modes in FP plateout and reentrainment will need to be evaluated.

DATABASE USED IN MODEL DEVELOPMENT

The reference diffusivities are derived primarily from diffusion tube experiments in the GAIL IV in-pile loop (Hanson, 1977). The source data from which the reference values for Cs diffusivity were calculated are presented in Figs. 8.2.1 and 8.2.2, taken from Busch (1966).

Experimental information on the interdiffusion of Kr and Xe in helium can be obtained from Campana et al. (1979).

8.3 MASS TRANSFER COEFFICIENT

function

This model provides values for the mass transfer coefficient of FP atoms in the coolant as a function of the Reynolds and Schmidt numbers, flow geometry, and gas-phase diffusivity (§8.2), for input into calculations of FP mass flow into the coolant (§6.8).

Fig. 8.2.1. $^{134}\text{Cesium}$ and ^{137}Cs activity profile where flow rate is $4.34 \text{ cm}^3 \text{ s}^{-1}$ at 350 psia and 513°C (from Busch, 1966).

Fig. 8.2.2. Diffusion coefficients vs absolute temperature for ^{137}Cs in helium at 350 psia (from Busch, 1966).

present status	The model for mass transfer across a solid/gas boundary layer has long been established in classical transport theory. However, "the appropriateness of the empirical coefficients is uncertain given HTGR operating conditions and complex geometry" (General Atomic, 1976a).
model uncertainty	The model uncertainty is that related to classical transport theory, and will not be evaluated here. The uncertainty inherent in the application of this model to mass transport into the coolant of a MHTGR (§6.8) is of greater concern, but has not been quantified.
references	Hudritsch et al. (1977); Treybal (1980); Bird et al. (1960)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

Expressions for the mass transfer coefficient within three forced convection regimes are commonly used, two for the laminar flow regime (Reynolds number < 2100) and one for the turbulent flow regime (Reynolds number ≥ 2100) (FDDM/F; Hudritsch et al., 1977):

$$H_i = 3.66 \frac{D_i}{d} \quad \text{for } Re < 2100 \text{ and } \frac{L}{d Re Sc} \geq 0.7^{(1)}, \quad (8.3.1)$$

$$H_i = 1.86 \left(\frac{d}{L} \right)^{0.33} Re^{0.33} \left(\frac{D_i}{d} \right) Sc^{0.33} \quad \text{for } Re < 2100 \text{ and } \frac{L}{d Re Sc} < 0.7^{(1)}, \quad (8.3.2)$$

$$H_i = 0.023 Re^{0.83} \left(\frac{D_i}{d} \right) Sc^{0.44} \quad \text{for } Re \geq 2100, \quad (8.3.3)$$

- H_i = mass transfer coefficient for FP species i (m s^{-1}),
 D_i = diffusion coefficient for species i in helium ($\text{m}^2 \text{s}^{-1}$),
 d = hydraulic diameter of conduit (m),
 L = hydrodynamic entry length (m),
 Re = Reynolds number,
 Sc = Schmidt number.

D_i is calculated as discussed in §8.2 above, and the Reynolds and Schmidt numbers are determined from their classical definitions. Equations for these dimensionless parameters will be provided in the "Discussion" section below. Equation (8.3.3) is usually employed in

(1) this value may be 0.07; see "Discussion."

simulations for the turbulent coolant flow typical under normal operating conditions (e.g., Hanson, 1977).

Range of validity

The above equations are valid for the forced convection regime for annular flow in a tube of constant cross-sectional area. Equations (8.3.1) and (8.3.2) are valid for laminar flow, Eq. (8.3.3) for turbulent flow. For other geometries and for the free convection regime, other sets of equations are valid as presented in the "Discussion" section.

The Reynolds number regime appropriate for the NP-MHTGR design is stated to be >5000 (CEGA, 1990). In contrast, Wichner (1991) mentions a typical MHTGR value of 180,000. The correlation given by Eq. (8.3.3) is stated to be applicable for Reynolds numbers between 2000 and 35,000 (General Atomic, 1976a; Treybal (1980). If Wichner's value is accurate, typical MHTGR conditions may fall outside the range of validity of Eq. (8.3.3).

Assumptions

The above equations are based on classical mass transfer considerations. The assumptions which go into their development and derivation are not considered here but can be determined from standard references (Treybal, 1980; Bird et al., 1960).

Uncertainty

The uncertainty of this model has not been quantified. A qualitative statement regarding the uncertainty is provided by General Atomic (1976a): "The convective mass transport process occurring in the primary coolant circuit is believed to be quite complex. However ... the process is simplistically modeled by use of an empirically determined correlation which gives a mass transfer coefficient analogous to a film heat transfer coefficient."

MODEL CHRONOLOGY

The model equations are available in standard mass transport references such as Treybal (1980), Bird et al. (1960), and others. Hudritsch et al. (1977) also refer to unpublished GA data, but the significance of this data is unknown. The formulation presented in FDDM/F is almost identical to that presented in Appendix A of Hudritsch et al. (1977).

DISCUSSION

Table 8.3.1 is taken from Appendix A of Hudritsch et al. (1977). In addition to flow in a tube as represented by the above equations, Table 8.3.1 also provides parameters for

Geometry	KCF	Flow Regime		a_1	a_2	a_3	a_4	a_5
Flow in tube and annular flow	1	Re<2100 (laminar)	$\frac{L}{d Ra Sc} \geq 0.07$	0	3.66	0	0	0
			$\frac{L}{d Ra Sc} < 0.07$	0	1.86	0.33	0.33	0.33
		Re>2100 (turbulent)	0	0.023	0	0.8	0.33	
Aligned tube bundles in cross flow (use d = outer tube diameter)	2	$(Ra)_{max} < 1000$	$f(Ra; 0.43, 0, 10^3)$	$f(Ra; 0.52, 0.27, 10^3)$	0	$f(Ra; 0.5, 0.63, 10^3)$	0.36	
		$1000 \leq (Ra)_{max} < 200000$	0	0.27	0	0.63	0.36	
		$(Ra)_{max} > 200000$	0	0.02	0	0.84	0.36	
Staggered tube bundles in cross flow (use d = outer tube diameter)	3	$(Ra)_{max} < 1000$	$f(Ra; 0.43, 0, 10^3)$	$f(Ra; 0.60, 0.40, 10^3)$	0	$f(Ra; 0.5, 0.60, 10^3)$	0.36	
		$1000 \leq (Ra)_{max} < 200000$	0	0.40	0	0.60	0.36	
		$(Ra)_{max} > 200000$	0	0.021	0	0.84	0.36	
Flat plate (use plate length for Reynold's number evaluation)	4	Re<3.2×10 ⁵ (laminar)	0 ≤ Sc ≤ 0.6	0	f(Sc; 1.128, 0.664, 0.6)	0	0.5	f(Sc; 0.5, 0.33, 0.6)
			0.6 < Sc ≤ 10	0	0.664	0	0.5	0.33
			Sc > 10	0	0.678	0	0.5	0.33
		Re>3.2×10 ⁵ (turbulent)	0	0.037	0	0.8	0.33	
					$f(x; a, b, c) = a - \frac{(a-b)(2c-x)x}{c^2}$			

evaluating mass transfer coefficients in tube bundles and across flat plates. The parameters α_1 through α_5 are applied to the general governing equation:

$$H_i = \frac{D}{\chi} \left[\alpha_1 + \alpha_2 \left(\frac{d}{L} \right)^{\alpha_3} Re^{\alpha_4} \right] Sc^{\alpha_5} , \quad (8.3.4)$$

$\chi = L$ for flat plates,
 $\chi = d$ for other geometries,
 all other variables as defined previously.

Application of the parameters in Table 8.3.1 for annular flow in a tube to Eq. (8.3.4) will reproduce Eqs. (8.3.1) and (8.3.2). Rather than Eq. (8.3.3), Table 8.3.1 provides the following equation:

$$H_i = 0.023 Re^{0.80} \left(\frac{D_i}{d} \right) Sc^{0.33} \quad \text{for } Re \geq 2100 . \quad (8.3.5)$$

Treybal (1980) states that the term $Sc^{0.44}$ in Eq. (8.3.3) provides better correlations for gas data than does the term $Sc^{0.33}$ in Eq. (8.3.5). In addition, both Hudritsch et al. (1977) and Schwartz et al. (1974) specify the criteria for choosing between Eqs. (8.3.1) and (8.3.2) in the laminar flow regime as:

$$\frac{L}{d Re Sc} = 0.07 , \quad (8.3.6)$$

rather than the value 0.7 as specified in FDDM/F. The reason for this discrepancy is unknown, and whether any of these represents a misprint is unknown at this time.

For those situations in which free convection should be considered, Table 8.3.2 is presented from Hudritsch et al. (1977). The governing equation in which the parameters of Table 8.3.2 should be used is (Hudritsch et al., 1977):

$$H_i = \frac{D}{\chi} \beta_1 Re^{\beta_2} Sc^{\beta_3} Gr^{\beta_4} \left(\frac{d}{L} \right)^{\beta_5} , \quad (8.3.7)$$

Gr = Grashof number (defined below),
 all other variables as defined previously.

Acharya (1984) presents mass transfer coefficients appropriate to simulations of pebble-bed reactors. He presents a coefficient for forced convection around a sphere of diameter D , referenced to a 1966 edition of Bird et al. (1960):

Table 8.3.2. KGN and β values for free convection (from Hudritsch et al., 1977)

Geometry	KGN	Flow Regime	β_1	β_2	β_3	β_4	β_5
Flow in tube and annular flow	1	$Re\ Sc\ d/L \leq 30$ $Re\ Sc\ d/L > 30$	6 1.78	0 0.357	0 0.357	0 0	0 0.357
Vertical tube banks and vertical flat plates (KCNFP=1)	2	$Gr\ Sc \leq 10^4$ $10^4 < Gr\ Sc < 10^9$ $Gr\ Sc \geq 10^9$	1.295 0.59 0.33	0 0 0	0.1646 0.25 0.13	0.1646 0.25 0.33	0 0 0
Horizontal tube banks and horizontal flat plates (KCNFP=1)	3	$Gr\ Sc \leq 10^{-5}$ $10^{-5} < Gr\ Sc < 10^4$ $10^4 < Gr\ Sc < 10^9$ $Gr\ Sc \geq 10^9$	0.4 1.962 0.53 0.13	0 0 0 0	0 0.1381 0.25 0.33	0 0.1381 0.25 0.33	0 0 0 0

$$H_i = \frac{D_i}{D} [2.0 + 6.0 Re^{0.5} Sc^{0.33}] , \quad (8.3.8)$$

although inspection of the 1960 edition suggests the coefficient 6.0 in the above equation should actually be 0.60. Acharya also mentions the HRB organization uses a different equation for pebble bed mass transfer coefficients:

$$H_i = \left(\frac{D_i}{D} \right) 0.58 Re^{0.5} Sc^{0.33} , \quad (8.3.9)$$

although he indicates this correlation would probably be inappropriate for core heatup conditions.

The dimensionless flow parameters are defined in Schwartz et al. (1974) and in Appendix A of Hudritsch et al. (1977) as follows. The Reynolds number is defined as:

$$Re = \frac{v \rho d}{\mu} , \quad (8.3.10)$$

- v = average coolant velocity (cm s^{-1}),
- ρ = helium density (g cm^{-3}),
- μ = dynamic viscosity of helium ($\text{g cm}^{-1} \text{s}^{-1}$),
- d = coolant channel diameter (cm).

The Schmidt number is defined as:

$$Sc = \frac{\mu}{\rho D_i} . \quad (8.3.11)$$

The Grashof number is defined as:

$$Gr = g L^3 |\rho_m - (\rho_m)_\infty| \frac{\rho_m}{\mu_m^2} , \quad (8.3.12)$$

- index m = mixture of FP and helium coolant,
- $(\rho_m)_\infty$ = average density in the free stream (g cm^{-3}),
- g = acceleration due to gravity (cm s^{-2}).

Additional detail and interpretation of these parameters is given by Bird et al. (1960), Treybal (1980), and other reference works.

In some representations (General Atomic, 1976a; Treybal, 1980) Eq. (8.3.3) is defined in terms of a Sherwood number, Sh , rather than a mass transfer coefficient:

$$Sh = H_i \frac{d}{D_i} \quad (8.3.13)$$

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The expected regime for Reynolds number in MHTGR design should be verified with respect to the range of validity of Eq. (8.3.3). The value of 0.7 stated as a criterion in the use of Eqs. (8.3.1) and (8.3.2) should be verified with respect to the value of 0.07 mentioned in the footnote to those equations.

DATABASE USED IN MODEL DEVELOPMENT

Apparently, experiments have not been conducted to confirm the validity of the correlations which are assumed to apply to MHTGR conditions. The database relevant to the diffusivity D_i which enters into calculations was discussed in §8.2 above.

8.4 SORPTION ON PRIMARY CIRCUIT ALLOYS

function	This model uses sorption isotherms to calculate the equilibrium FP surface concentration on metallic surfaces as a function of the FP partial pressure (or vice versa), temperature, metal, and oxidation state of the metal surface.
present status	Model equations have been derived for Cs, Ag, and I. Sorption of other FP has not been measured, so metallic surfaces are assumed to act as perfect sinks for these species. The available sorption data are well studied, but all model equations require significant extrapolation. Existing data were usually obtained at pressures significantly higher than those expected in MHTGRs ($\approx 10^{-10}$ Pa), and sorption data on non-MHTGR metals are frequently used in extrapolations. Data have not been obtained at the lowest expected coolant and alloy temperatures. Effects of surface conditions on sorption are not well known.
model uncertainty	Although the many assumptions used in deriving sorption isotherms could lead to uncertainties greater than 10^3 , actual comparison of sorption predictions with experiment provides uncertainties in the range of 25 to 50 (Myers, 1988). The differences between test conditions and reactor conditions introduce additional uncertainty due to the possible sorption effects of dust and aerosols within the coolant loop. One effort at

numerically simulating a plateout experiment concluded that "our data base and/or methodology appear to be grossly inadequate" (Acharya et al., 1984).

reference Myers (1984b); FDDM/F

INTRODUCTION

Refer to §6.1 for a general introduction to sorption theory. Fission product sorption data on metals is available only for Cs, Ag, and I, at pressures typically orders of magnitude larger than those expected within the MHTGR coolant circuit. The only metals studied were tungsten and the alloys Incoloy 800, Hastelloy B, Hastelloy X, T-22 low chromium steel, SS-304, and INOX 347. According to Myers (1984b) the primary alloys of interest for MHTGR technology are Incoloy 800, Hastelloy X, T-22, SS-304, and the carbon steel SA-36. Sorption on several of the alloys was studied for both oxidized and unoxidized surfaces. Sorption data is available over only limited temperature and pressure ranges. The available data for sorption isotherms is summarized in Table 8.4.1, from Myers (1984b). Sorption of Cs and I is considered only for their elemental forms; any existence as chemical compounds would negate the accuracy of using these sorption models.

The PC alloys specified for use in NP-MHTGR design are Alloy 800H (temperature range of 400 to 700°C), 2-1/4% Cr-1% Mo (200 to 450°C), and SA-533 (300 to 400°C under NOC, 300 to 550°C under AC). Alloy 2-1/4% Cr-1% Mo is also referred to as either T-22 or SA-387 alloy (CEGA, 1990; FDDM/F); the label T-22 will be used here for consistency with Myers (1984b). Alloy 800H is the same as Incoloy 800 (FDDM/F); the label Incoloy 800 will be used here.

Coolant NOC temperatures are expected to range from 300 to 700°C although AC temperatures may extend beyond this range. Accident condition temperatures of the PC alloys are not expected to differ significantly from the predicted NOC maxima except for SA-533. The temperature and pressure dependencies of sorption isotherms are included in the NOC formulation, therefore the sorption isotherms as given for NOC are also valid for AC.

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

Either of two expressions for the isotherm equation can be used, depending on applicability. One expression is based on the Langmuir isotherm equation:

$$p = \frac{C}{a_1(K_1 - C)} \quad , \quad (8.4.1)$$

Table 8.4.1. Source data for model development: sorption on metals and alloys (from Myers, 1984b)

Fission product	Metal or alloy	Pressure range (Pa)	Temperature range (°C)	Reference	Oxidation state ^(a)
Cs	Tungsten	$10^{-12} - 1$	527 - 927	Taylor et al. (1933)	U
Cs	Incoloy 800 ^(b) , Hastelloy X	$2 \times 10^{-6} - 2 \times 10^{-1}$	800	Gas Turbine (1976a, 1976b)	U,O
Cs	SS-304	$2 \times 10^{-5} - 5 \times 10^{-1}$	345 - 735	Milstead et al. (1966)	U,O
Cs	Incoloy 800 ^(b) , INOX 347, Hastelloy B	$10^{-5} - 10^{-4}$	400 - 600	Abassin et al. (1976)	U,O
Ag	Tungsten	$5 \times 10^{-7} - 5 \times 10^{-5}$	800 - 1000	Ionov et al. (1975)	U
I	T-22 low chromium steel ^(c)	$10^{-6} - 10^{-2}$	400 - 800	Osborne et al. (1982)	U,O

(a) U = unoxidized surface.

O = oxidized surface.

(b) Also referred to as Alloy 800H.

(c) Also referred to as SA-387 and as 2-1/4% Cr-1% Mo.

$$a_1 = a_1^{\circ} \exp\left(-\frac{Q_1}{RT}\right) , \quad (8.4.2)$$

while the other takes the form:

$$p = b_1 C + b_2 C^{n_2} + b_3 C^{n_3} , \quad (8.4.3)$$

$$b_i = b_i^{\circ} \exp\left(-\frac{Q_i}{RT}\right) , \quad i = 1, 2, 3 , \quad (8.4.4)$$

- p = partial pressure of the fission product species (Pa),
 C = surface concentration of the fission product species ($\mu\text{g}/\text{cm}^2\text{-geom}$),
 Q_i = activation energy, $i = 1, 2, 3$ (J mol^{-1}),
 R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$),
 a_1° = constant (Pa^{-1}),
 b_i° = constant, $i = 1, 2, 3$ ($\text{Pa } \mu\text{g}^{-1} \text{ cm}^2\text{-geom}$),
 K_1 = constant ($\mu\text{g}/\text{cm}^2\text{-geom}$),
 n_i = constant, $i = 1, 2, 3$ (dimensionless).

A correction for the surface roughness factor, δ_r , is appropriate when the geometric surface area of the alloy under study is different from that of the specimen used to derive the sorption isotherms. A correction is made to the concentration as given by:

$$C' = \frac{\delta_r'}{\delta_r} C , \quad (8.4.5)$$

with the primed quantities referring to the test surface and the unprimed quantities referring to the reference experimental conditions.

Parameters for the sorption isotherm equations for unoxidized PC alloys are given in Table 8.4.2, and for oxidized alloys in Table 8.4.3 (Myers, 1984b).

Range of validity

The experimental data were obtained under equilibrium conditions, thus the model given above is valid for steady-state and near-steady-state conditions. Specifically, Eq. (8.4.1) is not valid whenever the denominator is less than or equal to zero. This problem has been reported for calculations which use large time steps (Jovanovic, 1988). The validity of Eq. (8.4.3) weakens as pressures increase above approximately 1 Pa.

The experimental range of validity of the data was reviewed in Table 8.4.1. Data for Cs and I have been obtained over most of the temperature range expected to be

Table 8.4.2. Parameters for use in the design equations for fission product sorption isotherms on unoxidized primary circuit alloys, Eqs. (8.4.1) through (8.4.4) (from Myers, 1984b)

Element	Alloy	$K_1^{(a)}$	$a_1^{(b)}$	$b_1^{(c)}$	$b_2^{(c)}$	$b_3^{(c)}$	$Q_1^{(d)}$	$Q_2^{(d)}$	$Q_3^{(d)}$	n_2	n_3	δ_r
Cs	SA-36 carbon steel	-	-	2.65×10^{10}	1.57×10^{15}	1.25×10^{22}	273,000	262,000	216,000	3	8	7
	T-22 ^(e)	-	-	2.65×10^{10}	1.57×10^{15}	1.25×10^{22}	273,000	262,000	216,000	3	8	7
	Incoloy 800	-	-	2.65×10^{10}	1.57×10^{15}	1.25×10^{22}	273,000	262,000	216,000	3	8	7
	Hastelloy X	-	-	2.65×10^{10}	1.57×10^{15}	1.25×10^{22}	273,000	262,000	216,000	3	8	7
	SS-304	-	-	5.31×10^{10}	1.26×10^{16}	$3.19 \times 10^{24(1)}$	273,000	262,000	216,000	3	8	7
Ag	SA-36 carbon steel	0.20	5.22×10^{-7}	-	-	-	-254,000	-	-	-	-	7
	T-22 ^(e)	0.20	5.22×10^{-7}	-	-	-	-254,000	-	-	-	-	7
	Incoloy 800	0.20	5.22×10^{-7}	-	-	-	-254,000	-	-	-	-	7
	Hastelloy X	0.20	5.22×10^{-7}	-	-	-	-254,000	-	-	-	-	7
	SS-304	0.10	5.22×10^{-7}	-	-	-	-254,000	-	-	-	-	7

Table 8.4.2, continued

Element	Alloy	$K_1^{(a)}$	$a_1^{\circ (b)}$	$b_1^{\circ (c)}$	$b_2^{\circ (c)}$	$b_3^{\circ (c)}$	$Q_1^{(d)}$	$Q_2^{(d)}$	$Q_3^{(d)}$	n_2	n_3	δ_r
I	SA-36 carbon steel	3.0	3.49×10^{-5}	-	-	-	-111,000	-	-	-	-	7
	T-22 ^(e)	3.0	3.49×10^{-5}	-	-	-	-111,000	-	-	-	-	7
	Incoloy 800	3.0	3.49×10^{-5}	-	-	-	-111,000	-	-	-	-	7
	Hastelloy X	3.0	3.49×10^{-5}	-	-	-	-111,000	-	-	-	-	7
	SS-304	1.5	3.49×10^{-5}	-	-	-	-111,000	-	-	-	-	7

(a) Units of $\mu\text{g}/\text{cm}^2\text{-geom.}$

(b) Units of Pa^{-1} .

(c) Units of $\text{Pa } \mu\text{g}^{-1} \text{ cm}^2\text{-geom.}$

(d) Units of J mol^{-1} .

(e) FDDM/F also recommends the use of these parameters for sorption on SA-533 alloy.

(f) FDDM/F recommends a value of 3.26×10^{24} .

Table 8.4.3. Parameters for use in the design equations for fission product sorption isotherms on oxidized primary circuit alloys, Eqs. (8.4.1) through (8.4.4) (from Myers, 1984b)

Element	Alloy	$K_1^{(a)}$	$a_1^{(b)}$	$b_1^{(c)}$	$b_2^{(c)}$	$b_3^{(c)}$	$Q_1^{(d)}$	$Q_2^{(d)}$	$Q_3^{(d)}$	n_2	n_3	$\delta_r^{(e)}$
Cs	SA-36 carbon steel	-	-	2.65×10^9	1.57×10^{12}	1.25×10^{14}	273,000	262,000	216,000	3	8	7
	T-22 ^(f)	-	-	2.65×10^9	1.57×10^{12}	1.25×10^{14}	273,000	262,000	216,000	3	8	7
	Incoloy 800	-	-	5.31×10^9	1.26×10^{13}	3.19×10^{16}	273,000	262,000	216,000	3	8	7
	Hastelloy X	-	-	5.31×10^9	1.26×10^{13}	3.19×10^{16}	273,000	262,000	216,000	3	8	7
	SS-304	-	-	5.31×10^9	1.26×10^{13}	3.19×10^{16}	273,000	262,000	216,000	3	8	7
Ag	SA-36 carbon steel	2.0	5.22×10^{-7}	-	-	-	-254,000	-	-	-	-	7
	T-22 ^(f)	2.0	5.22×10^{-7}	-	-	-	-254,000 ^(g)	-	-	-	-	7
	Incoloy 800	1.0	5.22×10^{-7}	-	-	-	-254,000 ^(g)	-	-	-	-	7
	Hastelloy X	1.0	5.22×10^{-7}	-	-	-	-254,000 ^(g)	-	-	-	-	7
	SS-304	1.0	5.22×10^{-7}	-	-	-	-254,000 ^(g)	-	-	-	-	7

Table 8.4.3, continued

Element	Alloy	$K_1^{(a)}$	$a_1^{\circ (b)}$	$b_1^{\circ (c)}$	$b_2^{\circ (c)}$	$b_3^{\circ (c)}$	$Q_1^{(d)}$	$Q_2^{(d)}$	$Q_3^{(d)}$	n_2	n_3	$\delta_r^{(e)}$
I	SA-36 carbon steel	0.40	5.11×10^{-6}	-	-	-	-111,000	-	-	-	-	7
	T-22 ^(f)	0.40	5.11×10^{-6}	-	-	-	-111,000	-	-	-	-	7
	Incoloy 800	0.40	5.11×10^{-6}	-	-	-	-111,000	-	-	-	-	7
	Hastelloy X	0.40	5.11×10^{-6}	-	-	-	-111,000	-	-	-	-	7
	SS-304	0.40	5.11×10^{-6}	-	-	-	-111,000	-	-	-	-	7

(a) Units of $\mu\text{g}/\text{cm}^2\text{-geom.}$

(b) Units of Pa^{-1} .

(c) Units of $\text{Pa } \mu\text{g}^{-1} \text{ cm}^2\text{-geom.}$

(d) Units of J mol^{-1} .

(e) FDDM/F recommends the assumption that $\delta' = \delta$; Myers (1984b) recommends using the same factor as for unoxidized surfaces.

(f) FDDM/F also recommends the use of these parameters for sorption on SA-533 alloy.

(g) FDDM/F recommends a value of -215,000.

encountered within the coolant and PC alloys. However, no sorption data have been obtained for Cs below 345°C, I below 400°C, or Ag below 800°C, although coolant and alloy temperatures decrease to 300°C and lower. With sorption often pronounced at colder temperatures and the limited range of pressures and metallic samples tested, the potential exists for significant uncertainties in the use of these model equations. Because of the paucity of comparative data, these model equations can be considered valid throughout the range of expected reactor conditions but with the proviso that significant uncertainty exists for predictions obtained using these equations. The model equations for Ag must be considered the most questionable as data were obtained beyond both temperature and pressure ranges of interest for the MHTGR, and without the use of metallic samples of interest to MHTGR design.

Assumptions: general

1. Because the use of either the simple Langmuir isotherm or a modified Langmuir isotherm can be used to represent the available sorption data, it is assumed that this formulation is valid for describing the sorption behavior in temperature and pressure ranges outside those used in the reference experiments.
2. Isotherms are derived for the sorption of single species only. Synergistic effects are not considered, although these effects may not be important for the low FP pressures expected within the MHTGR.
3. The effect of possible sorption by dust and aerosols within the coolant on the sorption behavior of the metallic surface is not considered.
4. No chemical reactions of the fission products within the coolant or on the metallic surface which could alter sorption behavior are considered.
5. Equilibrium conditions exist at the interface such that FP plateout on the surface can be accurately modelled using these sorption isotherms.
6. Parameter values for sorption on T-22 (SA-387) alloy can also be used to model sorption on SA-533 alloy (FDDM/F).

Assumptions: unoxidized alloys

1. The sorptivity of any FP is the same for carbon steel SA-36, low-chromium T-22, Incoloy 800, and Hastelloy X, but differs for SS-304.
2. The sorptivities of Cs and Ag are the same on carbon steel SA-36, low-chromium T-22, Incoloy 800, and Hastelloy X as on tungsten.
3. The sorptivity of Cs on unoxidized SS-304 is about a factor of two smaller than on tungsten. This factor of two is assumed to also apply for Ag, and for I on unoxidized T-22.
4. The data on which Ag sorption isotherms are based are assumed to apply to an unoxidized surface.
5. The surface roughness factor as determined for T-22 is assumed to be the same for all alloys.

Myers (1984b) suggests that assumption 3 is supported by experimental data. Experimental support for the other assumptions is less clear.

Assumptions: oxidized alloys

1. Cesium sorptivity is increased by a factor of five on unoxidized surfaces relative to oxidized surfaces for the alloys Hastelloy X and Incoloy 800.
2. The increased sorptivity of Cs on oxidized surfaces of carbon steel SA-36 and low-chromium T-22 is the same as that for SS-304.
3. Cesium sorptivity is increased by a factor of ten on oxidized SS-304 relative to unoxidized SS-304 for MHTGR conditions.
4. On any specific alloy, the sorptivity of Ag increases on oxidized surfaces to the same extent as Cs.
5. The sorptivity of I decreases by a factor of ten on oxidized T-22 relative to unoxidized T-22.
6. The relative sorptivities of I on any oxidized vs. unoxidized surfaces is the same as for T-22.
7. The surface roughness factors for oxidized and unoxidized surfaces are the same.

Myers (1984b) suggests that assumptions 1, 3, and 5 are supported by experimental data. Experimental support for assumption 2 is less clear. Apparently experimental data relating to assumptions 4, 6, and 7 are not available.

Uncertainty

The uncertainties in sorption are given by (Myers, 1984b):

$$\sigma(\log C) = 1 + \frac{N}{1 + e^{1.1(\log P - 14)}} \quad (8.4.6)$$

in which $N = 3$ for SS-304 and $N = 2$ for all other alloys. This equation suggests uncertainties in sorption predictions on the order of 10^3 for MHTGR conditions.

MODEL CHRONOLOGY

Isotherm equations presented in open-literature sources prior to Myers (1984b) were based on Freundlich and Henrian isotherm formulations, unlike the Langmuir isotherm formulation employed by Myers. According to Myers (1984b) FDDM/D contained no data on sorption of fission products on metallic alloys, and the sorption isotherms presented by Myers (1984b) were to replace those in FDDM/E. The sorption isotherms and parameter values presented in FDDM/F are largely identical to those presented in Myers (1984b) except in some minor details as noted in Tables 8.4.2 and 8.4.3.

DISCUSSION

Langmuir isotherm

The Langmuir isotherm is used to describe most of these isotherm equations because it adequately fits the experimental data. The applicability of other forms of the isotherm equations under MHTGR-specific conditions cannot be ruled out. In fact, earlier isotherm model equations derived from the same data were based on a combined Freundlich and Henrian isotherm formulation until replaced by this Langmuir formulation (Myers, 1981c).

The typical form for the Langmuir isotherm is:

$$\theta = \frac{ap}{1 + ap} \quad , \quad (8.4.7)$$

with θ the fractional surface coverage, a the temperature-dependent constant, and p the pressure. The fractional surface coverage is related to the surface concentration by a constant K :

$$C = K\theta \quad , \quad (8.4.8)$$

and combination with Eq. (8.4.7) gives:

$$C = \frac{Kap}{1 + ap} \quad . \quad (8.4.9)$$

Equation (8.4.1) can be obtained from this equation. More information on the Langmuir isotherm and sorption theory can be obtained from Osborne et al. (1982).

Acharya et al. (1984) comment that at the low pressures used in MHTGR simulations, all the isotherms derived from experimental data tend to exhibit perfect sink behavior (i.e., desorption is insignificant). This observation suggests that any sorptive effects by the dust present in the coolant circuit could be significant. Hanson (1977) comments on experimental evidence that volatile metal iodides might form with the sorption of iodine on metals, which could affect iodine sorptivity. In a related comment, Myers (1991) notes evidence that iodine reacts with metallic impurities in the graphite and "will enter the primary circuit as metallic iodides and be distributed accordingly."

Cesium

The Langmuir isotherm assumes the heat of adsorption is independent of surface coverage. The available data indicate this assumption is not correct in the case of Cs. To accurately represent the Cs sorption data, another form for the isotherm equation was chosen [Eq. (8.4.3)]. However, this representation of the Cs data will give increasing error at pressures above 1 Pa, although that should not be a concern for MHTGR conditions.

In 1933, Taylor et al. (1933) obtained detailed data for Cs sorption on tungsten. Myers (1984b) fit these data to Eq. (8.4.3) and obtained the calculated results shown in Figure 8.4.1 for unoxidized surfaces. These results are assumed to accurately describe Cs sorption on all other alloys except SS-304. The sorptivity on unoxidized SS-304 was found to be a factor of two smaller than on tungsten. Cesium sorptivity on oxidized surfaces was found to be five times that of unoxidized surfaces for Hastelloy X and Incoloy 800 (Gas Turbine, 1976a; Abassin et al., 1976). Cesium sorptivity on oxidized SS-304 is a factor of 10 higher than on unoxidized SS-304 at pressures of 10^{-11} to 10^{-10} Pa, and a factor of 100 higher at pressures of 1 Pa. This information was used to obtain the Cs isotherm parameters of Tables 8.4.2 and 8.4.3 as discussed under "Assumptions" above. Table 8.4.1 shows that the only sorption data within the range of expected MHTGR conditions ($\approx 10^{-10}$ Pa) was obtained with tungsten. Data was obtained on MHTGR-relevant alloys at much higher pressures.

Silver

The only reported data for Ag sorption were obtained using tungsten (Ionov et al., 1975). Myers (1984b) fit the data using Eq. (8.4.1), with the calculated results shown in Figure 8.4.2, and states that the data are assumed to apply to unoxidized surfaces. These results are assumed to accurately describe Ag sorption on all other alloys except SS-304. The sorptivity on unoxidized SS-304 is assumed to be a factor of two smaller than on tungsten, the same as Cs. Silver sorptivity on oxidized surfaces is assumed to increase analogously to that of Cs.

Table 8.4.1 shows that the silver on tungsten data were obtained at pressures orders of magnitude greater than that expected for MHTGRs, on a surface whose oxidation state may not have been well characterized. Extrapolation of this one set of data to MHTGR conditions and alloys can introduce significant uncertainty.

Iodine

Data for iodine sorption on T-22 low chromium steel was obtained in by Osborne et al. (1982). Some debate exists over which sorption isotherm (Langmuir, Freundlich, Temkin) best represents the data. The Langmuir isotherm was used by Myers (1984b), and the results for unoxidized T-22 are shown in Figure 8.4.3(a). Data were also obtained for oxidized T-22, and the calculated isotherms are shown in Figure 8.4.3(b). These results are assumed to accurately describe I sorption on all other alloys except SS-304. The sorptivity on unoxidized SS-304 is assumed to be a factor of two smaller than the other alloys. The sorptivity on oxidized T-22 is assumed to be ten times smaller than on unoxidized T-22, and this ratio is assumed to apply for all other oxidized vs unoxidized alloys. The combination of these assumptions with the use of pressures significantly larger than expected for MHTGR conditions introduces significant uncertainty into the model sorption isotherms for iodine.

Fig. 8.4.1. Sorption isotherms for cesium on unoxidized tungsten. Solid curves represent Taylor-Langmuir curves, symbols represent calculated points (from Myers, 1984b).

Fig. 8.4.2. Sorption isotherms for silver on tungsten. Solid curves represent data from Ionov et al. (1975), symbols represent calculated points (from Myers, 1984b).

Fig. 8.4.3.a. Sorption isotherms for iodine on unoxidized T-22. Solid curves represent fits to the data, symbols represent experimental data (from Myers, 1984b).

Fig. 8.4.3.b. Sorption isotherms for iodine on oxidized T-22. Solid curves represent fits to the data, symbols represent experimental data (from Myers, 1984b).

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The statement by Acharya et al. (1984) that "our data base and/or methodology appear to be grossly inadequate" for accurate plateout calculations suggests further model development would be helpful. They then review some of the limitations of the database for sorption on PC alloys, similar to those discussed above.

Acharya et al. (1984) and Jovanovic (1988) comment on the possible significance on the effects of dust and aerosols within the coolant on the concentration of FP sorbed on the metallic surfaces, and the existence of some experimental data which indicates iodine may chemically react with a metallic surface. The possibility of iodine circulation and retention in the form of metallic iodides has been previously mentioned. The potential effects of these factors on the sorption by PC alloy surfaces might be considered in more detail.

Tritium permeation into metals and alloys has been well studied in relation to engineering of fusion reactors, including the effects of surface conditions and oxidation on permeation rates (see §9.7). Available literature might provide insight into the effects of surface conditions on FP sorption on PC alloys.

The scientific literature in general has likely not been reviewed in recent years for new sorption data or phenomenological understanding. Such a review might be in order, although MHTGR-specific data might not be located. Relevant MHTGR-specific data is expected from the COMEDIE series of plateout/liftoff tests. COMEDIE involves several integral tests designed to validate the MHTGR design methodology and computer codes for plateout/liftoff calculations. The apparent contradiction of performing integral validation tests while questions remain unanswered such as those by Acharya et al. (1984) will not be commented on here.

DATABASE USED IN MODEL DEVELOPMENT

Table 8.4.1 is located within the text. Figures 8.4.1 through 8.4.3 are presented below.

8.5 DIFFUSION IN PRIMARY CIRCUIT ALLOYS

function	This model provides diffusion coefficients for Cs and Ag in primary circuit alloys as a function of temperature and oxidation state of the alloy surface.
present status	"The current data base is inadequate to estimate the importance of diffusion of deposited radionuclides into the interior of structural metals ..." (CEGA, 1990). Data for only Cs and Ag diffusion in nonreference alloys are available upon which to base models. The effect of surface oxidation of the alloys on indiffusion is largely unknown.

- model** For Cs, the uncertainty "is estimated to be $9 \times 10^{4\%}$ " (Myers, 1988). The
- uncertainty** uncertainty for Ag indiffusion is comparable. The potential effects of surface oxidation on indiffusion also introduce uncertainty.
- references** Iniotakis et al. (1984); Chawla et al. (1981)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

Transport of metallic FP in the PC alloys is defined by the traditional diffusion equation:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right), \quad (8.5.1)$$

- D = diffusion coefficient ($\text{m}^2 \text{s}^{-1}$),
 D_0 = pre-exponential factor ($\text{m}^2 \text{s}^{-1}$),
 Q = activation energy (J mol^{-1}),
 T = temperature (K),
 R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

Values for D_0 and Q have been determined for Cs and Ag in several alloys. These values are listed in Table 8.5.1. FDDM/F recommends using the values presented in Table 8.5.1 for Cs sorption on oxidized and unoxidized alloys and for Ag sorption on all alloys and surface conditions.

Range of validity

For lack of additional data, the parameters given in Table 8.5.1 are assumed to hold over all reactor operating conditions and temperatures.

Experimentally, the data for Ag indiffusion of Chawla et al. (1981) was obtained using the nickel-based alloys Rene 100 and Inconel 713C in the temperature range of 600 to 800°C for annealing times from 600 to 2760 h. The initial Ag surface concentration is represented by a deposited surface layer of Ag. The surface condition of the alloys (i.e., oxidized vs. unoxidized) is not commented upon in Chawla et al. (1981).

The data for Cs indiffusion is based on a loop experiment for Cs deposition on Nimocast 713 LC alloy "in the temperature range from 800°C to 90°C under turbulent gas flow conditions." However, the derived diffusion coefficient may be applicable over a much smaller temperature range for the alloy structure into which the Cs is diffusing. For example, analysis of Fig. 8.5.1 (from Iniotakis et al., 1984) suggests a relevant temperature range of 650 to 750°C. No other discussion of experimental conditions is available from Iniotakis et al. (1984).

Table 8.5.1. Parameters for calculation of metallic fission product diffusion coefficients in primary circuit alloys, Eq. (8.5.1)

Fission product	Alloy	Surface ^(a)	D_0 ($\text{m}^2 \text{s}^{-1}$)	Q (J mol^{-1})	Temp. range ($^{\circ}\text{C}$)	Ref.
Cs	Nimocast 713 LC	Unox.	2.1×10^{-13}	69,000 ^(b)	650-750 ^(c)	Iniotakis et al. (1984)
Cs	Nimocast 713 LC	Ox.	8.4×10^{-15}	110,000 ^(b)	650-750 ^(c)	Iniotakis et al. (1984)
Ag	Rene 100	Unox., ox. ^(d)	2.5×10^{-11}	137,000	600-800	Chawla et al. (1981)

- (a) Unox. = unoxidized surface,
Ox. = oxidized surface.
- (b) Iniotakis et al. (1984) give different values for Q , but do not specify the units; if given in cal mol^{-1} , conversion to J mol^{-1} gives the above values which appear in FDDM/F.
- (c) Estimated temperature range determined from Fig. 8.5.1 (from Iniotakis et al., 1984).
- (d) FDDM/F states that these diffusion parameters are applicable for both oxidized and unoxidized surface conditions; Chawla et al. (1981) do not comment on the state of the alloy surfaces.

Assumptions

1. Diffusion data for these alloys is representative of that expected for the reference alloys [800H, 2-1/4% Cr-1% Mo, SA-533 (CEGA, 1990)] to be used in the MHTGR PC.
2. This diffusion data can be accurately extrapolated to temperature ranges outside those of the experiments.
3. Diffusion of Ag into PC alloys is the same for oxidized and unoxidized alloy surfaces.
4. The diffusion coefficient will not vary as a function of surface concentration of diffusant (specifically, a thin layer of Ag on the surface is assumed to provide diffusion data representative of that from the lower surface concentrations expected under realistic MHTGR operating conditions).
5. The theoretical model used by Iniotakis et al. (1984) to approximate Cs deposition, diffusion into the alloy, growth of the surface oxide layer, and effect of the oxide layer on diffusion is sufficiently accurate to provide a reliable diffusion coefficient for Cs in Nimocast 713 LC.

Fig. 8.5.1. Saphir 11: deposition of ^{137}Cs and ^{134}Cs along the tube of experiment Pegase 11 (from Iniotakis et al., 1984).

Uncertainty

For both Cs and Ag, the standard deviation in the natural logarithm of the diffusion coefficient is given by (FDDM/F):

$$\sigma (\ln D) = 6.9 \quad (8.5.2)$$

MODEL CHRONOLOGY

The model equations for Cs and Ag indiffusion into PC alloys are taken directly from the source references, therefore no model development exists per se.

DISCUSSION

Potential diffusion of FP metals from the surface into the bulk of the primary circuit alloys as well as their incorporation into surface oxide layers could be significant in reducing the surface inventory available for resuspension during liftoff, as well as altering the boundary conditions of surface concentration under which the equilibrium sorption isotherms are evaluated.

Table 8.5.2 expands Table 8.5.1 to include additional diffusion information beyond that listed in FDDM/F, specifically diffusion coefficients for Ag in two other nickel-based alloys. Two quotes are appropriate here. In reference to DDN 11.50, CEGA (1990) states that the "diffusivities of cesium in primary-circuit metals are needed under normal operating conditions, with special attention to the effects of surface films, in order to determine whether or not indiffusion must be explicitly modeled under MHTGR operating conditions." Myers (1988) states: "Perhaps of more importance than diffusion of fission products in primary circuit alloys is their diffusion and incorporation in the oxide layers of the alloys formed during normal operation and in the oxide layers as restructured during reactor shutdown. Here again, a whole field of work has been neglected; a literature search and analysis would improve the state of local knowledge drastically ... The diffusion and incorporation of fission products in the oxide layers of the primary circuit alloys is directly connected to the sorption process and perhaps to the isotherms. If diffusion and incorporation do occur in oxide layers to an enhanced degree, the distribution of the fission products between the vapor and solid phases will be altered in a way not now taken into account."

Indiffusion of silver

The only data presently available for FP indiffusion into alloys relevant to gas-cooled reactors is given in two references, Chawla et al. (1981) and Iniotakis et al. (1984). Chawla et al. measured the diffusion of Ag into the nickel-based high-temperature alloys Rene 100 and Inconel 713C between 600 and 800°C. In addition, they report the diffusion coefficient for Ag in Inconel 713C at 800°C. Although experiments for Cs diffusion were also attempted, Chawla et al. report only limited success, largely due to "the weak specific activity

Table 8.5.2. Additional parameters for calculation of metallic fission product diffusion coefficients in primary circuit alloys

Fission product	Alloy	Surface ^(a)	D_0 ($\text{m}^2 \text{s}^{-1}$)	Q (J mol^{-1})	Temp. range ($^{\circ}\text{C}$)	Ref.
Cs	Nimocast 713 LC	Unox.	2.1×10^{-13}	69,000 ^(b)	650-750 ^(c)	Iniotakis et al. (1984)
Cs	Nimocast 713 LC	Ox.	8.4×10^{-15}	110,000 ^(b)	650-750 ^(c)	Iniotakis et al. (1984)
Ag	Rene 100	U	2.5×10^{-11}	137,000	600-800	Chawla et al. (1981)
Ag	Inconel 713C	U	4.75×10^{-8}	203,000	600-800	Chawla et al. (1981)
Ag	Inconel 738	U	$1.3 \times 10^{-18(d)}$	(d)	800	Chawla et al. (1981)

- (a) Unox. = unoxidized surface;
Ox. = oxidized surface; and
U = unknown.

- (b) Iniotakis et al. (1984) give different values for Q , but do not specify the units; if given in cal mol^{-1} , conversion to J mol^{-1} gives the above values which appear in FDDM/F.
(c) Estimated temperature range determined from Fig. 8.5.1 (from Iniotakis et al., 1984).
(d) Diffusion coefficient was only measured at 1800°C , therefore $D \equiv D_0$.

of Cs-137." The motivation for these experiments was to obtain data relevant to FP diffusion in turbine-like alloys for direct-cycle gas-turbine HTGRs. The experiment involved the deposition of a very thin layer of Ag metal (containing $^{110\text{m}}\text{Ag}$) on the surface of the alloy (semi-infinite specimen geometry), followed by a high-temperature anneal, after which surface layers were removed by grinding ($\pm 0.5 \mu\text{m}$ accuracy) and gamma-counted for $^{110\text{m}}\text{Ag}$ activity. Calculation of the diffusion coefficient from these results is described in Chawla et al. (1981). The individual diffusion coefficients measured at each temperature are given in Table 8.5.3 [refer to Chawla et al. (1981) for the raw data used to derive these diffusion coefficients], and these results are plotted in Fig. 8.5.2. The diffusion parameters listed in Tables 8.5.1 and 8.5.2 were obtained from the data of Fig. 8.5.2 using least squares analysis.

Table 8.5.3. Summary of data on silver diffusion experiments (from Chawla et al., 1981)

Run No.	Temp (°C)	Time (h)	Alloy	D(m ² /s)
3	800	1003.	IN 738	1.3(-18)
4A	800	714.	RENE 100	1.2(-17)
4B	800	714.		7.2(-18)
5A	800	337.		2.1(-18)
5B	800	337.		3.8(-18)
8A	600	2690.		9.8(-20)
8B	600	2690.		2.1(-19)
9A	600	2760.		~7.9(-19)
9B	600	2760.		~5.9(-20)
10A	600	816.		1.1(-19)
10B	600	816.		1.1(-19)
4A	800	714.	I-713C	6.4(-18)
4B	800	714.		4.2(-18)
5A	800	337.		1.4(-17)
5B	800	337.		3.8(-18)
7A	700	600.		3.9(-19)
7B	700	600.		9.0(-19)
10A	600	816.		(a)
10B	600	816.		(a)

(a) Fluctuations in data prevent estimate of diffusion coefficient.

Fig. 8.5.2. Dependence of the diffusion coefficients for Rene 100 ($\odot$) and Inconel 713C (Δ) on temperature (from Chawla et al., 1981).

Chawla et al. give the uncertainty for Ag diffusion in the form:

$$\sigma(\ln D) = \left[a + b \left(\frac{10^4}{T} \right) + c \left(\frac{10^4}{T} \right)^2 \right]^{1/2}, \quad (8.5.3)$$

$\sigma(\ln D)$ = standard deviation in the natural logarithm of the diffusion coefficient,
 T = temperature (K).

For Rene 100:

$$\begin{aligned} a &= 7.468, \\ b &= -1.395, \\ c &= 0.066. \end{aligned}$$

For Inconel 713C:

$$\begin{aligned} a &= 26.742, \\ b &= -5.533, \\ c &= 0.287. \end{aligned}$$

The uncertainty expression for Rene 100 differs from that recommended in FDDM/F (see "Uncertainty" above). The reason for this difference is unknown. Although Chawla et al. state that the dashed lines in Fig. 8.5.1 were obtained using Eq. 8.5.3 and represent 95% confidence bounds, it is obvious that two data points for Rene 100 lie well outside these confidence bounds. The larger uncertainty recommended by FDDM/F might better include these data points within the confidence bounds.

It should be noted that FDDM/F recommends using the diffusion parameters for the alloy Rene 100 in MHTGR design, rather than those reported for Incoloy 713C. The chemical composition of these two alloys is unknown to this writer, therefore the reason for the preference for Rene 100 data is unknown.

Indiffusion of cesium

The data for Cs indiffusion is based on results from the Saphir 11 loop experiment in the Pégase reactor in Cadarache. This loop experiment included stainless steels 4541 and 4961, Inconel 625, and Nimocast 713 LC. The plateout model described in Iniotakis et al. (1984) was used to predict deposition on the metallic surfaces and subsequent indiffusion of Cs into the Nimocast 713 LC alloy. Detailed discussion is not provided for the experimental conditions, the experimental Cs indiffusion data, or the methodology with which plateout, oxide layer growth, and indiffusion into the alloy were calculated. The results of the analysis are summarized in Fig. 8.5.3 and compared to the experimental results. By coupling an equation for the time-dependent growth of the oxide layer, a parametric evaluation of approximate diffusion coefficients, and comparison of these results

Fig. 8.5.3. Saphir 11: diffusion profile of ^{137}Cs in Nimocast 713 LC (from Iniotakis et al., 1984).

to the experimental data (Fig. 8.5.3), Iniotakis et al. (1984) were able to determine diffusion coefficients which provided agreement between their model and the experimental results. They comment that the "influence of the oxide layer, and consequently, of the oxidation rate, is important for the Cs diffusion. A compact oxide layer creates a considerable diffusion barrier for Cs. The destruction of the oxide layer (e.g., by erosion) reduces its protection effect against Cs diffusion."

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Both Myers (1988) and Iniotakis et al. (1984) comment on the significance that formation of an oxide layer can have on the diffusion of FP metals into the PC alloy structure. This phenomenon should be investigated and understood in more detail, beginning with the literature survey recommended by Myers.

The possible effect of surface concentration on diffusion should be considered for the Ag data (i.e., diffusion from a thin deposited layer vs diffusion from a surface concentration on the order of a monolayer). The additional uncertainty introduced by the lack of information on the surface state of the alloys used for the Ag diffusion measurements might also be considered, if possible.

A general review of the scientific literature for additional diffusion data of FP elements in structural alloys might expand the database beyond Cs and Ag and provide more information on the surface effects mentioned above.

DATABASE USED IN MODEL DEVELOPMENT

For Ag, the database is represented by Table 8.5.3 and Fig. 8.5.2 (from Chawla et al., 1981). The database for Cs consists of Fig. 8.5.3, with background information from Fig. 8.5.1 (from Iniotakis et al., 1984).

8.6 REMOVAL OF DEPOSITED FISSION PRODUCTS FROM PRIMARY CIRCUIT ALLOYS

8.6.1 INTRODUCTION

Depressurization of and water ingress to the primary circuit are important accident scenarios for the MHTGR (Myers, 1986). A significant coolant leak would disturb the coolant flow patterns (blowdown) and the resultant shear stresses at the walls with the potential for blowing deposited fission and activation products off the PC piping surfaces (liftoff) and generating a significant AC source term. Likewise, water ingress in the form of steam (steamoff) or liquid water (washoff) could wash the radioactive species from the surfaces and induce their subsequent transport. Although liftoff occurs to some extent under NOC, the magnitude is small and the steady-state relationship between plateout and liftoff mitigates concern over NOC liftoff. According to the reference model, liftoff becomes a concern under AC when the shear stress on the deposited activation products exceeds that

under NOC. Alternative models exist for plateout/liftoff phenomena such as the turbulent burst model (Wichner, 1991), with kinetic processes at the surface dominated by occasional turbulent bursts within the laminar sublayer. Steamoff and washoff can only occur under AC conditions in a helium-cooled system.

As discussed below, the data on which to base models for these phenomena is quite limited. Hanson (1983) recognized that the "most pressing fuel performance Design Data Need for the [MHTGR] appears to be defensible liftoff data" such as that envisaged by the current COMEDIE loop experiment (although that experiment is designed to validate existing models and codes rather than to develop improved models).

Sections 8.6.2, 8.6.3 and 8.6.4 will present the current reference models for liftoff, steamoff, and washoff as presented by Myers (1986) and incorporated into FDDM/F. Myers (1986) lists several phenomena relevant to liftoff and water ingress events: particle entrainment, desorption, diffusion, solution, vaporization, and aerosol formation, with particulates discussed in greatest detail. The relevance of particulates to liftoff and related modes of FP transport will be briefly presented in §8.7.

8.6.2 LIFTOFF

function	This model calculates the AC fractional liftoff of FP deposited on PC alloy surfaces as a function of the coolant shear stress along the surfaces.
present status	The present model is limited by large scatter in the available data and by the current limited understanding of the phenomena which may play a role in liftoff of deposited FP from primary circuit alloys.
model uncertainty	Because of the scatter in the data, only one data set is used to derive the current model (Myers, 1988), resulting in a very large uncertainty. The potential significance of release by liftoff during accident conditions mandates further analysis and experimentation.
references	Myers (1986, 1988); Hanson (1983); CEGA (1990); Wichner (1991)

ACCIDENT CONDITIONS

Model equations

The model equations for liftoff are given by (Myers, 1986; FDDM/F):

$$L = L_o + \Delta L \quad , \quad (8.6.2.1)$$

$$\Delta L = \frac{100 m (SR - 1)}{100 + m (SR - 1)}, \quad (8.6.2.2)$$

- L = fractional liftoff (%),
 L_o = fractional liftoff for $SR \leq 1.0$, based on experimental data (%),
 ΔL = incremental increase in liftoff for $SR > 1.0$ (%),
 SR = ratio of shear stress during blowdown to that during NOC (dimensionless),
 m = constant (dimensionless).

Values for L_o and m are given in Table 8.6.2.1. The incremental liftoff values for ^{137}Cs and ^{90}Sr as calculated from the above equations are shown in Fig. 8.6.2.1 (taken from Myers, 1986) as a function of the shear stress ratio.

Range of validity

1. This model is assumed to be valid for all shear stress ratios which may be experienced under accident conditions ($SR > 1.0$).
2. The model only considers liftoff from the reactor surfaces. The fraction of mobile activated species which actually escapes the reactor is not considered by this model.
3. This model should be used only under dry conditions. In the presence of steam or water, the models in §8.6.3 and §8.6.4 should be used.

Assumptions

The following assumptions are obtained from Myers (1986).¹

1. The available experimental data are adequate for providing, at least, a minimum value of liftoff.
2. All available liftoff data are considered equally valid for model development.
3. The experimental values of liftoff at $SR = 1$ for the out-of-reactor tests are attributed to the effects of sample handling.
4. The slope of each experimental curve of liftoff vs shear stress ratio at $SR = 1$ is assumed to represent the actual relationship of liftoff to SR in the absence of handling effects.
5. Data from the single in-pile experiment are assumed to represent the true liftoff for $SR \approx 1$.
6. 100% of the deposited FP can be removed by liftoff if SR is sufficiently large.

¹The relevance of these assumptions to the model as presented is discussed or inferred by Myers (1986). This is not to say that Myers (1986) supports or justifies the use of these assumptions.

Table 8.6.2.1. Constants for use in the model equations for fission product liftoff from primary circuit alloys, Eqs. (8.6.2.1) through (8.6.2.3) (from FDDM/F)

Isotope	L_o (%)	m	ℓ_1	ℓ_2
^{137}Cs	0.19	0.4	15	112
^{131}I	0.15	1.2	30	27
^{90}Sr	0.54	2.6	30	22
$^{110\text{m}}\text{Ag}$	0.01	1.2	18	65
$^{129\text{m}}\text{Te}$	0.09	1.2	18	65
^{125}Sb	0.09	1.2	18	65

In addition:

- Liftoff from all alloy surfaces can be represented by the same model and model parameters (Table 8.6.2.1) for each isotope.

Uncertainty

The upper limit for liftoff observed during the experiments is given by Myers (1986):

$$L_{ul} = \ell_1 + \frac{(100 - \ell_1) SR}{\ell_2 + SR}, \quad (8.6.2.3)$$

L_{ul} = experimental upper limit of liftoff (%),
 ℓ_1, ℓ_2 = constants (dimensionless).

Values for ℓ_1 and ℓ_2 are given in Table 8.6.2.1. The upper limit liftoff values for ^{137}Cs and ^{90}Sr as calculated from Eq. (8.6.2.3) are shown in Fig. 8.6.2.1 as a function of the shear stress ratio. Equation (8.6.2.3) represents the upper 95% confidence limit.

MODEL CHRONOLOGY

In past years GA typically used an assumption of 1% for fractional liftoff (Hanson, 1983). This assumption was only justifiable if it were assumed that all out-of-pile experiments are invalid, although such an assumption restricts model development to a single "valid" experiment (Myers, 1988). The current model was developed from all available data, presented by Myers (1986), and adopted by FDDM/F.

Fig. 8.6.2.1. Net nominal [$\Delta L(\%)$] and upper limit (ul) liftoff values for ^{137}Cs and ^{90}Sr as a function of the shear stress ratio (from Myers, 1986).

DISCUSSION

Design Data Needs

CEGA (1990) discusses some of requirements for model development in DDN 11.51, "Radionuclide Reentrainment Characteristics for Dry Depressurization." "Correlations are required which give the fractional liftoff of the radiologically important radionuclides I, Sr, and Cs as a function of the controlling system parameters. Test variables which must be investigated include shear ratio, absolute wall shear stress, blowdown duration, temperature, humidity, and surface oxidation state ..."

Database available for model development

CEGA (1990) goes on to summarize the current database for liftoff models. "The present data base for the validation of radionuclide liftoff methods is extremely limited and does not explicitly account for the effects of dust. In the single in situ blowdown test of the CPL 2/4 in-pile loop, <0.5% liftoff of the plateout activity was observed. However, the maximum shear ratio realized in the CPL 2/4 blowdown was only 1.08 so these data do not provide a comprehensive test of a candidate liftoff model. Moreover, the CPL 2/4 loop was known to contain an inordinate amount of metal oxide aerosol; consequently, the CPL 2/4 data are likely to be biased high.

"Despite their limitations, the CPL 2/4 data do provide reason to believe that the release from the primary circuit due to liftoff will be $\leq 1\%$ for the design basis events involving rapid depressurization. However, the existence of questionable ex situ blowdown data showing much higher liftoff ... and no comprehensive independent data base to refute these results have led to a liftoff model with excessive uncertainty and perhaps excessive conservatism for use in the analysis of depressurization transients."

Much of the experimental liftoff database is summarized in Table 8.6.2.2, taken from Myers (1986). In this table, the liftoff at $SR = 1$ is represented by "%I." Reference is made by Myers (1986) to a 1985 report by K. Downey ("Summary of Fission Product Liftoff Data Base," GA Technologies Document No. 908332/0) which probably provides a more complete compilation, but which has not been obtained by this writer for analysis.

Hanson (1983) provides more detail on the state of the liftoff database as of 1983: "... the current liftoff data base is badly scattered and contradictory ... The most extensive set of liftoff tests were the CPL 2 liftoff tests performed by the CEA ... The CPL 2 results were also badly scattered but generally indicate liftoff fractions an order of magnitude higher than the [earlier GA] reference 1% assumption" (i.e., 5 to 30% liftoff).

"With one exception all existing liftoff data are inherently flawed because they resulted from so-called 'out-of-pile' liftoff tests. In other words, the fission product activity was deposited in an inpile loop, and then sections of contaminated piping or heat exchanger tubes were mechanically cut out of the loop and blown down in an out-of-pile test rig. Not only could the cutting and handling operations compromise the test specimens but also exposure to ambient air may alter the chemical state of the deposited fission products and/or

Table 8.6.2.2. Analysis of experimental liftoff data in terms of the normal dependence of liftoff on the shear stress ratio (slope) and of the absolute liftoff (%I) (from Myers, 1986)

Source	Ca-137			I-131			Sr-90, -85		
	Metal	Slope(a)	$\chi I(b)$	Metal	Slope(a)	$\chi I(b)$	Metal	Slope(a)	$\chi I(b)$
GAIL IV		0.31	0.0	--	--	--		3.75	0.0
DEP LOOP 4		0.02	0.02	(loop3)	0.06	0.22	(loop5)	2.80	23.0
CPL 2/1		0.75	10.5		0.27	29.4		4.21	23.7
CPL 2/3	Inc800	0.58	2.0	Inc800	1.33	2.3	Inc800	3.30	20.8
CPL 2/3	T22	0.56	0.5	T22	?	0.7			
CPL 2/4	Inc800	0.80	7.6	Inc800	1.23	7.6			
CPL 2/4	Inc800	0.65	8.6	Inc800	1.05	19.0			
CPL 2/4	Hast. B	0.03	7.7	Hast. B	2.50	31.0			
CPL 2/4	SS410	0.05	7.8	SS410	0.10	5.3			
CPL 2/4	T22	0.04	2.4	T22	0.0	1.9			
CPL 2/4	SS347	0.00	16.9	SS347	4.25	31.5			
CPL 2/1 BIS		0.29	2.2	--	--	--			
P.B.	Inc800	0.65	0.7	--	--	--	Inc800	0.93	0.0
P.B.	Carbon Steel	0.92	4.5	--	--	--	Carbon Steel	0.86	3.1
AVERAGE		0.40	5.5(c)		1.20	12.9		2.64	14.1
$\pm$ SD		± 0.33	± 4.9		± 1.40	± 13.4		± 1.43	± 11.6

(a) Slope in χ liftoff/SR

(b) χI is intercepted Sr=1 in percent

(c) GAIL IV data excluded because of full flow filter in circuit

the plateout surfaces. The effects on the liftoff behavior is unknown, but the attendant results have been advertised as conservative.

"The above limitations in the liftoff data base have long been recognized, and a series of in situ liftoff tests were planned as part of the CPL 2/4 test [in the Pegase reactor in Cadarache, France] ... fission products were to be deposited in an inpile loop, and then the entire loop was to be subjected to a series of blowdowns at successively higher shear ratios. (... intuitively, no liftoff should occur if the $SR \leq 1.0$). The first of the planned CPL 2/4 in situ blowdowns, at the shear ratio of ~ 1.0 , was completed, and the results were encouraging: the measured liftoff fractions for Sr-90 and I-131 were 0.5% and 0.15%, respectively, at a maximum $SR = 1.02$. Unfortunately, equipment failure prevented further blowdowns at higher shear ratios so no liftoff correlation resulted."

Myers (1986) recognizes the likelihood of the explanation presented above for the high liftoff values of the out-of-pile experiments, but also postulates the possibility that "the large liftoff values are intrinsic to the constant liftoff and redeposition of large particles occurring during loop or reactor operations" rather than arising from an inherent flaw of the experiments. This hypothesis can be supported as follows. "For the ex situ tests, the particulates removed during the blowdown tests were collected immediately down stream so that removal of larger particulates prior to reaching the collector was improbable. During the in situ test, the particulates made about 15 trips around the circuit before collection ... thus, large particulates would have been redeposited ... and would not have been collected. Contributing to this possible behavior was the decreasing flow speed during blowdown." Another point is made that "[a]nother difficulty with the first hypothesis is the absence of a large initial liftoff, generally, in the GAIL IV and GA Deposition Loops [see Table 8.6.2.2]. Were the samples from these loops treated differently?" Additional discussion is provided by Myers (1986).

Model development

The reference assumption of 1% for fractional liftoff used by GA in the early 1980s became untenable in light of the data mentioned above. As stated in "Assumptions" above, the experimental values of liftoff at $SR = 1$ for the out-of-reactor tests are attributed to the effects of sample handling, while the slope of each experimental curve of liftoff vs SR at $SR = 1$ is assumed to represent the actual relationship of liftoff to SR in the absence of handling effects. These values are listed in Table 8.6.2.2 for each experiment. According to Myers (1986), the slope and liftoff at $SR = 1$ increase in the series $Cs < I < Sr$.

The general form of an ideal liftoff curve is shown in Fig. 8.6.2.2, taken from Myers (1986). For $SR \leq 4$, the experimental data is cast in the form:

$$L = a + b (SR - 1) , \quad (8.6.2.4)$$

L = fractional liftoff (%),

SR = ratio of shear stress during blowdown to that during NOC (dimensionless),

a, b = constants (%),

Fig. 8.6.2.2. Idealized experimental liftoff profile for the ex situ experiments (from Myers, 1986).

and plotted in Fig. 8.6.2.3 for Cs, I, and Sr (from Myers, 1986). To develop a model which predicts 100% liftoff at very large values of SR, the incremental component of Eq. (8.6.2.4) was recast in the form of equation (8.6.2.2), which extended the model to the SR values shown in Fig. 8.6.2.1. Myers (1986) reports that use of Eq. (8.6.2.2) rather than Eq. (8.6.2.4) "entails an error of 10% or less for the isotopes listed in Table [8.6.2.1] at shear ratios of 10 or less except for Sr-90 where the error is 23% or less."

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Several phenomena are recommended (Myers, 1988) for consideration in evaluating future liftoff experiments and data: spallation of surface layers and scales from the primary circuit alloys during reactor shutdown, cyclic redeposition and liftoff of particulate matter during NOC, the behavior of particulate matter in general (composition, formation, and distribution), and the sources of particulate matter (oxide layers, carbon dust from the core graphite, and clustering of FP and alloy atoms). Myers (1986) discusses these recommendations in more detail. Particulate phenomena are discussed further in §8.7.

If the large liftoff values from the out-of-pile blowdown tests result from constant liftoff and redeposition of large particles, as postulated by Myers (1986), then these large particles have the potential of quickly settling out rather than enhancing dispersal of the radioactive species from the reactor as the large liftoff values would suggest.

A comprehensive review on plateout and liftoff in MHTGR systems has recently been completed by R. P. Wichner (1991). This review has not yet been incorporated into this compilation but should be referred to for detailed discussion of suggestions and approaches to model development.

DATABASE USED IN MODEL DEVELOPMENT

The existing liftoff database is indicated by Table 8.6.2.2, although not all the source data is provided by this table. More detailed presentation of the database would be expected in the document by K. Downey referenced above.

8.6.3 STEAMOFF

function	This model provides a value for fractional removal by steam of FP deposited on PC alloy surfaces, without functional dependencies.
present status	The present model for steamoff is based on one experiment for the fractional removal of iodine, the results of which varied widely. No other fission products have been evaluated, and the resulting model is very approximate.

Fig. 8.6.2.3. Liftoff vs shear stress ratio for Sr, I, and Cs (from Myers, 1986).

model uncertainty	The uncertainty is very large and has been stated to range from 0 to 1 (Myers, 1988).
references	Myers (1986, 1991)

ACCIDENT CONDITIONS

Model equations

The fractional removal of FP from PC alloy surfaces by steam is assumed to be (Myers, 1986):

$$S = 60 \% , \quad (8.6.3.1)$$

S = fractional steamoff (%).

This 60% removal rate is assumed to hold for all FP, due to lack of data.

Range of validity

The model is assumed to be valid under all conditions. In the experiment, the initial iodine loading on one-inch tubes of T-22 alloy (also referred to as SA-387 alloy or 2-1/4% Cr-1% Mo) by approximately 0.11 Pa iodine was approximately $10 \mu\text{g}/\text{cm}^2$ of geometric surface area at 310°C , followed by steamoff at 200°C with steam flowing at the rate of 7.1 L min^{-1} (STP) from 400 ml of water. Visual inspection after loading suggested the presence of oxidation on the T-22 surface.

Assumptions

1. Steamoff of all FP will be comparable to that of iodine.
2. Steamoff from the surface of T-22 alloy is characteristic of steamoff from other PC alloys.
3. Kinetic effects of the steamoff process are not significant.
4. The experimental conditions provide results characteristic of in-reactor conditions.

Uncertainty

The uncertainty is assumed to range from 0 to 100% (Myers, 1986).

MODEL CHRONOLOGY

The current model for steamoff was presented by Myers (1986) and incorporated into FDDM/F.

DISCUSSION

This steam-induced removal has also been referred to as steam cleaning (Myers, 1986). Steamoff was previously subsumed as a subcategory of washoff, but steamoff is now frequently differentiated from washoff, reportedly on the basis of a recommendation by R. P. Wichner of ORNL (Myers, 1986) [although CEGA (1990) still categorizes washoff as including steamoff].

Model development

The only data available with which to develop a model for steamoff are reported (Myers, 1986) to be from a scoping study to determine an approximate value for the fraction of sorbed iodine removed from the surface of T-22 alloy by steam. This experiment is attributed to F. C. Montgomery and K. E. Partain, but no references are given. Details of the experiment are presented by Myers (1986) and are briefly summarized above in "Range of validity." Analysis of the sorbate indicated that no molecular iodine was sorbed (i.e., only iodide was sorbed). The experimental data is given in Table 8.6.3.1 (from Myers, 1986). Two tests were conducted, with the first test showing 60% removal of the sorbed iodide and the second test showing no iodide removal. However, the second test was considered uncharacteristic and was not considered in development of the model. The T-22 specimens in this second test were soaked in an acidic solution for 1.5 h followed by "active scrubbing" of the surfaces to remove oxide layers. After treatment with steam, the surfaces of these specimens were visually different from those of the first test (see Fig. 8.6.3.1). The conditions under which the first test were conducted are considered to be more typical of in-reactor conditions than those of the second test, thus only the first test results were considered in development of the model (Myers, 1986).

Several other observations are made by Myers (1986) that might be relevant for a steamoff model.

1. In the first test, of the total iodide removed by the steam, only 13% was found in the water condensate. Most of the iodide must have escaped as a vapor. The question then arises, could redeposition of these gaseous iodine species within the PC reduce the steamoff fraction available for release from the reactor under actual conditions?
2. The observation is made that "the amount of iodide removed is roughly linearly proportional to the amount of steam passing the surface up to the point where steam no longer removes iodide." Thus the fractional steamoff may be a function of the exposure conditions to the steam, rather than a constant value as the model suggests.
3. The concentration of sorbed iodide exceeds the maximum predicted ($0.4 \mu\text{g}/\text{cm}^2\text{-geom}$) using the model equations for sorption provided in FDDM/E (Myers, 1986). The model equations were modified in FDDM/F in such a way that results are invalid for concentrations greater than $0.4 \mu\text{g}/\text{cm}^2\text{-geom}$ (refer to §8.4). This large experimental concentration may be due to (Myers, 1986): (1) a large surface roughness factor for the oxide surface (see §8.4) or (2) the possible formation of FeI_2 on the surface due to the large iodine vapor pressure.

Table 8.6.3.1. Summary of experimental results on iodine loading and steam cleaning experiments (from Myers, 1986)

A. Iodine Loading Experiments (310°C)

Test No.	Sample No.	Total Iodine Loading (μg)	Total Iodide Loading (μg)	Geometric Surface Conc. (μg/cm ²)
1	1	0	440	9.9
	2	0	420	9.5
2	1	0	350	7.9
	2(a)	0	525	11.8

B. Steam Cleaning Experiments (200°C)

Test No.	Loading of Companion Sample (μg)	Loading of Test Sample After (μg)(b)	Condensate Fraction		
			No.	Vol (ml)	Iodide Conc. (μg)
1	430 ± 10	176	1	100	18
			2	100	5
			3	200	0
2	350	-525	1	400	0

(a)Data for this sample are post steam-cleaning values.

(b)Loading of test sample after completion of the steam cleaning experiment.

(A) FIRST TEST SAMPLE AFTER STEAM CLEANING; THE GREY SCALE HAS BEEN REMOVED FROM THE NARROW, VERTICAL DARK REGION.

(B) THE FIRST TEST SAMPLE A MONTH AFTER POST-TEST ANALYSIS AND SUBSEQUENT EXPOSURE TO AIR AT ROOM TEMPERATURE; THE SURFACE HAS EXTENSIVELY RUSTED.

THE SECOND TEST SAMPLE A MONTH AFTER POST-TEST ANALYSIS AND SUBSEQUENT EXPOSURE TO AIR AT ROOM TEMPERATURE; A THIN GREY SCALE (DARKER REGION) AND THE EXPOSED ALLOY SURFACE WITHOUT VISIBLE SCALE (LIGHTER STRIP AT BOTTOM) ARE EVIDENT.

Fig. 8.6.3.1. Surface condition of T-22 test samples from steam cleaning experiments (from Myers, 1986).

Additional database available for model development

CEGA (1990) states that few measurements are available relevant to development of this model, but does mention additional sources for this limited database. "KFA has reportedly investigated the effects of water ingress on Cs plateout in the SMOC loop, but the data are not currently available to the U.S. program. Hochtemperatur Reaktorbau (HRB) has measured the washoff of Cs from test specimens removed from the LAMINAR plateout loop.

"Scoping Steam Induced Vaporization (SIV) measurements for iodine on 2-1/4% Cr - 1% Mo chromalloy steel were made at GA in 1985. However, only a limited number of data were obtained at low pressures and temperatures during these tests. Some LWR data on the behavior of radionuclides in a steam/liquid water system may be relevant to HTGRs." The GA scoping data on 2-1/4% Cr-1% Mo is probably the same as that discussed in detail above.

In a recent foreign travel report B. F. Myers (1991) comments on ongoing work in Germany as follows. "Experiments on the steam-induced removal of cesium from stainless steel at 250°C gave rates of removal 4 to 5 orders of magnitude higher than earlier studies at ORNL on removal of cesium from Incoloy 800 at water vapor pressures 3 to 14 times higher. The rates of removal in the case of stainless steel were in the range 10^{-5} to 10^{-4} /s under turbulent flow conditions. An experimental and theoretical program was begun on the basis of the large difference of the two experimental results."

Information on this previous work at ORNL and on the previous and ongoing work in Germany on steamoff of cesium should be pursued as a potential enhancement of the steamoff database. Hopefully more detailed information may be available for model development from these sources than that reported by Myers (1986) for iodine steamoff.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Several points are raised by Myers (1986) which raise questions, two specific to the model and two relating to the general phenomena governing sorption and washoff. The statement that "the amount of iodide removed is roughly linearly proportional to the amount of steam passing the surface ..." implies that the steam environment and kinetics of steamoff need to be considered in a more detailed model. The fact that most of the iodide must have escaped as a vapor raises questions on the possibility of redeposition within the PC under actual reactor conditions.

General issues which require consideration are (1) a measured sorption concentration much higher than that predicted by the existing model equations for iodine sorption and (2) very different steamoff fractions for the two differently prepared surfaces of the alloy (i.e., test 1 vs test 2).

The most promising avenue for near-term model refinement could be provided by the ORNL and German data on cesium steamoff, which were not presently available for inclusion in this database and analysis. The possible relevance of LWR data should also be considered.

DATABASE USED IN MODEL DEVELOPMENT

Until more information is obtained on the ORNL and German work on cesium steamoff, the present database used in development of the steamoff model consists of that presented in Table 8.6.3.1.

8.6.4 WASHOFF

function	This model provides a value for fractional removal by condensed water of FP deposited on PC alloy surfaces, without functional dependencies.
present status	The model is based on one experiment for cesium washoff. The model is reasonable for cesium, but its validity for other fission products is unknown.
model uncertainty	The uncertainty in the model for Cs is small, and stated to be about a factor of 1.3 (Myers, 1988). Due to lack of data, the uncertainty for the other fission products is very large, with a recommended uncertainty range from 0 to 1 (Myers, 1986).
references	Myers (1986); Röllig et al. (1985)

ACCIDENT CONDITIONS

Model equations

The fractional removal of fission products from PC alloy surfaces by the flow of water (droplets or bulk liquid) is assumed to be (Myers, 1986):

$$W = 50 \% , \quad (8.6.4.1)$$

W = fractional washoff (%).

This 50% removal rate is assumed to hold for all FP due to lack of data.

Range of validity

The model is assumed to be valid under all reactor conditions. The experiments were conducted using Cs vapor in helium, tubes made of Incoloy 800 and Inconel 617, temperatures of 600 to 900°C, and times from 20 to 60 d, followed by leaching of the tube surfaces with water at 80°C.

Assumptions

1. Washoff of all FP will be comparable to that of cesium.
2. Washoff from PC metallic surfaces will be comparable to that from Incoloy 800 and Inconel 617.
3. Leaching of the metallic surfaces by water at 80°C is representative of washoff within the reactor.
4. Washoff throughout the range of reactor conditions will be approximately constant.

Uncertainty

The uncertainty for Cs washoff is reported to be a factor of 1.3 (Myers, 1988). The uncertainty for all other isotopes is assumed to range from 0 to 100% (Myers, 1986).

MODEL CHRONOLOGY

The model for washoff is presented by Myers (1986) based on data presented by Röllig et al. (1985) and incorporated into FDDM/F.

DISCUSSION

The only data available was obtained for washoff of Cs by Röllig et al. (1985) under the conditions specified in "Range of validity" above. Leaching of the metallic surfaces by water at a temperature of 80°C is assumed to provide results representative of washoff under reactor conditions. The leach results as a function of the wall temperature of the sample tubes are plotted in Fig. 8.6.4.1. The data for leaching of the two alloys is given in Tables 8.6.4.1 and 8.6.4.2.

The results for leaching of Incoloy 800 in Fig. 8.6.4.1 suggest a decrease in washoff with increasing temperature, which is explained using Fig. 8.6.4.2 which gives the surface oxide layer thickness as a function of temperature. As temperature increases, the oxide layer thickness increases, and thus "the leachable cesium in the water leach experiments is inversely proportional to the oxide layer thickness suggesting that only a portion of the layer, that nearest to the surface, is accessible by water and that the cesium has been deposited as the oxide layer was growing" (Myers, 1986).

The results for Inconel 617 are more variable, with only a few percent of the Cs leached at 800°C but more typical amounts leached at the other temperatures. An explanation is proposed that at 800°C the oxide layers were strongly fissured, possibly exposing stronger binding sites for the Cs and preventing their washoff, but at 900°C the oxide layer was apparently degraded with possible implications for the increased washoff.

Additional experiments are obviously required to reduce the uncertainties and determine the dominant variables which affect washoff. Experiments using FP other than Cs would also be recommended.

Fig. 8.6.4.1. The percent water leaching of cesium sorbed on oxidized surfaces of the alloys Incoloy 800 and Inconel 617 (from Myers, 1986; attributed to Röllig et al., 1985).

Table 8.6.4.1. Water leach experiments on Incoloy 800 with sorbed cesium (from Myers, 1986; attributed to Röllig et al., 1985)

Test No.	$T_s (^{\circ}\text{C})^{(a)}$	$T_G (^{\circ}\text{C})^{(b)}$	$T (^{\circ}\text{C})_{\text{Nominal}}$	$P_{\text{Cs}} (\text{Pa})^{(c)}$	$t (\text{d})$
1	620-590	627-605	600	3.4(-7)	23
2	618-590	628-600	600	4.1(-7)	43
3	697-707	706-668	700	1.6(-6)	50
4	693-704	720-698	700	1.3(-6)	50
5	800-750	854-758	775	1.1(-7)	27

Test No.	$A_s^{(d)}$ (nCi/cm ²)	% H ₂ O ^(e) Lead	Oxide Layer Thickness (μm) External (f) Internal (g)
1	8 - 20	48-64	1-2 NA(h)
2	4 - 14	40-54	1-2 NA
3	2 - 4.5	19-22	2-4 NA
4	0.7-1.5	38-41	2-4 NA
5	0.03-0.08	22-40	10-20 20

(a) T_s : wall temperature at inlet and outlet of sample tubes ($^{\circ}\text{C}$).

(b) T_G : inlet-outlet gas temperature ($^{\circ}\text{C}$).

(c) P_{Cs} = partial pressure of cesium (Pa)

(d) A_s = Cs-134 activity at end of experiment (nCi/cm²); (Cs-133/Cs-134 = 8000 to 12000)

(e)Fraction of A_s accessible to and soluble in water at 80 $^{\circ}\text{C}$.

(f)Oxide layer above initial surface of alloy.

(g)Oxide layer below initial surface of alloy.

(h)NA = not available.

Table 8.6.4.2. Water leach experiments on Inconel 617 with sorbed cesium (from Myers, 1986; attributed to Röllig et al., 1985)

Test No.	$T_s (^{\circ}\text{C})^{(a)}$	$T_G (^{\circ}\text{C})^{(b)}$	$T (^{\circ}\text{C})_{\text{Nominal}}$	$P_{\text{Cs}} (\text{Pa})^{(c)}$	$t (\text{d})$
6A	700	725-691	700	NA	22
6B	800	818-784	800	NA	2.4
7	710-694	710-692	700	1.4(-6)	46
8	808-804	823-785	800	1.4(-6)	31
9	803-799	811-793	800	4.0(-6)	60
10	906-902	893-881	900	2.1(-6)	35

Test No.	$A_s^{(d)}$ (nC1/cm ²)	% H ₂ O ^(e) Lead	Oxide Layer Thickness (μm)	
			External (f)	Internal (g)
6A	0.3-0.7	NA	NA(h)	NA
6B	0.1-0.2	1-4	NA	NA
7	5-9	41	NA	NA
8	1-2	NA	2-5(i)	10
9	10-25	3-5	4-10(i)	15
10	3-4	40-60	NA(j)	20

(a), (b), (c), (d), (e), (f), (g), (h): See corresponding footnote in Table 4-2; note that for footnote (d) here Cs-133/Cs-134 = 700 to 1000 except for test No. 6 where the ratio was 7000.

(i) The oxide layers has strongly fissured outer contour with some isolated protrusions.

(j) The outer oxide layer had a degraded appearance.

Fig. 8.6.4.2. The thickness of the external oxide layer on Incoloy 800 as a function of temperature (from Myers, 1986).

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The original source of the reported data (Röllig et al., 1985) has not been reviewed by this author, thus it is assumed that the salient features of this experiment have been reported by Myers (1986). The existence of a single data set hinders further development of this model. Without additional data, refinement of the model can only be pursued using analogies available from the scientific literature (e.g., sorption of Cs on oxide layers, the distribution of implanted Cs within oxide layers, the effects of high-temperature exposure of water to the oxide layers on metallic surfaces, the structural integrity of these oxide layers, etc). However, such analogies cannot guarantee accuracy of a model under reactor-specific conditions and events.

DATABASE USED IN MODEL DEVELOPMENT

The available database is apparently limited to that reported by Röllig et al. (1985). This data, as presented by Myers (1986), has been presented above in Figures 8.6.4.1 and 8.6.4.2, and in Tables 8.6.4.1 and 8.6.4.2.

8.7 TRANSPORT BY DUST AND AEROSOLS

function	No model is presently employed to simulate FP transport by dust and aerosols within the primary circuit for MHTGR design calculations.
present status	Current models assume that FP are transported within the coolant as gas atoms (Myers, 1988). As such, no models for FP transport by dust or aerosols within the primary circuit are presently used in U.S. design calculations. A German model has been developed for the effects of dust on FP transport.
model uncertainty	The effects of dust and aerosols are frequently mentioned as a potentially significant source of uncertainty in estimations of FP plateout and liftoff within the primary circuit (CEGA, 1990). This uncertainty remains unquantified because of the limited reactor-relevant data available.
references	Wichner (1991); von der Decken et al. (1980); IAEA (1985); Craig (1975)

DISCUSSION

This discussion considers FP transport by dust and aerosols within the coolant and primary circuit only. Models for transport within the reactor building are not considered here.

Because no models of FP transport by dust or aerosols within the primary circuit are presently used in design calculations in the U.S., a detailed exposition of the governing equations or phenomena involved will not be presented here. Rather, a brief introduction is provided to the source references which can serve as a starting point in future model development and data analysis. CEGA (1990) summarizes DDN 11.53 as follows. "The presence of circulating and/or deposited particulate matter in the primary circuit of an HTGR may alter the plateout distributions in the primary circuit during normal operation and may increase the extent to which condensible radionuclides are released from the primary circuit during dry and wet depressurization transients. Consequently, the effects of dust on the transport of condensible radionuclides in the primary coolant circuit must be characterized ..."

Database available for model development

CEGA (1990) continues with a discussion of the current database. "The available data on the effects of dust on radionuclide transport in the primary coolant circuit are largely from reactor surveillance measurements made at Peach Bottom, Dragon and AVR. However, the particulate matter in the primary circuits of the PB and AVR reactors is mainly carbonaceous so the relevance of these data is questionable for the MHTGR-NPR wherein a metal-oxide aerosol is more likely ..."

"There are also British data on the transport of metal-oxide aerosols in AGRs, but no data on the effects of such aerosols on radionuclide transport.

"Limited data are also available from the GA deposition loop program. In one test, a quantity of graphite powder was added to the out-of-pile loop, and the result was to alter the plateout distribution of the Cs-137 and Sr-90 and to increase significantly (>10X) the amount of liftoff observed in ex situ blowdown tests.

"Finally, there is an extensive amount of open-literature data related to aerosol formation, transport, deposition, and reentrainment, but none relates directly to the conditions expected in the primary circuit of the MHTGR-NPR."

Although the phenomena relevant to FP transport via dust and aerosols in the PC are known, major uncertainties arise from the lack of information on the quantities of dust and the particle size distribution expected in the MHTGR. Wichner (1991) has recently provided a comprehensive review of data and phenomena relevant to FP plateout and liftoff in the MHTGR PC system, and states that: "there is only sparse information available on dust types, quantities and other characterization data representative of real HTGR dust. Therefore, a fairly heavy reliance is placed here on the relatively comprehensive dust examinations conducted in the Peach Bottom, Core 2 Surveillance Program. Peach Bottom HTGR dust data tend to be discounted due to the sporadic lubricating oil ingresses during the early stages of Core 2 operation. However, dust formation mechanisms generally expected in HTGRs operated as well in Peach Bottom, and the oil ingress events are not sufficiently significant to warrant discarding the information, especially since there is very little else." Wichner also mentions dust data from the German AVR program, but that the dust levels arising from this pebble-bed design are much larger than expected for the prismatic MHTGR design.

Myers (1991) comments briefly on ongoing work in the FRG: "In the evaluation of the AVR dust experiments, the activity of iodine on dust was found to be relatively high; iodine preferred to deposit on the readily mobilized dust." Information on the analysis of dust taken from the Fort St. Vrain HTGR is given in a report by Sparks et al. (1990). Craig (1975) provided a review of particulate behavior and relevant phenomena within HTGR primary coolant systems but did not address the associated FP transport. Additional non-HTGR information is available on the general behavior of dust and aerosols and the attachment of radionuclides. Wichner (1991) mentions safety studies in the LMFBR and LWR programs which consider FP transport via aerosols. In nonreactor applications, the increasing interest in radon as a radiological hazard has generated studies of the attachment of radon daughters to particles and aerosols.

Several papers presented at the 1985 IAEA Specialists' Meeting on Fission Product Release and Transport in Gas-Cooled Reactors are relevant to dust and aerosol behavior. Garland et al. (1985) presented a paper entitled "Behaviour of Particles in a Commercial Advanced Gas-Cooled Reactor." Reed et al. (1985) presented a paper entitled "The Variation of Particle Gas-Borne Concentration with Time in a Gas Cooled Reactor." Skyrme (1985) presented a paper entitled "Attachment of Gaseous Fission Products to Aerosols."

Model development

Wichner (1991) summarizes the current state of aerosol liftoff models as follows. "Particle liftoff has been one of the traditional difficult areas of fluid mechanics for at least the past 50 years ... However, HTGR liftoff presents a unique set of circumstances which precludes a direct carryover from published studies. The HTGR situation is unique in that liftoff flows act on particles plated out under the high surface shear conditions existing during normal operation. In contrast, most studies involve either quiescently deposited particles or deposits formed under unspecified conditions."

A brief but useful introduction to relevant phenomena and modelling of FP/dust behavior in HTGRs is given by von der Decken et al. (1980). Iniotakis et al. (1984) implement this model into the FRG codes PATRAS and PATRAS-S, and some computational results for the influence of dust are presented in Figure 8.7.1. Iniotakis et al. (1984) summarize this study as follows. "Curve 1 refers to the case without dust, curve 2 to the case with dust. Curve 3 represents the amount of Cs-137 which is sticking on the dust particles which are themselves deposited on the surfaces. An adhesional distance $y_0 = 300 \text{ \AA}$ and a particle radius of $r_p = 1 \text{ }\mu\text{m}$ had been chosen. The circuit contamination in low temperature regions is significantly reduced through the presence of dust. This is due on one hand to a quasi-decontamination of the surface due to dust desorption and on the other hand through the binding of the depositable atomic cesium on dust in the gas phase. The overall influence of dust on the deposition of fission products is very complex. In addition to the size spectrum and nature of the dust particles, the mass flow and temperature dependences as well as the composition and morphology of the wall surface play an important part."

Fig. 8.7.1. Influence of dust on deposition of ^{137}Cs (PNP-500, HKV-loop, operation time 30 years) (from Iniotakis et al., 1984).

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

A program of model development would first consider the modelling approach employed by Iniotakis et al. (1984) and discussed in more detail in von der Decken et al. (1980). This approach should then be compared to the discussion and analysis presented by Wichner (1991) and the references therein. The other references mentioned above can be reviewed for supplementary information.

As of 1991, the codes TDAC and MELCOR were under consideration for modelling aerosol transport within the containment building. The modelling methodology used by these codes could be evaluated with respect to its relevance for aerosol behavior within the primary circuit.¹

DATABASE USED IN MODEL DEVELOPMENT

The database relevant to model development can be obtained from the above-mentioned references and from additional references mentioned therein.

8.8 UPDATE

Preliminary testing of washoff of iodine from 2 1/4 Cr-1 Mo was performed and documented in the following report:

Beahm, E. C., and W. E. Shockley (1991), "Fission Product Washoff from Structural Alloys: Preliminary Tests," Oak Ridge National Laboratory Report ORNL/NPR-90/45.

This report should be reviewed for consistency with the contents of §8.6.

Very useful data will be obtained from the completion of the initial COMEDIE plateout and liftoff test. Those data have yet to be reported in detail, and the PIE of the loop and fuel components has yet to be completed. Although this test was designed as an integral validation test, it will provide valuable information on the accuracy of the plateout/liftoff models used for design purposes. Unfortunately, the COMEDIE experiments planned for validation of design methods for steamoff and dust effects will probably not be completed.

¹Barthold (1993) comments that the TDAC code does not model the formation and behavior of dust and aerosols, but requires a particle size to be input for the calculation of settling losses in the containment building. Additional depletion mechanisms are condensation and plateout in the building. TDAC converts all depletion processes into equivalent filter efficiencies.

9. TRITIUM TRANSPORT IN THE REACTOR

9.1 INTRODUCTION

Because tritium is often more mobile and exhibits behavior different than other fission products, tritium transport is often modelled differently. As an example, tritium can be produced through neutron capture by several materials other than fissile and fertile fuels, and only tritium raises concerns of escape by permeation through the primary circuit alloys during normal reactor operations. Sorption of tritium on graphite is modelled using an equation unlike that of other sorption model equations for fission products. For these reasons, and because of the importance of tritium behavior specific to the NP-MHTGR program, modelling of tritium behavior is included as a separate chapter of this compilation. Although tritium transport in target particles is of great relevance to the NP-MHTGR program, the associated models have not been presented in the open literature and are therefore not discussed here.

Tritium can be produced by several neutron interactions, the predominant mechanisms being (Yang et al., 1977):

- (1) ternary fission of the fuel,
- (2) neutron capture by ^3He present within the helium coolant,
- (3) neutron capture by ^6Li and ^7Li present as impurities within the graphite or within target materials, and
- (4) neutron capture by ^{10}B present as control material.

Gainey (1976) discusses in some detail each source of tritium. If target materials are not present, the largest source of tritium is the ternary fission of fissile materials. The fractional yield of tritium per fission has been estimated to be on the order of 1.0×10^{-4} (Acharya, 1988). Barthold (1993) comments that the tritium activity from these sources is low and the dose consequences even lower, impacting the requirements for tritium model accuracy.

Because of the previous lack of emphasis on modeling of tritium behavior in the MHTGR, the following sections include much of the available data on tritium behavior as presented in the references. This inclusion should facilitate future model development and refinement.

9.2 TRITIUM TRANSPORT IN INTACT FUEL PARTICLES

function

This model provides permeation coefficients for the transport of tritium through the kernel and coating layers, with the only temperature dependence for transport through SiC.

$$D = D_0 \exp\left(-\frac{Q}{RT}\right), \quad (9.2.1)$$

D_0 = pre-exponential diffusion factor ($\text{m}^2 \text{s}^{-1}$),
 Q = activation energy (J mol^{-1}),
 T = temperature (K),
 R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

The ratio Q/R is sometimes included as a single term in this equation.

For tritium, FDDM/F recommends an analogous formulation for the effective permeation coefficient:

$$K = K_0 e^{-Q/RT}, \quad (9.2.2)$$

K = effective permeation coefficient ($\text{m}^2 \text{s}^{-1}$),
 K_0 = pre-exponential permeation factor ($\text{m}^2 \text{s}^{-1}$),
 Q = activation energy (J mol^{-1}),
 R, T = defined as above.

Permeation coefficients are often used to include any solubility effects in the diffusion-like formulation. Recommended values for K_0 and Q in the kernel and coating layers as recommended by FDDM/F are given in Table 9.2.1. FDDM/F comments that the "quantity K may be used in place of the diffusion coefficient in codes [COPAR] which use solutions of the classical diffusion equation to calculate transport."

Table 9.2.1. Parameters for calculation of tritium permeation coefficients in particle kernel and coating layers, Eq. (9.2.2) (from FDDM/F)

Particle component	K_0 ($\text{m}^2 \text{s}^{-1}$)	Q (J mol^{-1})
Kernel	1.0×10^{-6}	0.0
Buffer	1.0×10^{-6}	0.0
PyC layers	1.0×10^{-6}	0.0
SiC	4.7×10^{-15}	76,500

Range of validity

The model is assumed to apply to all reactor temperatures and conditions. Experimentally, tritium retention was measured after 900 to 1400°C anneals on particles with burnups of 12 to 75% FIMA at irradiation temperatures of 850 to 1575°C, for kernels of UO_2 , UC_2 , and $(\text{Th,U})\text{C}_2$.

Assumptions

FDDM/F references internal GA memoranda for these model parameters; therefore, only the following general assumptions can be inferred.

1. The effects of the kernel and the buffer and PyC layers on tritium transport is insignificant with respect to those of the SiC layer.
2. The quantitative effects of neutron irradiation and in-reactor conditions on tritium transport are unknown; therefore, the transport parameters must be assumed to be independent of the irradiation and reactor conditions.
3. Apparently the tritium transport experiments were conducted no later than the 1970s; therefore, the coating deposition techniques used in the 1970s must be assumed to result in diffusion coefficients and solubilities which approximate those of modern coatings.

Uncertainty

The standard deviation in the release is stated to be 0.55 (FDDM/F).

MODEL CHRONOLOGY

FDDM/F references internal GA memoranda as the source for the model parameters listed in Table 9.2.1. These memoranda have not been reviewed by this writer; therefore, the logic and database used in the development of this model are unclear. FDDM/E presented a curve for experimental tritium retention in TRISO particles at the end of irradiation as a function of irradiation temperature, with Gainey (1976) mentioned as the reference. However, the data presented by Gainey is the same as that presented by General Atomic (1972). Thus, it seems conceivable that the model developed for FDDM/F may be based on a computational fit of an effective permeation coefficient through the SiC layer to this experimental retention curve based on early 1970s data, with the assumption that all other particle components do not significantly affect the release of tritium.

DISCUSSION

Although the model presented in FDDM/F disregards the effects of the kernel and PyC layers on tritium transport, data does exist for the tritium diffusion coefficient through these components. In addition, independent measurements of tritium diffusivity and solubility in

SiC do exist. These data will be presented below to permit future comparison with the reference model.

Diffusion in UO₂ kernels

Gainey (1976) reports a diffusion coefficient for tritium in UO₂:

$$D_{\text{UO}_2} (m^2/s) = 3.7 \times 10^{-6} \exp \left(- \frac{7200 \pm 450}{T} \right) . \quad (9.2.3)$$

Wheeler (1971) determined this diffusion coefficient by using single crystal UO₂ in the temperature range 500 to 1000°C, and he reported the solubility of hydrogen in UO₂ to vary from 0.03 to 0.4 µg per gram of UO₂; the solubility of tritium should approximate that of hydrogen. With UCO predominantly composed of UO₂, one could assume the same diffusion coefficient in UCO as in UO₂ in approximating tritium diffusion in UCO kernels.

Myers (1988) justifies the approach used by FDDM/F for kernel release as follows. "All tritium formed in the kernel is assumed to be immediately released. This assumption is acceptable in regard to the regulatory limits on tritium release from the core since the fraction of exposed kernels is sufficiently small so that the absolute quantity of tritium escaping from the core in this manner does not exceed the limit or contribute to exceeding the limit." Whether this approach is too conservative for the specifics of the NP-MHTGR design is a question for future analysis.

Diffusion in PyC layers

Gainey (1976) also reports a diffusion coefficient for tritium in pyrolytic carbon:

$$D_{\text{PyC}} (m^2/s) = (0.07 \pm 0.058) \exp \left(- \frac{38,000}{T} \right) , \quad (9.2.4)$$

but he mentions that PyC layers can be very effective in trapping tritium, apparently by chemisorption.

Causey et al. (1979) irradiated lithium-coated PyC with neutrons, and the resulting tritons recoiled into the PyC for subsequent diffusion anneals. They report the diffusion coefficient for tritium in LTI PyC (obtained from General Atomic Co.) but note distinctly different results if hydrogen is added to the sweep gas. For pure helium, the diffusion coefficient is given by:

$$D_{\text{PyC}} (m^2/s) = 4.4 \times 10^{-10} \exp \left(- \frac{134,000}{RT} \right) , \quad (9.2.5)$$

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}.$$

However, with hydrogen added to the helium the diffusion coefficient became:

$$D \text{ (m}^2\text{/s)} = 0.1 \exp\left(-\frac{268,000}{RT}\right) . \quad (9.2.6)$$

These differing results "appeared to be caused by rate controlled tritium desorption from radial pores throughout the material. When tritium is recoiled into the samples, many of the tritons would be stopped on or very near pore surfaces. The diffusion coefficients measured when hydrogen was used in the sweep gas is postulated to be controlled by the isotopic exchange rate of hydrogen for tritium atoms chemisorbed on the carbon pore surfaces ... When hydrogen was not used in the sweep gas, the tritium release was controlled by the desorption rate of tritium atoms from the chemisorption sites ... It must be noted that because of these pores, neither of the Arrhenius relations for LTI pyrolytic carbon represents a true diffusion coefficient because tritium release may be controlled by the ambient surface conditions."

Although the implantation of tritium into PyC in this experiment may affect the experimental diffusion coefficients compared to MHTGR conditions, the pronounced effects of surface conditions (oxidizing vs reducing atmosphere) is a variable relevant to tritium transport through the carbonaceous materials in the MHTGR core. Causey et al. (1979) also provide data on the solubility of hydrogenic species in laminar PyC, but the direct quantitative applicability of this data to LTI PyC is uncertain. In summary, the "solubility of deuterium in the laminar pyrolytic carbon was surprisingly high and showed a negative heat of solution ... The square root of pressure dependence for the solubility implies that the deuterium molecules dissociate as they enter the pyrolytic carbon."

A suggestion from M. L. Russell (1991) may provide additional information on the transport of tritium in PyC. Specific references are made to the work of R. A. Causey et al. (Eighth International Conference on Plasma-Surface Interactions, Jülich, Germany, May 1988; and articles in the *Journal of Nuclear Materials*) and to H. Atsumi et al. (articles in the *Journal of Nuclear Materials*). This work has not been reviewed by this writer, but future model evaluation should consider this additional information.

Diffusion and solubility in the SiC layer

Causey et al. (1978) measured the diffusion coefficient and solubility of tritium, deuterium, and hydrogen in several types of SiC. The SiC samples were recoil-injected with tritons, followed by isothermal anneals. For vapor-deposited β -SiC samples (obtained from General Atomic Co.), the diffusion coefficient of tritium was reported to be:

$$D_{\text{SiC}} \text{ (m}^2\text{/s)} = 1.58 \times 10^{-4} \exp\left(-\frac{308,000 \pm 8000}{RT}\right) , \quad (9.2.7)$$

R = ideal gas constant (8.314 J mol⁻¹ K⁻¹).

Here Causey et al. report an upper value of 3.41×10^{-4} m²/s for the D_0 term in Eq. (9.2.7) and a lower value of 0.73×10^{-4} m²/s, as determined by the standard deviation of $\ln D_0$.

Causey et al. (1978) also determined the solubility of deuterium in vapor-deposited β -SiC using the governing equation:

$$S = S_o \exp\left(-\frac{Q_s}{RT}\right) P^\alpha, \quad (9.2.8)$$

with the result:

$$S = 8.77 \times 10^{-9} \exp\left(+\frac{155,000 \pm 14,000}{RT}\right) P^{0.61}, \quad (9.2.9)$$

- S = solubility (deuterium atoms per silicon atom),
- S_o = pre-exponential solubility factor (deuterium atoms per silicon atom),
- P = deuterium pressure (atm),
- α = exponential constant,
- Q_s = heat of solution (J mol^{-1}),
- R, T = defined as above.

In Eq. (9.2.9) the upper and lower limits on S_o were reported to be 2.71×10^{-8} and 2.85×10^{-9} , respectively. The negative heat of solution results in reduced solubility of deuterium in SiC as the temperature increases. With respect to the range of validity of Eq. (6), the values of S_o and Q were determined for a deuterium pressure of 1 atm, at temperatures from 1000 to 1400°C, and the exponent α was determined at 1200°C, using pressures from 0.02 to 1 atm. The solubility of tritium can be expected to approximate that of deuterium, as their chemical behavior should not significantly differ.

If surface effects are not rate-limiting for transport, the permeability, P , of tritium through the SiC layer can be calculated as the product of the solubility and the diffusivity (Causey et al., 1978):

$$P = D_o S_o \exp\left(-\frac{Q + Q_s}{RT}\right) P^{0.61}. \quad (9.2.10)$$

The pre-exponential terms are commonly combined into a single pre-exponential permeation factor, P_o :

$$P_o = D_o S_o. \quad (9.2.11)$$

To calculate the permeability in common units ($\text{atoms cm}^{-1} \text{s}^{-1}$), S_o should be converted into units of tritium atoms cm^{-3} . The rate of tritium permeation escaping the SiC layer is then given by:

$$J = \frac{P}{d}, \quad (9.2.12)$$

J = rate of mass transfer across the SiC surface (tritium atoms $\text{cm}^{-2} \text{s}^{-1}$),

d = thickness of the SiC layer (cm).

Whether injection of tritium by recoil into the SiC affects subsequent measurements of diffusion (relative to reactor-like transport) is unknown. It should be noted that the experimental results for tritium diffusion and permeability discussed above do not appear to correlate with the model parameters for the tritium permeation coefficient in SiC as given in Table 9.2.1. As mentioned previously, this fact suggests that the model permeation coefficient in SiC may not be based on experimental data for transport in SiC but may instead be based on tritium release profiles from TRISO particles.

Measurements of tritium release from TRISO particles

The available data on tritium retention in the early TRISO particles at the end of irradiation is presented in Table 9.2.2, taken from General Atomic (1972). Figures 9.2.1 and 9.2.2 show the tritium release from UO_2 and UC_2 particles during postirradiation anneals. In general, tritium retention decreases with higher irradiation and annealing temperatures and higher burnups, although quantitative models are difficult to derive because of the limited data available. Gainey (1976) summarizes the TRISO results:

- (1) UO_2 and UC_2 particles were only studied at high burnup (>60% FIMA) while $(\text{Th,U})\text{C}_2$ particles were studied at low burnup (<25% FIMA),
- (2) tritium release exhibited dependencies on burnup and irradiation temperature, and
- (3) tritium release is greatest for UO_2 , intermediate for UC_2 , and least for $(\text{Th,U})\text{C}_2$ (although inspection of the data would suggest that Gainey was here referring to retention rather than release).

The qualitative conclusions which can be drawn from Table 9.2.1 and Figures 9.2.1 and 9.2.2 will be quoted directly from General Atomic (1972) below.

In the end-of-irradiation retention measurements, "the TRISO coated $(\text{Th,U})\text{C}_2$ particles, irradiated to 12 to 26% FIMA burnup, retained essentially all the tritium at 950°C, and the percentage of tritium retained decreased with fuel (irradiation) temperature. The TRISO coated UO_2 particles, irradiated to 60 to 75% burnup, showed similar behavior, [i.e., high retention at low temperature (around 900°C) and decreasing retention with increasing temperature]. By comparison, the TRISO coated UC_2 particles appeared to be less effective in retaining tritium.

"In general, the retention data ... indicate that tritium is highly retained in fuel material, even in fuel compacts containing failed particles, during irradiation to high burnup for up to 450 days at temperatures around 900°C, and that the retention decreases with increasing temperature. Irradiation, by the creation of sorption sites, may account, in part, for the high retention of tritium.

"The total percentage releases of tritium from the TRISO UC_2 and TRISO UO_2 particles during the anneal experiments were 44 and 29%, respectively ... These release values, obtained in short-term experiments, are relatively high and would appear to be inconsistent with the low release (high retention) values observed for similar particles in the

Table 9.2.2. Retention of tritium in TRISO fuel particles (from General Atomic, 1972)

Sample No.	Average Fuel Temp. (°C)	Days Capsule at Power	Capsule No.	Fuel Kernel	FIMA Burnup (%)	No. of Fuel Part. Per Run	Batch No.	Experimental Values			
								Z Retained Based on		Average Percent Retained Based on	
								Cs-137	Total Zr	Cs-137	Total Zr
40 41	950	281	P22	(Th,U)C ₂	19	3 3	4155-151E	96 91	95 111	94	103
47 48 49 50 50A	1240	127	P21	(Th,U)C ₂	12	3 3 3 3 1	3923-113E	86 85 74 81 94	96 92 69 81 --	84	85
64 65	1575	253	P13L	(Th,U)C ₂	26	7 6	4263-75E	30 28	-- --	29	--
44 45 46A	875	253	P13L	UO ₂	60	3 3 1	4413-67E	100 92 101	97 138 --	98	117
79 80	1275	253	P13L	UO ₂	75	3 3	4413-67E	75 68	-- --	72	--
76 77	1450	253	P13L	UO ₂	75	5 5	4413-67E	53 46	-- --	50	--
53 54 27	850	253	P13L	UC ₂	60	3 3 3	4413-5E	73 75 --	-- -- 74	74	74
62 63	1250	253	P13L	UC ₂	75	6 5	4413-5E	32 35	23 24	34	24

Fig. 9.2.1. Release of tritium during anneal of TRISO-coated UO_2 particles (from General Atomic, 1972).

Fig. 9.2.2. Release of tritium during anneal of TRISO-coated UC_2 particles (from General Atomic, 1972).

long-term capsule tests ... The high release in the anneal tests suggests that the coatings were permeable to tritium. The irradiation effect, mentioned above, may account in part for the relatively low in-pile release." Not much can be added to this discussion until additional data become available on modern particles.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Predictions of tritium release using the model equation should be compared with predictions which use the experimental diffusion and solubility coefficients for kernel and coatings as presented in "Discussion" above. These results should be compared with the General Atomic (1972) data presented in "Database ..." below to determine whether the two approaches show any consistency.

The data presented here should be scrutinized to determine if any approximate dependencies can be determined for irradiation temperature vs burnup effects on end-of-irradiation tritium retention, and if any approximate model can be developed for tritium release during postirradiation annealing as a function of annealing temperature and irradiation conditions.

With this tritium transport data developed during the 1970s, a search of the scientific literature for newer data on tritium transport in kernel and coating materials and the effects of irradiation might be useful. Specifically, the recent references mentioned above for tritium transport in PyC should be evaluated. The greatest need is in experimental confirmation that tritium transport in present-day particles can be described by models derived from 20-year-old particles.

DATABASE USED IN MODEL DEVELOPMENT

Refer to Table 9.2.2 and Figures 9.2.1 and 9.2.2.

9.3 TRITIUM RELEASE FROM FUNCTIONALLY FAILED PARTICLES

function	This model provides a simple conservative estimate for fractional tritium release from particles with nonintact SiC layers, without functional dependencies.
present status	Apparently a very conservative model is employed for tritium release from defective particles. Little is known about the origin or justification for this model.
model uncertainty	The source of the model is unknown, and whether any data exist relevant for model comparisons is unknown; therefore, the model uncertainty cannot be commented upon.

references Acharya (1978); Gainey (1976); General Atomic (1972)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

Acharya (1988) states that tritium is "completely released" from failed particles and from particles with SiC coating defects. From this a model equation for tritium release from particles with failed or defective SiC layers under all irradiation and heating conditions is given as (FDDM/F):

$$f = 1.0 , \quad (9.3.1)$$

f = fractional release of tritium.

Range of validity

The model is assumed to apply to all fuel temperatures and reactor conditions. No experimental range of validity for this equation can be presented without knowledge of what, if any, data exist upon which this model is based (see "Discussion" below).

Assumption

The SiC layer is the only significant barrier to tritium release (i.e., no significant kernel retention, tritium solubility, PyC sorption or chemisorption occurs).

Uncertainty

There are "insufficient data to estimate the uncertainty in this value" (FDDM/F).

MODEL CHRONOLOGY

No historical development of this model is known, therefore it appears to be a deliberately overconservative prediction of tritium release based on limited data.

DISCUSSION

The only apparent data relating to tritium release from failed particles is reported by General Atomic (1972) and restated by Gainey (1976). A compact irradiated in fuel element D13-05 of the Peach Bottom HTGR core was measured for tritium retention. Apparently these "pyrolytic-carbon coated (Th,U)C₂ particles" were BISO particles, not TRISO particles. These particles were determined to be 80 to 100% failed, but only 20 to 30% of the tritium was released from the compacts. This retention data is given in Table 9.3.1, taken from General Atomic (1972). Irradiation conditions for this compact were

Table 9.3.1. Retention of tritium in Peach Bottom Compact No. 18, irradiated in fuel element D13-05 (from General Atomic, 1972)

Sample Location	Ru-106 Found (g)	Tritium Found (dpm)	Tritium Calculated (dpm)	Tritium Retained (%)
Top	1.5×10^{-7}	1.2×10^7	1.7×10^7	71
Upper middle	1.8×10^{-7}	1.4×10^7	2.0×10^7	70
Lower middle	2.4×10^{-7}	2.0×10^7	2.7×10^7	74
Bottom	1.3×10^{-7}	1.2×10^7	1.5×10^7	80
Average				$74 \pm 7\%$

reported to be an irradiation time of 450 EFPD at an average temperature of 980°C, with a ^{235}U burnup of 40% and a thorium burnup of 2 to 3% (total % FIMA was not reported). As compact retention is not a direct measure of release from the failed particles, a model suggesting 100% release may have been chosen to overcompensate for the lack of data.

If this model is incorporated into any computer code, that code would be TRITGO. Acharya (1988) comments on complete tritium release from failed particles, but notes that "the contribution from the failed particles (5×10^{-5}) and from SiC defects (5×10^{-5}) is negligible as compared to the diffusive release of ~5% from intact particles." From this it cannot be inferred that the model is formally incorporated into TRITGO.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The significance of tritium solubility in kernel and SiC and sorption on the PyC layers, as discussed in §9.2, would need to be considered for a more realistic assessment of tritium retention in failed particles.

DATABASE USED IN MODEL DEVELOPMENT

Refer to Table 9.3.1.

9.4 TRITIUM RELEASE FROM B_4C CONTROL MATERIAL

function	This model calculates the fractional release of tritium from B_4C pellets as a function of temperature.
present status	Data exists for tritium release from B_4C pellets over a specific temperature range. The model equation approximates this data and extrapolates to 100% release beyond the experimental range.
model uncertainty	The uncertainty of this model is quantified below, but requires comparison of the physical characteristics of modern B_4C pellets with those used in the 1970s.
references	Gainey (1976); Acharya (1988); Pitner et al. (1973).

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The fractional release of tritium formed in B_4C is given by (FDDM/F):

$$f = 1 - \frac{1}{g_1 g_2} , \quad (9.4.1)$$

$$g_i = 1 + \exp \left[a_i \left(\frac{10^4}{T} - \frac{10^4}{T_{oi}} \right) \right] , \quad i = 1, 2 , \quad (9.4.2)$$

f = fractional release of tritium from B_4C ,
 a_i = constant (K^{-1}),
 T = temperature (K),
 T_{oi} = reference temperature, $i = 1, 2$ (K).

Values for the parameters are given in Table 9.4.1.

Range of validity

Measurements of tritium release were made between 593 and 871°C. At those temperatures, release was above 80%. The release behavior at temperatures significantly outside that range has not been measured. Due to the limited data, the range of validity of the model must be assumed to cover all reactor temperatures and conditions.

Assumptions

1. The physical form of the experimental samples (B_4C pellets) used in the tritium release experiments is comparable to the form used in the MHTGR.
2. The operating temperature range of B_4C control material within the MHTGR approximates that of the experimental temperature range.
3. The possible existence of a significant retentive regime for tritium in B_4C at

Table 9.4.1. Parameters for calculation of fractional release of tritium from B_4C and uncertainties in the parameters [Eqs. (9.4.1) and (9.4.2)] (from FDDM/F)

Parameter	Units	Value	Standard deviation
a_1	K^{-1}	0.65	0.050
a_2	K^{-1}	-6.26	0.26
$10^4/T_{o1}$	K	11.6	0.60
$10^4/T_{o2}$	K	8.87	0.10

temperatures below 593°C is not significant for the operating temperatures within the reactor.

Uncertainty

The uncertainty of the model is represented by the standard deviation in each of the model parameters as given in Table 9.4.1. The equivalence of the physical characteristics of modern B₄C pellets with those used for model derivation in the 1970s has not been determined and could impact model uncertainty.

MODEL CHRONOLOGY

Models for tritium release from B₄C control material are apparently based on the same data set [i.e., that reported by Gainey (1976)]. Although the model presented above is more detailed than that presented previously in FDDM/E, a source document which discusses derivation of this model is not referenced in FDDM/F.

DISCUSSION

Data presented by Gainey (1976) for tritium release from B₄C pellets shows a minimum tritium fractional release of about 20% at approximately 760°C, with increasing release at hotter and colder temperatures. Tritium release between 80 and 85% was measured at temperatures of 593 and 871°C.

Details of the physical characteristics of the B₄C pellets used in these experiments have not been determined at this time. The source reference for these experiments is Pitner et al. (1973). Determination of the similarity of these B₄C samples to those used in the MHTGR should be made to assure the direct applicability of the experimental results.

The experimental results from Pitner et al. (1973) as reported by Gainey (1976) are shown in Figure 9.4.1. The apparent temperature dependence of tritium retention in B₄C pellets as determined by Pitner et al. (1973) is shown in Figure 9.4.2.

Gainey (1976) summarizes the experimental results from Pitner et al. (1973): "The results ... show between 20 and 80% of the tritium produced by the $^{10}\text{B}(n,2\alpha)^3\text{H}$ reaction is retained, the amount being dependent upon a complex function of irradiation temperature but not the burnup level. This retention effect was thought to be due to the way in which tritium combined chemically with the B₄C. Annealing at temperatures well above the irradiation temperature was necessary to release tritium from the B₄C pellets."

Myers et al. (1985c) mentioned the irradiation and inspection of wafers containing BISO-coated B₄C particles. Only structural integrity of the particles was examined, and no information is presented relevant to this model for tritium release.

In his analysis of tritium distribution in the MHTGR, Acharya (1988) mentions that in using "the FDDM correlation ... an estimate of about 5% release from intact particles can be arrived and was used in the analysis."

Fig. 9.4.1. Tritium retained in boron carbide (from Gainey, 1976).

Fig. 9.4.2. Temperature dependence of tritium retention in B₄C pellets (from Gainey, 1976).

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The only data used in the development of this model was reported in 1973. The scientific literature should be reviewed to determine whether additional information on tritium behavior in B_4C might be available. Confirmation should be made that modern B_4C pellets are the same as those from which data was obtained.

DATABASE USED IN MODEL DEVELOPMENT

Refer to Figures 9.4.1 and 9.4.2.

9.5 TRITIUM SORPTION ON THE COMPACT MATRIX MATERIAL AND GRAPHITE

function	This model calculates the concentration of sorbed tritium on graphite above 650°C as a function of temperature, hydrogen/tritium partial pressure, and fast neutron fluence. Below 650°C no tritium is sorbed.
present status	One model for tritium sorption on graphite has been presented without discussion. Apparently no model for tritium sorption on the fuel compact matrix material has been presented. As a first approximation, the model for sorption on graphite can also be applied to sorption on the compact matrix material.
model uncertainty	No discussion of the model is presented. The only statement regarding the uncertainty is that by Acharya (1988): "The uncertainty in the sorption isotherms is expected to be large, since it is based on very meager data base." The model as presented applies to graphite, thus its application to the fuel compact matrix material may introduce significant additional uncertainty.
references	Acharya (1988); Gainey (1976); General Atomic (1972)

NORMAL OPERATING AND ACCIDENT CONDITIONS

Model equations

Apparently the only model for tritium sorption on graphite that has appeared in the open literature is one presented by Acharya (1988) and attributed to B. F. Myers. No model for tritium sorption on the fuel compact matrix material has been located in the open literature. As a first approximation, the model for sorption on graphite can be assumed to

also apply to sorption in the fuel compact. Existing data which qualitatively justify such an approximation are presented in "Discussion" below.

Acharya (1988) presents the model equation for tritium sorption on graphite as:

$$C_i = 0, \quad T < 650^\circ\text{C}, \quad (9.5.1)$$

$$C_i = \frac{A_o (1 + \beta \gamma_H f)}{1 + e^{a(T - T_o)}} P, \quad T > 650^\circ\text{C}, \quad (9.5.2)$$

- C_i = sorbate concentration in irradiated graphite (units not stated, see below),
- f = fast fluence (n m^{-2}),
- P = partial pressure of hydrogen and tritium (units not stated, see below),
- T = temperature (units not stated, see below),
- T_o = reference temperature (value and units not stated, see below),
- a = constant (value and units not stated, see below),
- A_o = $1.38 \times 10^3 \text{ cm}^3(\text{STP}) \text{ m}^{-2} \text{ torr}^{-1}$,
- B = 2.6×10^{-25} ,
- γ_H = annealing factor (dimensionless), given by:

$$\gamma_H = \frac{1}{1 + e^{0.0439(T - 1423)}}. \quad (9.5.3)$$

The unit of temperature for T in Eqs. (9.5.1) and (9.5.2) is not stated by Acharya (1988), but it can be assumed to be Kelvin by standard usage (and thus the constant a would have units of K^{-1}). The unit of pressure is not stated by Acharya (1988), but can be inferred to be torr. The unit of concentration is also not stated; the units for A_o would suggest the tritium concentration is given in $\text{cm}^3(\text{STP})$ of tritium gas per m^2 of surface area, but this inference needs to be verified. No values for T_o or a in Eq. (9.5.1) are given by Acharya (1988). Approximate values might be inferred from the statement that one expects the "onset of desorption at about 1500 K." In addition, the similarity of form between Eq. (9.5.3) and the denominator of Eq. (9.5.2) suggest the value of 1423 K might be appropriate for T_o . Whether a value of 0.0439 K^{-1} can be ascribed to a will not be speculated upon until this model equation and related data have been evaluated in more detail.

Range of validity

Without analysis of the source data, no experimental range of validity can be ascribed to this equation. Lack of information on the model requires an assumption that the model is applicable over all reactor temperatures and conditions.

Assumptions

As stated by Acharya (1988), the following assumptions were used in the derivation of this model:

1. No tritium sorption on graphite occurs below 650°C.
2. Temperature-dependent sorption occurs above 650°C.
3. Sorption is a function of the fast fluence, with sorption increasing with fluence.
4. Desorption comes into play at about 1223°C.

In addition:

5. Tritium sorption in the fuel compact matrix material will approximate that in the graphite.

MODEL CHRONOLOGY

No model of this effect has been located in any open-literature reference prior to Acharya (1988). Acharya provides no firm reference upon which the above model is based, thus its development cannot be commented upon. FDDM/E suggests a very simple and conservative model equation for tritium release from graphite with none of the dependencies suggested in the above model, and does not discuss tritium sorption on the compact matrix material. FDDM/F does not comment on or present a model for tritium sorption on graphite or compact material.

DISCUSSION

Model discussion

The only statement regarding this model is given by Acharya (1988) and is quoted below in full: "This isotherm developed by Myers, assumes no sorption at temperatures below 650°C, fluence dependence of sorption, with sorption increasing with increase in fluence and onset of desorption at about 1500 K. Because of the last assumption no desorption will take place in the MHTGR, since graphite component temperatures will not exceed 1500 K during normal operation. In other words once H-3 [tritium] is sorbed on to the graphite surface, it will not desorb even if the temperatures change in the graphite components during normal operation of the MHTGR."

Tritium release from graphite and compact materials

To compare the model equation for sorption in graphite to experimental data of sorption in the fuel compact material, reference must be made to the results of tritium release from fuel element D13-05 irradiated in the Peach Bottom HTGR core (Gainey, 1976). This compact apparently contained BISO (Th,U)C₂ particles which were 80 to 100%

failed. Measurements indicated only 20 to 30% of the tritium was released from the compacts. This data was given previously in Table 9.3.1. The compact was irradiated at an average fuel temperature of 980°C.

Another statement which might provide information against which this model could be compared was provided by Gainey (1976), based on unpublished work by T. S. Elleman: "Elleman's results ... indicate that about 20% of the tritium produced could be permanently held in the graphite structure." Gainey goes on to discuss other work in tritium retention and release from graphite. He mentions work at KFA and HRB, and that "KFA explained their results by assuming that a combined diffusion/desorption mechanism was responsible for the release. They considered chemisorption and molecule dissociation at the graphite surface and absorption and diffusion into the graphite bulk." Results from this work are presented in Figure 9.5.1, taken from Gainey (1976). Other results for hydrogen desorption from another type of graphite are presented in Figure 9.5.2, again taken from Gainey (1976). Gainey also speculates that the known reaction of graphite with hydrogen could provide an additional retention mechanism for tritium in HTGRs (although gaseous methane is stated to be the principal product).

Chemisorption on graphite

In another section Gainey (1976) discusses tritium removal from the coolant system by chemisorption on graphite, and presents the available data as of 1976. The following quotes, figures, and tables are taken from Gainey (1976).

"It is known that both tritium and hydrogen can be chemisorbed onto graphite at high temperatures. However, only one set of measurements has been made in the temperature range of interest for HTGR operation. No information is available on the influence of neutron flux and irradiation upon the sorption properties of tritium on graphite ... it might be expected that a radiation field would ... increase the amount of chemisorption.

"Out-of-pile measurements made on A-3 graphite at HRB showed that tritium chemisorption increases with temperature and time. Further, the BET surface of the graphite also gradually increased [Table 9.5.1 from Gainey (1976)]. The temperature dependency of tritium chemisorption is shown in Fig. 9.5.3 (Gainey, 1976). In another test, a 6-cm graphite 'pebble' was equilibrated at 873°K for 100 hr with helium containing 570 dps/cm³ (STP) helium [1.54×10^{-2} μCi tritium/cm³ (STP) helium]. The tritium concentration profile through the graphite sphere is shown in Fig. [9.5.4]. A comparison of these results with the tritium concentration observed in graphite balls from the [German] AVR indicates that a much larger chemisorption of tritium occurs at reactor operating conditions ...

"Measurements made on Graphon, a graphitized carbon black, and on nuclear-grade graphite type TSP are given in Figures [9.5.5] and [9.5.6]. The results are limited to below 873°K and a pressure of 67 Pa (6.7×10^{-4} atm). It is important to notice that tritium and hydrogen chemisorption both increase with temperature.

"The kinetics of chemisorption of hydrogen on carbon and graphites is complex. Barrer and Rideal ... established that at about 873°K the rate of chemisorption of hydrogen on carbon changed from an exponential dependence upon temperature to a square root temperature dependence. This indicates that the diffusion of hydrogen to inner graphite

Fig. 9.5.1. Influence of annealing temperature on tritium release from graphite (from Gainey, 1976).

Fig. 9.5.2. Elovich plot of hydrogen desorption from nuclear graphite (TSP) at different temperatures (from Gainey, 1976).

Table 9.5.1. Tritium sorption on A-3 graphite at 873 and 1073 K (from Gainey, 1976)

Exposure Time (hr)	Temp (°K)	Adsorbed Amount (μCi/g)	BET After Loading (m ² /g)
0	873	0.47	0.85
4		0.63 0.87	
12.5	973	1.25 1.41	
24	873	1.44 1.55	
47	873	1.76 2.67	
96.5	873	2.57 2.93	
168	873	4.12	1.1-1.5
190	873	5.2 6.42	2.1
333	873	10.0 20.6 23.3 24.3	6-8
10	1073	1.7 1.8	
24	1073	2.2 2.2	1.8
49.5	1073	3.6 4.4	1.8
120	1073	5.1 5.2	1.7
300	1073	11.5	2.4

Fig. 9.5.3. Temperature dependence of tritium sorption on A-3 graphite (from Gainey, 1976).

Fig. 9.5.4. Tritium concentration profile through an AVR graphite sphere (from Gainey, 1976).

Fig. 9.5.5. Sorption of hydrogen on Graphon (from Gainey, 1976).

Fig. 9.5.6. Sorption of hydrogen on TSP nuclear graphite between 1100 and 1770 K (from Gainey, 1976).

surfaces is slower than the rate of chemisorption and therefore is rate limiting in this temperature region.

"In summary, the mechanisms by which tritium is held in graphite are poorly understood. Unfortunately, because so little information is available, it is not possible to incorporate tritium retention by graphite (or control materials) into model calculations. However, graphite could prove to be a very significant sink for tritium under reactor operating conditions ..."

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

More hard data needs to be located, if possible, for the sorption of tritium on graphite to permit comparison with the quantitative predictions of the model, and to confirm an approximate value for a in Eq. (9.5.2). For present purposes, the data presented in Figures 9.5.5 and 9.5.6, might be compared to the model to test their consistency, as well as verifying the inferred units of sorbed concentration in Eqs. (9.5.1) and (9.5.2).

After an appropriate value for a is determined, the Peach Bottom compact retention data can be compared to model predictions for the sorption of tritium on the compact matrix material and to determine the validity of applying the graphite model to the compact matrix material.

No comprehensive review of tritium behavior has apparently been undertaken since Gainey's report in 1976. Some review of the scientific literature with respect to tritium behavior in graphites might provide data not presently assimilated into the MHTGR database. Specifically, a suggestion from M. L. Russell (1991) may provide additional information on the interaction of tritium with graphite. Specific references are made to the work of R. A. Causey et al. (Eighth International Conference on Plasma-Surface Interactions, Jülich, Germany, May 1988; and articles in the *Journal of Nuclear Materials*) and to H. Atsumi et al. (articles in the *Journal of Nuclear Materials*). This work has not been reviewed by this writer, but future model evaluation should consider this additional information.

DATABASE USED IN MODEL DEVELOPMENT

Refer to Table 9.5.1 and Figures 9.5.1 through 9.5.6.

9.6 TRITIUM TRANSPORT IN THE COMPACT MATRIX MATERIAL AND GRAPHITE

function

This model provides a simple approximation for the rapid distribution of tritium within the fuel compact and graphite without functional dependencies.

present status	Apparently only a very simple model for tritium transport in graphite has been previously presented (FDDM/E), and no model has been presented for transport in the compact matrix material. A model can be suggested here in analogy with the model for metallic FP transport through the compact and graphite, consistent with existing computational methodology.
model uncertainty	Because this transport model depends on the model for sorption on graphite whose level of uncertainty is expected to be large, the uncertainty of this transport model must also be considered significant.
references	Acharya (1988)

NORMAL OPERATING AND ACCIDENT CONDITIONS

Model equations

Because only limited data is available for tritium behavior in the compact matrix material and graphite, a simple model can be postulated which assumes rapid and uniform dispersion of the tritium throughout the compact and graphite structure at all times:

$$C(x) = \bar{C} \quad , \quad (9.6.1)$$

- $C(x)$ = tritium concentration at position x within the fuel compact and/or graphite structures (arbitrary units),
 $\bar{C}$ = average tritium concentration throughout the fuel compact and graphite structures (arbitrary units).

By assuming this concentration to represent the surface concentration at the graphite/coolant interface, the sorption isotherm presented in §9.5 can be adapted to the methodology presented in §6.8 for transport across the interface into the coolant. The time-dependent balance between this rate of tritium loss to the coolant and the tritium source term within the core materials will provide the time-dependent average concentration throughout the compact/graphite structure. Because of the assumption of identical sorption isotherms for compact matrix material and graphite, tritium flow across the compact/graphite interface does not require calculation.

For example, at coolant interface temperatures above 650°C some fraction of tritium will be sorbed (§9.5) and the vapor pressure at the interface will determine the rate of tritium flow into the coolant. At temperatures less than 650°C the tritium should be rapidly released into the coolant.

Range of validity

This model is assumed to be valid over the range of the sorption model presented in §9.5 (i.e., over all reactor temperatures). The lack of experimental data prevents a more realistic range of validity based on experimental results.

Assumptions

The assumptions listed in §9.5 and §6.8 apply to this model. In addition:

1. The sorption isotherm presented in §9.5 is accurate.
2. Diffusion of tritium within the compact matrix material and graphite structures is insignificant.
3. The average tritium concentration throughout the compact/graphite structure is representative of that at the coolant interface.

Uncertainty

The uncertainty in the model cannot be quantified due to lack of data. Refer to the comments in "model uncertainty" above.

MODEL CHRONOLOGY

The statement of "Model Chronology" in §9.5 is applicable here.

DISCUSSION

This model is presented as a simple approximation to provide some modelling approach where little or none previously existed. This model should be analyzed and refined in the future as needed. The limited data on tritium release from graphite presented in §9.5 should be analyzed with respect to the sorption model. Such an analysis might allow information on the transport process itself to be inferred (e.g., diffusive transport vs instantaneous release). The only statement located which directly reflects on the method of transport is given by Gainey (1976): data for tritium release from lithium-containing graphite as a function of temperature "imply that tritium release from graphite is a diffusion-limited process since the release is proportional to the square root of time." These results are shown in Figure 9.6.1, taken from Gainey (1976). For tritium which is produced from lithium impurities within the graphite, the fission recoil would be expected to implant the tritium atoms into the graphite structure, and subsequent diffusive release would be required.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The considerations mentioned above in §9.5 also apply here. Modelling of tritium release from graphite and fuel compacts analogous to that for metallic FP seems reasonable

Fig. 9.6.1. Tritium release isotherms from annealed/irradiated graphite probes (from Gainey, 1976).

(i.e., representation of transport phenomena as a combination of sorptive and diffusive mechanisms). Some quantitative separation of the effects of sorption and transport are required, if such insight is possible from the limited database. For example, is the assumption of instantaneous transport of tritium throughout the compacts and graphite reasonable? Such questions may be difficult to answer considering the available data.

DATABASE USED IN MODEL DEVELOPMENT

Refer to Figure 9.6.1.

9.7 TRITIUM PERMEATION IN STEAM GENERATOR TUBES

function	This model calculates the rate of tritium permeation through steam generator tube alloys as a function of the tritium concentration in the coolant, concentration gradient across the tube, tube wall thickness, and temperature.
present status	"The present data base on tritium permeation is incomplete and shows a pressure dependence and a strong effect of surface films that are not understood" (CEGA, 1990). "The effects of impurities in the coolant and of an oxide layer on the coolant side of the tubes have not been determined" (Myers, 1988). There is "relatively little information available on the temperature and pressure region of interest for HTGRs" (Gainey, 1976). However, considerable data and theory exist which have not been considered for model development, including that for hydrogen and deuterium permeation.
model uncertainty	"The uncertainty is estimated to be 6" (Myers 1988).
references	Yang et al. (1977); FDDM/F; Gainey (1976); Le Claire (1981-1983)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The tritium permeation rate through steam generator (SG) tubes is described by the model equation (FDDM/F):

$$P_r = P_o \left(\frac{C_T}{C_{T_o}} \right)^n \left(\frac{\Delta C_T}{\Delta \tau_w} \right) e^{-Q/RT} \quad (9.7.1)$$

$$n = n_o e^{Q_o/RT} , \quad (9.7.2)$$

- P_r = tritium permeation rate ($\mu\text{Ci m}^{-2} \text{h}^{-1}$)
 P_o = constant (m mm h^{-1}),
 C_T = tritium concentration on coolant side of tube ($\mu\text{Ci m}^{-3}$, at STP),
 C_{T_o} = reference tritium concentration on coolant side of tube ($\mu\text{Ci m}^{-3}$, at STP),
 $\Delta C_T / \Delta \tau_w$ = tritium concentration gradient across the tube wall ($\mu\text{Ci m}^{-3} \text{mm}^{-1}$),
 τ_w = wall thickness of the SG tube (mm),
 Q, Q_o = activation energies (J mol^{-1}),
 T = temperature (K),
 R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$),
 n_o = constant (dimensionless).

Values of the parameters to be used for calculations of tritium permeation through Incoloy 800 and T-22 alloys are given in Table 9.7.1, as listed in FDDM/F. Note that T-22 alloy is also referred to as SA-387, and these labels can be used interchangeably; T-22/SA-387 is generally represented as 2-1/4 Cr-1 Mo alloy (Gainey, 1976).

Range of validity

Based on the limited database, the model is assumed to apply over all expected operating conditions of the reactor. The experimental data were obtained using Incoloy 800 and low carbon steel alloys with oxide layers on the steam side of the tubes and tritium source concentrations of $600 \mu\text{Ci/m}^3$ and $10^4 \mu\text{Ci/m}^3$ (STP) in helium with impurity concentrations listed in Table 9.7.2. (The impurity concentrations referred to in FDDM/F correspond to those for the $10^4 \mu\text{Ci m}^{-3}$ tritium source in Table 9.7.2.) The Incoloy 800 had a tube wall thicknesses of 3.175 mm and permeation was measured from 400 to 700°C. The

Table 9.7.1. Parameters for calculation of tritium permeation in steam generator tubes, Eq. (9.7.1) (from FDDM/F)

Alloy	P_o (m mm h ⁻¹)	C_{T_o} ($\mu\text{Ci m}^{-3}$, STP) ^(a)	n_o	Q (J mol ⁻¹)	Q_o (J mol ⁻¹)
Incoloy 800	9.10	600	0.935	53,500	2,290
T-22 (SA-387)	1.42	600	0.935	42,000	2,290

(a) FDDM/F mentions units of $\mu\text{Ci/cm}^3$; comparison with Yang et al. (1977) indicates units of $\mu\text{Ci/m}^3$ are correct.

Table 9.7.2. Characteristics of the tritium sources used in tritium permeation tests on Peach Bottom steam generator tubes
(from Yang et al., 1977)

	Simulation of Peach Bottom Coolant		Simulation of Large HTGR Coolant	
	In Reactor at 2.330×10^6 Pa or 23 atm Operating Pressure	Source Prepared	In Reactor at 5.065×10^6 Pa or 50 atm Operating Pressure	Source Prepared
Tritium specific activity ($\mu\text{Ci}/\text{m}^3$)	5.8×10^2	6×10^2	1×10^4	1×10^4
Impurities (0.101 Pa or microatm)				
H ₂	230	200	1500	1450
N ₂	23	27	50	54
CH ₄	23	22	50	50
CO	12	11	50	48
CO ₂	2.3	2.7	5	5
H ₂ O	0.23	<1	5	5
O ₂	0	<0.5	0	<0.5

low carbon steel alloys had tube thicknesses of 3.15 mm and permeation was measured from 221 to 352°C.

Assumptions

1. Tritium permeation through T-22 alloy is comparable to that measured through the low carbon steel.
2. The tritium permeation rate varies linearly with the source concentration.
3. The tritium concentration on the steam side of the tubes is assumed to be zero.
4. Variations in the impurity contents of the reactor coolant from those of the experiments will not significantly affect the tritium permeation rate.

Uncertainty

The uncertainty is presented in FDDM/F as the standard deviation in the natural logarithm of the permeation rate. The reported uncertainty values are the same for both Incoloy 800 and T-22:

$$\sigma (\ln P_r) = 1.1 \quad . \quad (9.7.3)$$

MODEL CHRONOLOGY

FDDM/E used the phenomenological model equation and parameter values as provided by Yang et al. (1977) (see "Discussion" below). FDDM/F revised this model equation to incorporate additional experimental variables and detail, but the revision is apparently also based on the original data of Yang et al. (1977). FDDM/F lists the source reference for this revision as an internal GA memo which has not been reviewed by this writer.

DISCUSSION

The design needs for this model parallel the data needs as summarized in DDN 11.54 of CEGA (1990): "Correlations describing the permeation of tritium through Alloy 800H and T22 (2-1/4% Cr 1% Mo steel) as a function of temperature, H^3 partial pressure, system pressure, coolant impurity concentrations and tube surface state. The effects of thermal cycling ... also must be determined."

The model equation provided in FDDM/F provides more detailed dependencies of tritium permeation on experimental parameters than that suggested in the reference document of Yang et al. (1977). For analysis of their data, Yang et al. used the phenomenological permeation equation:

$$P = P_o e^{-Q/RT} \quad , \quad (9.7.3)$$

P = tritium permeation rate ($\mu\text{Ci m}^{-2} \text{ h}^{-1}$),
 P_o = pre-exponential factor ($\mu\text{Ci m}^{-2} \text{ h}^{-1}$),

and all other terms defined as above.

Although more detailed, the FDDM/F model equation includes dependencies for only temperature and tritium concentration in the coolant. The effects of coolant impurity concentration, tube surface state, and thermal cycling are not considered by the model equations.

One limitation of the data is the low level of impurity concentrations in the experiments (Table 9.7.2) compared to those expected in the MHTGR. The coolant impurity levels listed in CEGA (1990) are 126 $\mu\text{atm H}_2\text{O}$, 315 $\mu\text{atm CO}$, 126 $\mu\text{atm CO}_2$, and 630 $\mu\text{atm H}_2$. Except for H_2 , these impurity concentrations are one to two orders of magnitude greater than those listed in Table 9.7.2.

The permeation data presented by Yang et al. (1977) is summarized in Tables 9.7.3 through 9.7.5. In these tables, the Incoloy 800 samples are identified by the prefix SU under Sample Designation and the low carbon steel alloys are identified by the prefix EC. Details on the two simulated helium coolants (Peach Bottom and Large HTGR) were presented in Table 9.7.2. Figures 9.7.1 and 9.7.2 (from Yang et al., 1977) are graphs of the data for the low carbon steel alloy for different surface conditions (tritium source of 600 $\mu\text{Ci m}^{-3}$ STP). Figures 9.7.3 and 9.7.4 (Yang et al., 1977) are graphs of the data for the Incoloy 800 alloy for different surface conditions (tritium source of 600 $\mu\text{Ci m}^{-3}$ STP), while Figures 9.7.5 and 9.7.6 (Yang et al., 1977) show the effect from two different tritium source concentrations for various surface conditions.

Gainey (1976) shows additional data for the effects of temperature and hydrogen pressures on hydrogen permeation through low carbon steel and T-22 from work by Yang and coworkers, which is reproduced in Fig. 9.7.7, and comparable data for hydrogen permeation through Incoloy 800 as shown in Fig. 9.7.8. Analogous data obtained by H. D. Röhrig and coworkers for Incoloy 800 are presented by Gainey (1976) are reproduced in Fig. 9.7.9. Gainey compares the work of Yang et al. with that of Röhrig et al. and comments that where "a comparison of these results is possible (873° and 973°K), good agreement is observed at hydrogen pressures below 133 Pa (1 torr). Above this pressure, the Germans report higher permeation rates."

Gainey (1976) presents additional ORNL data (attributed to R. A. Strehlow and H. C. Savage, *Nucl. Technol.* 22 (1974) 127) for deuterium permeation through several unoxidized and oxidized metals and alloys including Incoloy 800 and T-22; this data is reproduced in Table 9.7.6. Gainey also presents information and figures describing the effects of oxidation and coating thickness for hydrogen and tritium permeation through Incoloy 800. Figure 9.7.10 is attributed to unpublished data of T. S. Elleman at GA, and Figs. 9.7.11 and 9.7.12 are attributed to H. D. Röhrig et al. Finally, Gainey comments on the variation of tritium concentration in the helium coolant with respect to the background hydrogen, water, and methane concentrations in the Dragon, Peach Bottom, and AVR reactors. More discussion can be obtained in Gainey (1976) for consideration in model evaluation.

A very useful compilation of data and theory for the permeation of hydrogen and its isotopes was written by Le Claire (1981, 1982, 1983). Briefly, Table 9.7.7 summarizes other permeation data for Incoloy 800, and Table 9.7.8 summarizes data for several ferritic alloys.

Table 9.7.3. Tritium permeation rates of as-received Peach Bottom samples^(a)
(from Yang et al., 1977)

Test No.	Sample Designation	Temperature (K)	Tritium Permeation Rate ^(b) ($\mu\text{Ci}/\text{m}^2, \text{hr}$)
3	SU-I-6	673	1.19 (-1), 1.48 (-1)
4		773	4.34 (-1), 4.75 (-1)
5		873	1.04 (0), 8.28 (-1)
6		973	1.29 (0), 1.47 (0)
8	SU-O-6	673	9.25 (-2), 9.33 (-2)
9		773	4.35 (-1), 4.83 (-1)
10		873	1.75 (0), 1.69 (0)
11		973	2.90 (0), 2.68 (0)
15	EC-I-87	494	8.40 (-3)
16		564	1.40 (-2), 170 (-2)
17		625	6.61 (-2), 6.35 (-2), 6.29 (-2)(c)
18		493	1.28 (-2)
19	EC-O-76	566	3.31 (-2), 3.67 (-2)
20		563	3.09 (-2)
21		623	6.90 (-2), 6.51 (-2), 5.80 (-2)(c)
22		563	2.26 (-2), 2.06 (-2)
23	EV-I-26	523	1.72 (-2), 1.38 (-2)
24		573	4.55 (-2), 4.75 (-2)
25		634	1.53 (-1), 1.37 (-1)
26		694	3.84 (-1), 3.59 (-1)

(a) All tests were carried out with simulated Peach Bottom helium coolant outside the tubular sample (total pressure = 1.013×10^5 Pa or 1 atm) and helium-steam mixture inside (total pressure = 1.013×10^5 Pa or 1 atm, steam pressure = $6.66 - 8.00 \times 10^4$ Pa or 500 - 600 torr). The simulated Peach Bottom coolant has a tritium activity of $6 \times 10^2 \mu\text{Ci}/\text{Std m}^3$ and impurity partial pressures (in 0.101 Pa or microatm) of H_2 200, CO 11, N_2 27, CO_2 2.7, CH_4 22, H_2O <1, O_2 <0.5.

(b) The tritium permeation rate is calculated on the basis of the effective surface area of the sample. The numbers in parentheses represent an exponent of 10.

(c) The third measurement was carried out by using an extended tritium collection time (16 hours versus 2 hours for the other measurements).

Table 9.7.4. Effect of surface films on tritium permeation rates of Peach Bottom steam generator samples^(a)
(from Yang et al., 1977)

Test No.	Sample Designation	Surface Condition	Temperature (K)	Tritium Permeation Rate ($\mu\text{Ci}/\text{m}^2, \text{hr}$)
27	EC-O-76	Coolant-side film removed	493	1.06 (-2)
28			493	8.19 (-3) ^(b)
29			563	3.40 (-2), 3.80 (-2)
30			630	8.29 (-2), 8.90 (-2)
31	EC-O-76	Coolant-side and steam-side films both removed	513	9.67 (-2), 7.94 (-2)
32			562	2.44 (-1), 2.43 (-1)
33			628	7.33 (-1), 7.10 (-1)
37	EV-I-27	Coolant-side and steam-side films both removed	631	7.14 (-1), 6.73 (-1)
38			692	2.06 (0), 1.92 (0)
39	EV-I-26	Steam-side film restored	693	6.32 (-2), 9.09 (-2)
40			693	8.63 (-2), 9.28 (-2)
41			633	2.64 (-2), 2.66 (-2)
49	EV-I-26	Coolant-side surface cleaned further by polishing; steam-side film intact	633	2.53 (-2), 2.83 (-2)
50			693	1.14 (-1), 1.30 (-1)
51			573	9.40 (-3), 8.24 (-3)
62	EV-I-26	Coolant-side surface removed 1 mil mechanically; steam-side film intact	573	9.35 (-3), 5.36 (-3)
63			693	1.46 (-1), 1.37 (-1)

Table 9.7.4. (continued)

Test No.	Sample Designation	Surface Condition	Temperature (K)	Tritium Permeation Rate ($\mu\text{Ci}/\text{m}^2, \text{hr}$)
52	SU-I-6	Coolant-side film removed	773	2.25 (-2), 1.36 (-2)
52B			773	2.05 (-2), 1.62 (-2)
53			871	3.18 (-2), 3.09 (-2)
54			973	1.39 (-1), 1.09 (-1)
55	SU-I-6	Coolant-side and steam-side films both removed	673	6.33 (-2), 5.31 (-2)
56	SU-I-6	Steam-side film restored	873	6.63 (-1), 6.33 (-1)
57			873	2.92 (-2), 2.64 (-2)

(a) Measurements were made with the same simulated Peach Bottom helium coolant outside the tubular sample (at 1.013×10^5 Pa or 1 atm pressure) as that used for the measurements shown in Table 5-1. For cases where only the helium-coolant-side film was removed, the inside of the sample was exposed to a mixture of helium plus steam (total pressure = 1.013×10^5 Pa or 1 atm, steam pressure = $6.66 - 8.00 \times 10^4$ Pa or 500 - 600 torr). For cases where both the coolant-side film and the steam-side film were removed, the inside of the sample was exposed only to helium.

(b) The measuring was carried out by using an extended tritium collection time (16 hours versus 2 hours for the other measurements).

Table 9.7.5. Tritium permeation rate of Peach Bottom superheater samples from LHTGR helium coolant^(a)
(from Yang et al., 1977)

Test No.	Sample Designation	Surface Condition	Temperature (K)	Tritium Permeation Rate ($\mu\text{Ci}/\text{m}^2, \text{hr}$)
42	SU-0-6	As-received, after Test No. 11	673	6.20 (-1), 6.62 (-1)
43			773	2.89 (0), 2.94 (0)
44			873	9.23 (0), 9.23 (0)
45			973	1.42 (1), 1.57 (1)
46			973	1.84 (1), 1.32 (1)
58	SU-I-6	Coolant-side film removed, after Test No. 57	673	8.92 (-2), 1.00 (-1)
59			773	1.91 (-1), 2.24 (-1)
60			873	3.09 (-1), 4.15 (-1)
61			973	1.20 (0), 1.24 (0)

(a) Measurements were made with simulated large HTGR helium coolant outside the tubular sample at (1.013×10^5 Pa or 1 atm pressure) and helium plus steam (total pressure = 1.013×10^5 Pa or 1 atm, steam pressure = 500 - 600 torr). The simulated large HTGR coolant has a tritium activity of $1 \times 10^4 \mu\text{Ci}/\text{std m}^3$ and impurity partial pressures (in 0.101 Pa or microatm) of H_2 1450, N_2 54, CH_4 50, CO 50, CO_2 50, H_2O 5, O_2 <0.5.

Fig. 9.7.1. Tritium permeation rates of as-received Peach Bottom economizer samples (low carbon steel) (from Yang et al., 1977).

Fig. 9.7.2. Effect of surface films on tritium permeation rates of Peach Bottom economizer sample EC-0-76 (low carbon steel) (from Yang et al., 1977).

Fig. 9.7.3. Tritium permeation rates of as-received Peach Bottom superheater samples (Incoloy 800) (from Yang et al., 1977).

Fig. 9.7.4. Effect of surface films on tritium permeation rates of Peach Bottom superheater sample SU-I-6 (Incoloy 800) (from Yang et al., 1977).

Fig. 9.7.5. Effect of tritium concentration on tritium permeation rate of Peach Bottom superheater sample SU-I-6 after the removal of the surface deposit on the helium coolant side (Incoloy 800) (from Yang et al., 1977).

Fig. 9.7.6. Effect of tritium concentration on tritium permeation rate of as-received Peach Bottom superheater sample SU-0-6 (Incoloy 800) (from Yang et al., 1977).

Fig. 9.7.7. Hydrogen permeability through T-22 and low carbon steel at various temperatures (from Gainey, 1976).

Fig. 9.7.8. Permeation of hydrogen through Incoloy 800 (from Gainey, 1976).

Fig. 9.7.9. Permeation of hydrogen through Incoloy 800 vs temperature and pressure (from Gainey, 1976).

Table 9.7.6. Deuterium permeation through unoxidized and oxidized metals and alloys (from Gainey, 1976)

Material	Temp (°K)	Permeation Rate ^(a) at 1 Torr, Metal Thickness = 1 mm [cm ³ (STP)/hr-cm ²]	Pressure Range (torr)
Ni	896	$(1.6 \pm 0.2) \times 10^{-2}$	9×10^{-4} to 750
Hastelloy N	878	$(2.7 \pm 0.2) \times 10^{-3}$	4×10^{-3} to 31.4
304L stainless steel (initial)	970	$(2.3 \times 10^{-3})^{(b)}$	31.4
304L stainless steel (after 18 hr)	970	$(2.6 \pm 0.5) \times 10^{-4}$	3×10^{-2} to 31.4
304L stainless steel	1058	$(4.5 \pm 0.4) \times 10^{-4}$	5×10^{-2} to 31.4
406 stainless steel (oxidized with D ₂ -2.6% D ₂ O, 72 hr)	915	$(1.6 \pm 0.3) \times 10^{-5}$	1 to 750
Incoloy 800	922	$(1.6 \pm 0.2) \times 10^{-3}$	1 to 750
Incoloy 800 (after oxidation with D ₂ -2.6% D ₂ O at 1017°K)	922	$(4.7 \pm 0.4) \times 10^{-6}$	10 to 750
Incoloy 800 (exposed to H ₂ O at 811°K, 233 bars, 10 ³ hr before testing)	804	$(6.3 \pm 0.4) \times 10^{-4}$	1.3 to 750
Croloy T9 ^(c) (oxidized with D ₂ -2.6% D ₂ O, 72 hr)	846	$(6.6 \pm 0.5) \times 10^{-5}$	7 to 750
Croloy T9 (same specimen as above after 932°K oxidation)	843	$(5.7 \pm 0.4) \times 10^{-6}$	10 to 750
Croloy T22 ^(d)	558	$(1.8 \pm 0.1) \times 10^{-4}$	1 to 750
Croloy T22	853	$(8.0 \pm 0.1) \times 10^{-3}$	1 to 750
Croloy T22 (oxidized with D ₂ -2.6% D ₂ O at 853°K)	853	$(6.0 \pm 0.2) \times 10^{-3}$	3 to 750

(a) 95% confidence level from a least-squares fit.

(b) Extrapolated to 1 torr assuming half-power pressure dependence.

(c) ASTM-A-213-T9.

(d) ASTM-A-213-T22.

Fig. 9.7.10. Effects of oxidation and coating thickness on the release of tritium from Incoloy 800 (from Gainey, 1976).

Fig. 9.7.11. Influence of oxide film on hydrogen permeation (from Gainey, 1976).

Fig. 9.7.12. Hydrogen permeation vs $1/T$ for a clean oxide surface (from Gainey, 1976).

Table 9.7.7. Permeation constant measurements for hydrogen and isotopes in high nickel alloy steels (from Le Claire, 1983; references available therein)

$$P_m = P_m^* \exp(-Q_{pm}/RT) \text{ ccs.H}_2(\text{STP}) \text{ cm}^{-1}\text{s}^{-1}\text{atm}^{-1/2}$$

Unless otherwise stated: (i) P_m^* and Q_{pm} are for hydrogen.
(ii) for age hardenable alloys, results are for alloys in the solution treated condition.

No.	$P_m^* \cdot 10^2$	Q_{pm} (kcal $s\ mol^{-1}$)	Temp. range (°C)	Input Pressure range (atm.)	Authors
<u>Incoloy 800</u>					
1	7.49	17.7	600-950	$5 \cdot 10^{-5}$ -0.5	Röhrig et al (1974)
2	1.76	15.3	700-950	1-5	Mori & Nakada (1974)
3	7.58	16.8	760-960	1	Tanabe (1974)
4	40.3	20.58	600-1050	1-10	Narita (1977)
5	4.06	15.5)	450-950	5-10	Buchkremer et al (1978)
6	5.94	(a) 15.5)			
7	6.78	16.5	800-1000)	1	Masui et al (1979)
8	6.03	(b) 16.6	500-1000)		
9	H 0.24	13.1)	300-600	0.13-0.8	Tanabe et al (1979)
10	D 0.25	) 14.1)			
11	T 2.60	16.12)	350-750	(c)	Bell, Redman & Bittner (1980)
12	T 1.69	(e)) (d) 15.61)			
<u>Incolov 802</u>					
13	2.92	15.2	450-950	5-10	Buchkremer et al (1978)
<u>Incolov 807</u>					
14	3.61	15.2	450-950	5-10	Buchkremer et al (1978)
15	9.42	17.48	800-1000	1	Masui (1978)

Table 9.7.8. Permeation constant measurements for hydrogen and isotopes in ferritic FeCr alloys (from Le Claire, 1982; references available therein)

$$P_m = P_m^0 \exp(-Q_{pm}/RT) \text{ ccs (S.T.P.) cm}^{-1} \text{ s}^{-1} \text{ atm}^{-1}$$

(The P_m^0 and Q_{pm} are for hydrogen unless otherwise indicated).

No.	Alloy Type	Cr	Mn	C	Others ^(b)	$10^3 \times P_m^0$	Q (kcal/mol)	Authors
1	4130	0.7	-	0.3	0.2 Mo	2.08	9.49	Nelson & Stein (1973)
2	4130					2.1	9.0	Louthan et al (1976)
3	-	1.38	0.5	.04	0.33 Si	[3.71](a)	9.25	Chang & Bennett (1952)
4	Croloy 2		-	-	1 Mo .3 Ni	(T) 3.95	11.21	Bell et al (1979)
5	Croloy 2		0.4	.08	1 Mo .12 Ni .14 Si	(T) 2.45	9.35	Renner & Raue (1979)
6	-	2.51	0.57	.04	.37 Si	[4.74](a)	10.25	Chang & Bennett (1952)
7	-	4.25	0.53	.05	.25 Si	[.644](a)	10.30	Chang & Bennett (1952)
8	406	13			-	(T) 4.78	12.20	Bell et al (1979)
9	430	15.6	-	.04	-	1.16	11.44	Rudd & Vetrano (1960)
10	430	16			-	1.0	11.2	Flint (1951)
11	E.Brite 26		-	-	1 Mo	(T) 7.6	12.3	Bell et al (1979)
12	-	27.5	0.2	.06	0.47 Si	1.85	12.97	Geller & Sun (1950)

Notes on Table

(a) Square brackets indicate that numerical values were not explicitly reported by the authors. Values quoted for P_m^0 were calculated from tabulated Q_{pm} and graphs of P_m .

(b) Alloy contents in wt.%. Balance Fe, although authors do not always report detailed analyses.

Comparison of the alloy constituents in Table 9.7.8 with that of T-22 in Table 9.7.9 (taken from Gainey, 1976) shows that the data for some alloys could be compared with that for T-22 and the low carbon steels used by Yang et al. Future model analysis should consider the data and theory provided by this compilation by Le Claire.

Acharya (1988) employs the present model equations to calculate the tritium distribution throughout the MHTGR, including permeation through the SG tubes. His conclusion may be pertinent to further model analysis: tritium "permeation through the steam generator tubes is predicted to be less than 4 curies during the life of the plant. Compared to other permeation analysis results, this number appears to be very low and suggests that the permeation data given in the Fuel Design Data Manual which was used in this analysis should be re-evaluated." Acharya then used older permeation data and calculated a tritium permeation of approximately 250 Ci over the lifetime of the plant.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

From the above presentation, it would appear that significant data exist for the permeation of hydrogenic isotopes through Incoloy 800 and T-22 under a variety of experimental conditions which could be incorporated into a more detailed model. The compilations of Le Claire and Gainey represent an excellent starting point. More recent data may have been produced by the fusion energy program which shares comparable concerns for tritium permeation through metals and alloys; review of the scientific literature of the past decade could be promising.

The larger database for permeation of hydrogen and deuterium should be compared to that of tritium and incorporated into the model. In general, the permeation data should not be expected to vary by more than some constant, and the general dependencies of permeation with respect to experimental variables should be the same (with very similar chemical behavior of the isotopes, the main difference is their relative atomic weights).

Acharya's statement questioning the reliability of the model equations for tritium permeation are a concern. Perhaps comparison of the existing model equations with the expanded database recommended above might provide some insight into this issue.

DATABASE USED IN MODEL DEVELOPMENT

The database used in the development of the model equations presented in FDDM/F was taken from Yang et al. (1977) and is represented by Tables 9.7.2 through 9.7.5 and Figures 9.7.1 through 9.7.6 in "Discussion" above. Although apparently not considered in the development of these model equations, the data represented by Figures 9.7.7 through 9.7.12 and Tables 9.7.6 through 9.7.8 could be considered for future incorporation into the database during evaluation and revision of the existing model.

Table 9.7.9. Materials used in permeation studies (from Gainey, 1976)

Material	Nominal Composition ^(a) (%)
Nickel, ASTM B-161, Grade A	Ni; 0.25 max. Cu; 0.40 max. Fe; 0.35 max. Mn; 0.35 max. Si; 0.15 max. C; 0.01 max. S
304L stainless steel	Fe; 18 to 20 Cr; 8 to 12 Ni; 2.00 max. Mn; 1.00 max. Si; 0.045 max. P; 0.030 max. S; 0.03 max. C
406 stainless steel	Fe; 14 Cr; 3.9 Al; 0.4 Ni; 0.4 Mn; 0.4 Si; 0.3 Ti; 0.08 C
Incoloy 800	Fe; 32.0 Ni; 20.5 Cr; 0.35 Si; 0.75 Mn; 0.30 Cu; 0.04 C
Hastelloy N	Ni; 15 to 18 Mo; 6 to 8 Cr; 4 Fe; 0.04 to 0.08 C; 0.5 Al; 0.01 B
T9, ASTM A-213-T9	Fe; 8 to 10 Cr; 0.9 to 1.1 Mo; 0.30 to 0.60 Mn; 0.25 to 1.00 Si; 0.15 max. C; 0.03 max. P; 0.03 max. S
T-22, ASTM A-213-T22	Fe; 1.9 to 2.6 Cr; 0.87 to 1.3 Mo; 0.30 to 0.60 Mn; 0.5 max. Si; 0.15 max. C; 0.03 max. P; 0.03 max. S

(a) Composition given is that supplied by the manufacturer or obtained from the handbooks.

9.8 TRITIUM TRANSPORT IN TARGET PARTICLES

- function** The transport of tritium from its generation in the target kernel material through the TRISO coating layers and release from the particle must be calculated for NP-MHTGR target particles.
- present status** The models used to describe this transport are presently unknown to this writer. Future inclusion of such models in a revision of this compilation would be appropriate.

9.9 UPDATE

Although significant data on tritium transport were obtained as part of the NP-MHTGR target program, apparently those data have not been made available to the MHTGR fuel program. Therefore, the only new data relevant to this chapter might be the irradiation performance of the B₄C coated particles included in HRB-21 piggyback samples, provided PIE is performed on those samples.

10. HEAVY-METAL TRANSPORT THROUGH THE CORE MATERIALS

10.1 INTRODUCTION

The models for transport of heavy-metal atoms are similar to those of metallic FP in most cases. Other compilations (e.g., FDDM/F) often include HM transport as a subset of metallic FP transport models. Heavy-metal transport models are included here as a separate section for ease of analysis of HM-specific models. CEGA (1990) does not present any Design Data Needs which discuss HM transport in the core; therefore, these models and available data will only be briefly presented for reference.

No models for HM transport within the fuel compact are stated explicitly in FDDM/F. One can reasonably assume that HM transport in the compact would be modelled analogously to that of metallic FP (§6.3); i.e., establishment of an instantaneous average concentration throughout the compact upon release from the particles. For lack of information, one might assume that HM release from the compact surface might follow sorption isotherms such as suggested in §10.5 below for graphite. However, this is nowhere discussed explicitly and can only be inferred. As such, HM transport in the fuel compact will not be discussed further.

Homan et al. (1978) comment on the potential importance of Pu transport and release from an HTGR system. "Pu-238, which is derived from U-235, represents a potential radiological hazard if it is released in significant quantities to the primary circuit. Since the U-235 inventory in a LEU/MEU core is approximately the same as that in a HEU core, plutonium release is important to both LEU/MEU and HEU systems" although the yield of Pu is higher in LEU than in HEU fuel. "Plutonium release from intact TRISO particles is probably negligible at typical HTGR operating temperatures. For failed particles, the release should vary with the composition of the phases in the kernel ..."

General Atomic (1979) comments that "Plutonium migrates at a higher rate than uranium and thorium, and the tolerable release of plutonium into an HTGR primary circuit is small, mainly because Pu-238 has such a high bone inhalation effectivity (rem/Ci, about 500 times that of Sr-90)." As a footnote, this report discusses a MEU program with a stated uranium enrichment of about 20%, which corresponds to the present definition of LEU fuel.

An estimate of the amount of Pu which could be released into the primary circuit of a LHTGR was reported by K. J. Mysels in General Atomic (1978). The motivation of the estimate was "intended to show that even if, contrary to evidence, the transport through graphite was in no way limiting, the rate of evaporation of the plutonium into the helium would be sufficiently slow to reduce the release to an acceptable level."

Fellows et al. (1987) have conducted a more recent estimate. "The transport pathway of plutonium, generated from in-core conversion of tramp uranium in the fuel rods, through the HTR core and coolant system, has been examined in order to approximate the degree of plutonium holdup in the graphite. Estimates suggest that only about $2.9 \times 10^{-4}\%$ of this plutonium transmuted from the uranium outside of the fuel will be transported out of the core graphite during the lifetime of the HTR fuel elements in the reactor core. The remainder is held as chemisorbed or dissolved species in the graphite." Details of these

estimates will not be presented here, but can be referred to for useful insight into model approximations for Pu transport throughout the reactor core.

10.2 HEAVY-METAL TRANSPORT IN THE FUEL KERNEL

function	This model provides a diffusion coefficient for Pu in the kernel as a function of kernel material, burnup, and temperature.
present status	The reference diffusion coefficients for Pu in several kernel materials are the same as those given for Sr. Preliminary analysis of the data which exist for Pu suggested different values for the model parameters, but the Sr model is apparently used for convenience. Transport of Am and Pm are also briefly discussed.
model uncertainty	The uncertainties in metallic FP diffusion coefficients in kernels are "exceedingly large" (Myers, 1988) due to extrapolation of diffusion data in ThO ₂ and lack of data on burnup and fluence effects. The same can be said for HM diffusion as parameters for Sr are applied directly to Pu transport.
references	FDDM/F; Myers (1981b, 1981d, 1981e)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The effective homogeneous diffusion coefficient is given by (Myers, 1981d):

$$D = D' r^2 , \quad (10.2.1)$$

with the reduced diffusion coefficient in the kernel prior to irradiation given by:

$$D' = D'_0 \exp\left(-\frac{Q}{RT}\right) , \quad (10.2.2)$$

- D = effective homogeneous diffusion coefficient ($\text{m}^2 \text{s}^{-1}$),
- D' = reduced diffusion coefficient (s^{-1}),
- r = kernel radius (m),
- D'_0 = pre-exponential factor (s^{-1}),
- Q = activation energy (J mol^{-1}),
- T = temperature (K),
- R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

During irradiation, the reduced diffusion coefficient changes with burnup according to:

$$D'_o = C_1 [1 + (1 + n) C_2 F^n] \quad , \quad (10.2.3)$$

F = burnup (% FIMA),
 C_1 = constant (s^{-1}),
 C_2, n = constants (dimensionless).

Given the parameters C_1 , C_2 , n , and Q , the reduced diffusion coefficient can be calculated as a function of temperature and burnup. Values for C_1 , C_2 , n , and Q are given in Table 10.2.1 for Pu in several kernel materials.

Range of validity

The range of validity of this model must be considered to include all temperature regimes representative of NOC and AC and to apply to all reactor operating regimes in general. As the reference model is apparently based on Sr data rather than the existing Pu data, one might conclude that there is no experimental range of validity as such.

Assumptions

As the model parameter values for Pu and Sr are identical, most of the assumptions listed in §5.2 are applicable and will not be repeated here. Only Pu-specific assumptions are stated below.

Table 10.2.1. Parameters for calculation of plutonium diffusion coefficients in kernels, Eqs. (10.2.2) and (10.2.3)

Kernel material	$C_1 (s^{-1})^{(a)}$	$C_2^{(a)}$	$n^{(a)}$	$Q (J \text{ mol}^{-1})^{(a)}$	Ref.
UCO ($UC_{0.4}O_{1.6}$) ^(b)	1.1×10^9	0.0197	4	593,600	FDDM/F
ThO ₂ , UO ₂ ^(c)	7.6×10^8	0.0197	4	593,600	FDDM/F
UC ₂	(d)	(d)	(d)	(d)	Myers (1981d)

- (a) All values the same as those for Sr (see Table 5.2.1).
 (b) Myers (1981d) provided these values specifically for $UC_{0.4}O_{1.6}$ for Sr (see §5.2).
 (c) Values for UO₂ are assumed to be the same as those for ThO₂.
 (d) No retention by UC₂ or ThC₂ is assumed.

1. Plutonium transport is analogous to Sr transport within kernel materials.
2. The burnup dependence for Pu is assumed to be the same as that for Cs (i.e., $n = 4$).
3. Carbide fuels do not retain Pu.
4. The diffusion coefficient for Pu in UO_2 kernels is the same as that in ThO_2 kernels.
5. The diffusion coefficient of any metallic FP (and Pu) in UC_xO_y is derived from that in UO_2 by multiplication by the factor $[1 + (2 - y)/2]^2$, to incorporate the assumption that no retention in the UC_2 portion of the UC_xO_y fuel occurs (Myers, 1981d).

Uncertainties

FDDM/F reports the standard deviation in the natural logarithm of the diffusion coefficients as follows. For diffusion in UCO and ThO_2 kernels, the standard deviation is given as:

$$\sigma(\ln D) = 5.7 \quad (10.2.4)$$

This value is the same as that reported for Sr diffusion.

MODEL CHRONOLOGY

Myers (1981d) developed the model equations presented above. Myers (1981b) began deriving Pu-specific values for the model parameters and Myers (1981e) applied a different model formulation to the data. For some reason, this work is not considered by the present model which simply applies the Sr parameters to Pu.

DISCUSSION

This model is presented in a format identical to that of the metallic FP in §5.2. Homan et al. (1978) provides a review of the available data and analyses for Pu transport in kernel materials as of 1978.

Statements provided by Myers (1981b) are interesting in comparison with the recommended diffusion coefficients of Table 10.2.1. "Data on in-pile release of Pu from $(\text{Th},\text{U})\text{C}_2$ have been obtained by Buzzelli ... and preliminary, out-of-pile data on Pu release from UC_2 by Sterling ... The former data apply to burnups of 14-18% FIMA, the latter to a burnup of 60% FIMA. The reduced diffusion coefficient of [General Atomic Report GA-A14953, June 1978] for 1200°C is plotted in Fig. [10.2.1] along with the value of the reduced diffusion coefficient calculated from a fit to the data of [General Atomic Report GA-A14863, March 1978] ... the data are represented by

$$D' \approx 3.2 \times 10^{-24} F^{6.9}$$

Thus, the reduced diffusion coefficients are found to depend on the 6.9 th power of the burnup experienced, i.e., $n = 6.9$. In treating the Pu data of Fig. [10.2.1], kernel composition

Fig. 10.2.1. Burnup dependence of reduced diffusion coefficients for Cs and Pu in $(Th,U)C_2$ and ThC_2 kernels (from Myers, 1981b).

differences have been neglected." These statements are considerably different than the reference model presented above.

A more detailed analysis of the Pu release data is provided by Myers (1981e) and is summarized as follows. "A preliminary analysis of plutonium release data has been made with the following results and conclusions:

1. The release of plutonium from the kernels of laser-failed particles is controlled by the process of evaporation at 1050° and 1200°C for particles with WAR and UO₂ kernels and at 1050°C also for particles with UC₂ and (Th,U)O₂ kernels,
2. The release of plutonium from the kernels of laser-failed particles at 1200°C is controlled by diffusion for particles with UC₂ and (Th,U)O₂ kernels,
3. An expression for the rate of evaporation has been derived,
4. The reduced diffusion coefficients for plutonium in UC₂ and (Th,U)O₂ at 1200°C have been evaluated and
5. A discussion is presented on important factors which are not operative in the plutonium release experiments."

In addition, a diffusion coefficient for Pu in (Th,U)C₂ is given as:

$$D = 1.4 \times 10^{-3} \exp \left(- \frac{573,000}{RT} \right), \quad (10.25)$$

- D = diffusion coefficient (m² s⁻¹),
 T = temperature (K),
 R = ideal gas constant (8.314 J mol⁻¹ K⁻¹).

This expression was stated to be applicable for burnups from 14 to 18% FIMA. Additional details on this analysis can be obtained from Myers (1981e). The database for this analysis is presented in Table 10.2.2. These calculations for release from carbide kernels do not appear to be consistent with the assumption of no retention by carbide kernels.

Mehner et al. (1982) analyzed the transport of Pu and Am within fuel particles. "The transport behaviour of the transuranium elements plutonium and americium in low enriched coated particle fuel at high irradiation temperatures was investigated by means of mechanical separation of kernel and coating after irradiation ... The main results of the alphaspectrometry measurements are plotted in Fig. [10.2.2]. The observed scatter is not caused by the method of Pu and Am determination but is due to the inhomogeneous temperature distribution in the irradiation capsule. The diagramm shows clearly, that there is no diffusion of transuranium elements from UO₂ kernels, the amount of Pu and Am found in the coating was formed directly by the uranium contamination. Diffusion of both transuranium elements was observed from all carbide-containing kernels where the release of americium was always higher than that of plutonium. This can be explained by the higher vapour pressure of americium compared with plutonium over the carbide."

Chernikov et al. (1982) analyzed the transport of several metallic FP and of promethium within fuel particles. "Diffusion mobility of promethium in uranium dioxide with atomic ratio O/U = 2.001 and in the oxide, alloyed by imitators of fission products (rare-

Table 10.2.2. Plutonium release data: fractional release of α -emitters in post-irradiation annealing tests (from Myers, 1981e)

Kernel	Burnup (% FIMA)	Temp. (a) (°C)	Fractional Release (b)		
			200 h	800 h	1800 h
10-7	UC ₂	60	(0+0.8)(-4)	(5.9+1.6)(-4)	(1.2+0.2)(-3)
		60	(5.0+0.3)(-3)	(1.3+0.05)(-2)	(2.1+0.05)(-2)
	(Th,U)O ₂ 1:1	40	(0.0+7.4)(-5)	(1.2+1.0)(-4)	(2.2+1.0)(-4)
		40	(2.0+0.9)(-4)	(3.8+1.4)(-4)	(6.0+1.5)(-4)
	UO ₂	60	(2.6+1.4)(-4)	(6.9+2.2)(-4)	(1.4+0.2)(-3)
		60	(5.8+1.4)(-5)	(1.5+0.3)(-3)	(3.7+0.3)(-3)
	WAR O/U=1.6	59	(2.9+1.2)(-4)	(2.9+1.5)(-4)	(9.8+1.6)(-4)
		59	(6.6+1.4)(-4)	(3.6+0.3)(-3)	(8.2+0.3)(-3)
	WAR O/U=1.2	59	(2.4+1.3)(-4)	(7.2+2.0)(-4)	(1.3+0.2)(-3)
		59	(3.2+0.3)(-3)	(1.6+0.03)(-2)	(2.5+0.03)(-2)
	WAR O/U=0.9	11-16	(3.8+0.3)(-3)	(4.0+0.3)(-3)	(4.2+0.3)(-3)
		11-16	(8.0+0.2)(-3)	(2.9+0.07)(-2)	(4.0+0.07)(-2)
	WAR O/U=0.9	11-16	(9.0+0.4)(-3)	(1.5+0.05)(-2)	(1.8+0.05)(-2)
		11-16	(6.1+0.1)(-2)	(1.3+0.2)(-1)	(1.4+0.2)(-1)
	WAR O/U=0.0	28	(1.0+0.1)(-4)	(1.4+0.2)(-4)	(2.0+0.2)(-4)
		28	(7.0+0.1)(-3)	(2.2+0.02)(-2)	(3.5+0.02)(-2)

(a) Nominal temperature

(b) $(4 \pm 2)(-4) \equiv (4 \pm 2) \cdot 10^{-4}$

Fig. 10.2.2. Fraction of Pu (●) and Am (○) in the coatings of 30 irradiated LEU fuel particles (from Mehner et al., 1982).

earth metals, Y, Zr) is practically the same and near the value of uranium atomic mobility in UO_2 ... that is, probably, connected with alloyed admixture diffusion due to uranium dioxide lattice defects diffusion playing the main role in atom migration." The diffusion coefficient for ^{147}Pm in UO_2 is given by:

$$D = 2.00 \times 10^{-7} \exp\left(-\frac{82,000}{RT}\right), \quad (10.2.6)$$

- D = diffusion coefficient of ^{147}Pm in UO_2 ($\text{m}^2 \text{s}^{-1}$),
 T = temperature (K),
 R = ideal gas constant (not stated, but appears to be $1.987 \text{ cal mol}^{-1} \text{K}^{-1}$).

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

If the need arises in the MHTGR program for refinement of HM transport models, the work reported by Myers (1981b, 1981e) can be reviewed in detail. The work by Myers (1981e) represented significant effort toward providing a more detailed release model, and can be reviewed for its validity in relation to newer data, if any exist.

DATABASE USED IN MODEL DEVELOPMENT

Table 10.2.2 represents the available database as of 1981 as presented by Myers (1981e). Data from two additional experiments are reported by Myers (1981e) and can be reviewed in that reference.

10.3 HEAVY-METAL TRANSPORT IN THE PARTICLE COATING LAYERS

function	This model provides a diffusion coefficient for Pu in PyC layers as a function of temperature. No diffusion of HM atoms through intact SiC layers is assumed.
present status	The reference diffusion coefficient for Pu in PyC was obtained using unirradiated and nonreference HTI PyC. No diffusion through the SiC is assumed. Transport of U, Th, Am, and Pm in PyC is also briefly discussed.
model uncertainty	Although a value for the uncertainty of the diffusion coefficient of Pu in PyC is given in FDDM/F, the use of a diffusion coefficient obtained using unirradiated nonreference HTI PyC must introduce significant uncertainty. No uncertainty for the SiC transport model is stated.
references	Baldwin et al. (1978); Homan et al. (1978)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

Transport of heavy-metal atoms through PyC is modelled using the traditional formulation for the diffusion coefficient:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right), \quad (10.3.1)$$

- D = diffusion coefficient ($\text{m}^2 \text{s}^{-1}$),
- D_0 = pre-exponential factor ($\text{m}^2 \text{s}^{-1}$),
- Q = activation energy (J mol^{-1}),
- T = temperature (K),
- R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

For Pu in PyC, values for D_0 and Q as determined by Baldwin et al. (1978) are:

$$\begin{aligned} D_0 &= 4.47 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}, \\ Q &= 230,000 \text{ J mol}^{-1}. \end{aligned}$$

No diffusion of HM atoms is assumed to take place in intact SiC layers:

$$D_{\text{SiC}} = 0.0 \quad (10.3.2)$$

Range of validity

The model is assumed to apply over all reactor conditions. Experimentally, the data was obtained from approximately 1000 to 1800°C, using HTI PyC deposited onto graphite disks and a source solution of plutonium oxide dried onto the surface of the PyC.

Assumptions

1. Data for Pu diffusion in HTI PyC can be used to represent diffusion in LTI PyC.
2. Data for Pu diffusion in unirradiated PyC can be used to represent diffusion in irradiated PyC.
3. Temperature is the only significant variable affecting diffusive transport of Pu in PyC.
4. No significant diffusion of HM atoms takes place in intact SiC.

Uncertainty

The uncertainty in the diffusion coefficient of Pu in PyC is given by FDDM/F as the standard deviation, σ , of $\ln D$:

$$\sigma (\ln D) = 0.40$$

(10.3.3)

MODEL CHRONOLOGY

The only detailed study for the transport of Pu in PyC is that presented by Baldwin et al. (1978). Confirmatory experiments were also performed by Mehner et al. (1982). Earlier data exist for the diffusion of U and Th in PyC, as discussed below. For HM transport through SiC, the early belief that intact SiC would prevent release of Pu has not changed.

DISCUSSION

Homan et al. (1978) comment on the results of Baldwin et al. (1978): "The D values for plutonium are about an order of magnitude higher than those of uranium in isotropic pyrolytic carbon and two orders of magnitude higher than those of thorium. It would be highly desirable to extend these measurements to low-temperature-isotropic (LTI) coatings." Apparently this hope remains unfulfilled to the present. Homan et al. also comment that a "BISO coating is not a good barrier for plutonium release, but a TRISO coating retains plutonium."

These qualitative comments on Pu, U, and Th diffusion in PyC are quantified in a figure from Baldwin et al. (1978), reproduced as Fig. 10.3.1. The references for the Th and U data are given below in "Database."

Mehner et al. (1982) determined the range of diffusion coefficients for Pu and Am in PyC from the data presented in Fig. 10.2.2, previously shown in §10.2. "Diffusion coefficients of plutonium and americium in the pyrocarbon coating of the UC₂-BISO particles were obtained from the particle release in the range

$$\begin{aligned} 5.6 \times 10^{-16} < D_{\text{Pu}}/\text{m}^2 \text{ s}^{-1} < 2.5 \times 10^{-15}, \\ 7.4 \times 10^{-16} < D_{\text{Am}}/\text{m}^2 \text{ s}^{-1} < 7.1 \times 10^{-15}. \end{aligned}$$

These data agree with diffusion coefficients of plutonium in pyrocarbon coatings given by Baldwin, Winchell, and Langer" (1978).

The existence of detailed experiments to study the transport of Pu or other HM species in SiC has not been determined. The reference model for nonexistent transport in SiC is probably derived from experiments such as the following, quoted from Homan et al. (1978). "The effectiveness of SiC as a diffusion barrier for plutonium has been demonstrated in other high temperature irradiation experiments. For instance, TRISO coated plutonium oxide particles ... were irradiated in Studsvik to 20% FIFA [fissions per initial fissile atom] at 2123 K ... No evidence of plutonium release from the coated particles was detected by gamma-ray spectrometry." The reference provided for this data is P. Barr et al. ("High Temperature Irradiation Experiments on Plutonium-Bearing Coated Particle Fuel," *Plutonium as a Reactor Fuel*, International Atomic Energy Agency, Vienna, 1967).

Fig. 10.3.1. Diffusion coefficients of plutonium in isotropic pyrolytic carbon (from Baldwin et al., 1978).

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Any consideration of model refinement is limited by the available data. One cannot consider refinement of the model to consider, for example, transport through LTI PyC or the effects of irradiation on transport without additional experiments or data. The same is true for considerations of transport in SiC, although this model as it exists should have less uncertainty than the PyC transport model.

DATABASE USED IN MODEL DEVELOPMENT

The database used to derive the model parameters of Eq. (10.3.1) for Pu diffusion in PyC is presented in Table 10.3.1, taken from Baldwin et al. (1978). For the database related to diffusion of Th and U in PyC as presented in Fig. 10.3.1, Baldwin et al. (1978) provide the following references:

H. K. Lonsdale and J. N. Graves (1967), *J. Appl. Phys.* 38, 3620.

L. R. Zumwalt and J. N. Graves (1970), General Atomic Co., Private Communication.

For the database related to Pu transport through SiC, one can refer to the reference of Barr et al. (1967) quoted by Homan et al. (1978) above. Homan et al. (1978) also present some data on release of Pu, U, and Th from loose, intact, BISO and TRISO irradiated particles which was attributed to a private communication with G. Buzzelli (1977).

10.4 HEAVY-METAL TRANSPORT IN GRAPHITE

function	This model provides a diffusion coefficient for Pu in graphite as a function of temperature and fractional graphite oxidation.
present status	The model for diffusion of metallic FP in graphite (§6.4) is applied to the diffusion of plutonium in graphite. Refer to §6.4 for more detailed information on this model.
model uncertainty	Although the uncertainty of this model for Pu transport is presented quantitatively in FDDM/F, insufficient information is available for a qualitative statement on the uncertainty of the model.
references	FDDM/F; Fellows et al. (1987); Tallent et al. (1985)

Table 10.3.1. Results of plutonium diffusion in isotropic pyrolytic carbon
(from Baldwin et al., 1978)

Diffusion Time (h)	Diffusion Temperature (K)	Diffusion Coefficient (m ² /s)
1002.0	1260	7.79×10^{-18}
1002.0	1260	1.91×10^{-17}
102.0	1445	3.79×10^{-16}
102.0	1445	2.68×10^{-16}
40.5	1645	2.28×10^{-15}
40.5	1645	3.09×10^{-15}
1.0	1815	1.49×10^{-14}
1.0	1815	1.15×10^{-14}
0.1	2050	6.12×10^{-14}
0.1	2050	6.64×10^{-14}

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The standard Fick's law diffusion coefficient is used to model the diffusion of metallic FP in the structural graphite, H-451:

$$D = D_o \exp\left(-\frac{Q}{RT}\right), \quad (10.4.1)$$

- D = effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$),
- D_o = pre-exponential factor ($\text{m}^2 \text{s}^{-1}$),
- Q = activation energy (J mol^{-1}),
- T = temperature (K),
- R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

A recent refinement of the model considers the effect of graphite oxidation on diffusion (FDDM/F):

$$D = D_o [1 + d_o (1 - e^{-B})] \exp\left(-\frac{Q}{RT}\right), \quad (10.4.2)$$

- B = weight percent burnoff (extent of graphite oxidation),
- d_o = constant.

This model has also been applied to the diffusion of plutonium in H-451 graphite, with the model parameters given by:

$$\begin{aligned} D_o &= 4.36 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}, \\ Q &= 172,000 \text{ J mol}^{-1}, \\ d_o &= 3.0. \end{aligned}$$

Range of validity

The model is assumed to apply over all reactor conditions. Refer to Fellows et al. (1987) for discussion of the experimental range of validity.

Assumptions

With respect to model assumptions, an internal GA memorandum is referenced which has not been reviewed by this writer. Only one model assumption is obvious: the value for d_o obtained for strontium can also be applied to Pu transport (FDDM/F). Reference can be made to Fellows et al. (1987) for assumptions which went into derivation of the diffusion coefficients from the experimental data.

Uncertainty

The uncertainty is expressed in FDDM/F as the standard deviation, σ , of $\ln D$:

$$\sigma (\ln D) = 1.10 \quad . \quad (10.4.3)$$

MODEL CHRONOLOGY

A diffusion coefficient for Pu in H-451 graphite was presented by Fellows et al. (1987) in the form of Eq. (10.4.1). The data presented in this reference was apparently applied to the model of §6.4, but the reference for this analysis has not been reviewed by this writer. The reference values for D_0 and Q listed above are not the same as those presented by Fellows et al. (1987). The reason for this difference is unknown.

DISCUSSION

The data used in the determination of the diffusion coefficient of Pu in H-451 graphite are presented in Fig. 10.4.1, taken from Fellows et al. (1987). A model which assumed constant surface concentration was considered to be applicable to the experimental conditions, and the resulting diffusion coefficient for Pu was reported to be:

$$D = 2.02 \times 10^{-5} \exp \left(- \frac{82,250}{RT} \right) m^2 s^{-1} , \quad (10.4.4)$$

with all terms as defined previously. As this diffusion coefficient is different from the non-burnoff portion of Eq. (10.4.2), no additional analysis of this model is possible at this time. Experimental details and the data and models used to obtain Eq. (10.4.4) can be obtained from Fellows et al. (1987).

Tallent et al. (1985) reported diffusion coefficients for uranium in H-451 graphite. The data points and derived diffusion coefficients (given in units of $cm^2 s^{-1}$) are presented in Fig. 10.4.2. Different diffusion coefficients were calculated for an initial source of UC_2 vs UO_2 . The data were obtained between 900 and 1400°C. Additional details can be obtained from Tallent et al. (1985).

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Lacking information on the derivation of the reference model and parameters for Eq. (10.4.2), model refinement would be limited to review of the references mentioned above.

Fig. 10.4.1. Arrhenius plots of plutonium diffusion coefficients in H-451 graphite (from Fellows et al., 1987).

Fig. 10.4.2. Arrhenius plots of uranium diffusion coefficients in H-451 graphite (constant surface uranium concentration method) (from Tallent et al., 1985).

DATABASE USED IN MODEL DEVELOPMENT

The experimental database is available from Fellows et al. (1987) and Tallent et al. (1985). The data used to determine the value of d_o for Sr must also be considered part of the model database.

10.5 HEAVY-METAL SORPTION IN GRAPHITE

function	No analytical model is presented here for HM sorption on graphite. Instead, relevant data for Pu sorption on graphite is presented.
present status	No model for heavy-metal sorption in graphite is presented in FDDM/F. Fellows et al. (1987) have analyzed the measurements of Tallent et al. (1984) for the vapor pressure of Pu over H-451 graphite and derived a sorption isotherm from which a model could be developed.
model uncertainty	The uncertainty of the derived sorption isotherm is presented below in "Discussion."
references	Fellows et al. (1987); Tallent et al. (1984)

DISCUSSION

As no reference model for HM sorption on graphite has apparently been advanced, the relevant information from Fellows et al. (1987) will be quoted in full and can be used to develop a model as required.

"... The vapor pressure's dependency on the adsorbed plutonium concentration at 1673 K is strongly suggestive of a Langmuir isotherm relationship. This is helpful in that it offers a mechanistic framework for a vapor pressure correlation using the available data. The Langmuir isotherm has the form

$$C_s = \frac{k L P}{1 + k P} , \quad (10.5.1)$$

where

- C_s = plutonium surface concentration, $\mu\text{mol}/\text{m}^2$,
- P = plutonium vapor pressure, Pa,
- k = equilibrium constant for the adsorption reaction (see below), Pa^{-1} ,
- L = concentration of surface adsorption sites, $\mu\text{mol}/\text{m}^2$.

"The equilibrium constant, k , is defined by the adsorption reaction:

Pu (vapor) + active sites = Pu (adsorbed) ,

for which

$$k = \frac{C_s}{P(L - C_s)} \quad (10.5.2)$$

"Tallent, et al. [1984] have determined the concentration of active adsorption sites, L , to be $3.27 \mu\text{mol}/\text{m}^2$. Their procedure uses the measured heat of vaporization as a function of surface concentration and extrapolates to the concentration yielding the heat of vaporization of Pu_2C_3 , the likely plutonium species formed at coverages of a monolayer and greater.

"The data listed in Table [10.5.1] were used to determine the variation of the equilibrium constant with temperature, using the value $L = 3.27 \mu\text{mol}/\text{m}^2$. The following relationship was obtained:

$$\log k = \frac{22780}{T} - 5.5102 \quad (10.5.3)$$

"The standard deviation of the plutonium surface concentration, C_s , using the above correlation is 0.41 for 11 of the 12 data points in Table [10.5.1]."

More information on the above discussion and relevant experimental details can be obtained from Fellows et al. (1987) and Tallent et al. (1984).

DATABASE USED IN MODEL DEVELOPMENT

The data in Table 10.5.1 are plotted as a function of temperature in Fig. 10.5.1 and as a function of surface concentration in Fig. 10.5.2 (taken from Tallent et al., 1984).

10.6 UPDATE

No data relevant to the contents of this chapter have been generated by the MHTGR program in recent years.

Table 10.5.1. Plutonium vapor pressure measurements over graphite
(from Fellows et al., 1987)

Temperature (K)	Surface concentration ($\mu\text{mol}/\text{m}^2$)	Vapor pressure (Pa)
1273	0.138	1.05×10^{-14}
	0.690	9.77×10^{-14}
	1.159	6.31×10^{-14}
1473	0.0193	9.77×10^{-12}
	0.7176	4.16×10^{-11}
	0.9108	7.58×10^{-11}
1673	0.110	3.47×10^{-10}
	1.270	1.23×10^{-9}
	1.325	1.41×10^{-9}
	1.408	1.73×10^{-9}
	1.794	4.68×10^{-9}
	2.070	4.07×10^{-9}

Source: O. K. Tallent, R. P. Wichner, R. L. Towns, and
T. T. Godsey, Vapor Pressure of Plutonium Carbide Adsorbed on Graphite,
ORNL/TM-9161, September 1984.

Fig. 10.5.1. Comparison of vapor pressure of Pu₂C₃ adsorbed on H-451 graphite with vapor pressure of Pu₂C₃ (from Tallent et al., 1984).

Fig. 10.5.2. Plutonium sesquioxide adsorption isotherms on H-451 graphite (from Tallent et al., 1984).

11. HYDROLYSIS AND OXIDATION OF CORE MATERIALS

11.1 INTRODUCTION

Hydrolysis describes the reaction of the particle and core materials with water, while oxidation describes their reaction with molecular oxygen (FDDM/F). The mechanisms of reaction are not completely independent, as water has some oxidizing effect due to the inherent presence of oxygen. In fact, at times the terms "oxidation" and "hydrolysis" are used interchangeably [e.g., Velasquez et al. (1978) discuss the "oxidation of H-451 graphite by steam"].

Oxygen and water are always present as impurities in the helium coolant. Nominal impurity levels have been given as 126 μatm of water and $<630 \mu\text{atm}$ of all oxidants (O_2 , CO , CO_2) (CEGA, 1990). The typical oxygen impurity concentration in the helium coolant has been stated to be approximately 1 ppbv [R. D. Burnette, quoted by Myers (1986)]. The possible large-scale ingress of water and steam during an accident raise a much more serious concern than the ambient impurity levels. Air ingress into the reactor core is also a concern due to the presence of oxygen.

The models presented below are used in conjunction with the models on fission gas release from kernels (§4) and HM contamination (§7). This section discusses the models and mechanisms of hydrolysis and oxidation independently of their effect on FP release.

Particle coatings

Although the PyC layers can react with water or oxygen, the ability of the SiC layer to form a protective SiO_2 layer upon contact with oxidizing conditions mitigates concerns for release of FP from intact particles (assuming the conditions are conducive to passive oxidation of SiC rather than active oxidation; see §11.3). However, the lack of detailed data on the effect of oxidation and hydrolysis on intact and defective particles and coating layers does not permit one to unambiguously rule out the potential for induced particle failures from air/water ingress. The effect of OPyC (and potential SiC) degradation on pressure-vessel failure as well as anecdotal evidence of UC_2 particle "popping" during wet heating tests would suggest otherwise.

Fuel kernels

Both hydrolysis and oxidation result in enhanced release of fission gas from the kernel. Hydrolysis-enhanced fission gas release during NOC is described by steady-state release models, while the AC models describe the transient release of stored fission gas in the absence of a neutron flux. Models for the effects of hydrolysis and oxidation on fractional fission gas release from the kernel were presented and discussed in §4. Only the general mechanisms of kernel oxidation and hydrolysis will be discussed here. Reference should be made to §4 for information on the relation to fission gas release.

Fuel compact and graphite

Although the fuel compact matrix material and the core graphite can both react with oxygen and water, the compact is significantly more reactive. However, Myers (1988) suggests that the rate of hydrolysis of the fuel compact matrix "decreases significantly after the exposed matrix material surface becomes saturated with adsorbed H_2O or its dissociation products." For graphite, Myers (1988) comments: "During hydrolysis and oxidation, the binder of the graphite, wherein resides the sorbed fission products, are preferentially removed. Thus the fission products in the graphite could be nearly completely released at very small burnoffs (small degrees of hydrolysis or oxidation) ..." Any air or moisture ingress into the core will first cause reaction of the core graphite. Any reaction of the fuel compacts or particles will be delayed by the resistance of the graphite to the inward flow of oxidizing species into the core. More information on the reactions of the fuel compact and graphite with oxidizing species and the safety significance of such reactions are provided by GA Technologies (1986).

11.2 HYDROLYSIS AND OXIDATION OF FUEL KERNELS

11.2.1 INTRODUCTION

This section presents the model equations for the burnup-induced compositional change of the UCO kernel (ratio of UC_2 to UO_2) and for the fractional oxidation and hydrolysis of fuel kernels. The equations for fractional hydrolysis and oxidation are also incorporated into the models for enhanced fission gas release from kernels in §4.5 and §4.7. Refer to §4 for discussion of the practical significance of kernel hydrolysis and oxidation with respect to FP transport and release.

11.2.2 COMPOSITIONAL CHANGE OF UCO KERNEL WITH BURNUP

function	This model calculates the fraction of UC_2 remaining in the UCO kernel as a function of burnup and initial UC_2 fraction.
present status	This model is probably accurate in predicting the UC_2/UO_2 ratio during burnup, but no clear statement of its origin or derivation has been located.
model uncertainty	The uncertainty inherent in this model is unknown. The variation in the as-manufactured UC_2/UO_2 ratio is probably greater than the uncertainty in the model itself.
references	FDDM/F; Scheffel et al. (1989); Homan et al. (1977)

NORMAL OPERATING CONDITIONS

Model equations

The UCO kernel is considered to consist of distinct UC_2 and UO_2 components. Due to thermodynamic considerations, the ratio of UC_2 to UO_2 changes with burnup because of the change in oxygen potential with burnup (i.e., some of the oxygen released from UO_2 fission reacts with the UC_2 to form UO_2 , thus UC_2 is removed both chemically and by neutron capture). The composition of the UCO kernel at any point during the irradiation lifetime of the fuel is given by FDDM/F:

$$M = M_o - 0.625 F, \quad M \geq 0, \quad (11.2.2.1)$$

M = fraction of UC_2 in the UCO kernel (mole percent),

M_o = initial manufactured fraction of UC_2 in the UCO kernel (mole percent),

F = burnup (% FIMA).

Range of validity

This model equation is valid until UC_2 is completely removed from the kernel (i.e., until $M = 0$).

Assumptions

The assumptions required for this model derivation are unknown, as source references have not been reviewed. The assumptions are likely related to thermodynamic considerations such as those used by Homan et al. (1977). The effect of temperature on UC_2/UO_2 thermodynamic equilibrium must be assumed to be insignificant; the validity of this assumption is nowhere discussed.

Uncertainty

The uncertainty in this model is unknown. It should be noted that, although the nominal UCO composition is given as $UC_{0.3}O_{1.7}$ (technically a composition by weight; the nominal molar composition is approximately $UC_{0.31}O_{1.69}$), the manufacturing tolerance capabilities on carbon variation is stated to be $UC_{0.4}O_{1.6}$ (Scheffel et al., 1989). The tolerance for minimum carbon content is not stated. This upper tolerance level represents a 33% variation from the nominal UC_2 composition, which in practice probably renders the uncertainty of the model to a secondary status.

MODEL CHRONOLOGY

The chronology of the development of this model is unknown, as source references have not been reviewed.

DISCUSSION

This model is not relevant to accident conditions (no change in burnup) except in predicting the kernel composition at the time of the accident for AC models which are composition-dependent. For example, the kernel composition is relevant for AC gas release under hydrolyzing conditions because the rate of UC_2 hydrolysis is significantly greater than that of UO_2 (Myers, 1986). As the rates of oxidation of UC_2 and UO_2 are believed to be similar (Myers, 1986), no such distinction between UC_2 and UO_2 compositions is required for modelling of oxidation-enhanced fission gas release.

Two references for this model are mentioned in FDDM/F, one an internal GA memo and the second a proprietary GA document¹. However, a newer version of the proprietary document (Scheffel et al., 1989) has been distributed on a nonproprietary basis. Scheffel et al. (1989) do not present Eq. (11.2.2.1), but they do present a figure showing the calculated UC_2 content in UCO kernels as a function of initial UCO composition and burnup. This figure is reproduced as Fig. 11.2.2.1. It appears that this figure was likely calculated on the basis of Eq. (11.2.2.1).

Another reference for this UC_2 -content dependence on burnup is provided by Homan et al. (1977). Thermodynamic calculations were performed to estimate the removal of UC_2 from the UCO kernel during irradiation as a function of burnup and initial UC_2 content: "For example, consider the results at an initial 20% UC_2 content. Both UC_2 and UO_2 are initially present and these phases establish the μ_{O_2} [chemical potential of oxygen] up to -34% FIMA ... Once burnup exceeds -34% FIMA, UC_2 has disappeared ..." For complete removal of UC_2 at 34% FIMA, Eq. (11.2.2.1) predicts an initial UC_2 molar content of 21.25% (initial content by weight of 20.74%). These values for initial UC_2 content are very close to the stated value of 20% by Homan et al. (1977) which suggests that:

- (1) for this initial UC_2 content the model is consistent with the calculations of Homan et al. (1977),
- (2) Eq. (11.2.2.1) was likely derived based on thermodynamic considerations such as those employed by Homan et al. (1977), and
- (3) if necessary, the derivation of Eq. (11.2.2.1) could probably be reproduced by employing the methodology stated by Homan et al. (1977).

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Although detailed information on this model is limited, the model as stated is probably adequate because of the larger uncertainty in the as-manufactured UC_2/UO_2 ratio in UCO kernels. It might be interesting to speculate on potential effects of as-manufactured variation in the initial UC_2 content. An upper tolerance limit on initial UC_2 content is specified as $UC_{0.4}O_{1.6}$ by Scheffel et al. (1989), but no lower tolerance limit is given. If the

¹W. J. Scheffel, "Technical Support Document for Issue E of the HTGR Fuel Product Specification," GA Document 903728/C, July 1986.

Fig. 11.2.2.1. UC_2 content in UCO kernels as a function of initial UCO composition and burnup (from Scheffel et al., 1989).

compositional distribution around the nominal value is symmetric, then a lower limit for the initial UC_2 content would be closer to $UC_{0.2}O_{1.8}$. For such a UCO composition, Fig. 11.2.2.2 (taken from Homan et al., 1977) suggests that CO formation could occur above approximately 53% FIMA. The design value for maximum fissile particle burnup in the NP-MHTGR is 75% FIMA (CEGA, 1990). It is generally assumed that CO production is not a concern for UCO particle integrity in the MHTGR with respect to pressure-vessel model calculations (General Atomics, 1989). Although the limited production of CO suggested here should not have a significant effect on fuel performance, the assumption that no CO is produced within MHTGR fuel may not be strictly true.

DATABASE USED IN MODEL DEVELOPMENT

Lacking review of the original references to the model, the database, if any, used in deriving Eq. (11.2.2.1) is unknown. If direct experimental evidence is not available, Fig. 11.2.2.2 might be considered part of the database for this model although based on a thermodynamic rather than experimental analysis.

11.2.3 FRACTIONAL HYDROLYSIS OF FISSILE FUEL KERNELS

function	This model calculates the time-dependent fractional hydrolysis of the UCO kernel as a function of temperature and water vapor pressure.
present status	The hydrolysis of UCO kernels is modelled by considering the hydrolysis of the UO_2 and UC_2 portions of the kernel separately. Functional dependencies on temperature and water vapor pressure are derived from the experimental data and incorporated into classical nucleation theory.
model uncertainty	The model uncertainty has not been determined.
references	Myers (1986); Montgomery (1980, 1981b)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The fraction of UCO hydrolyzed after the time t is given by Myers (1986):¹

¹It appears the following equation should have a term related to the relative UC_2/UO_2 composition within the UCO kernel, otherwise the value for fractional hydrolysis could be as high as two. This is not discussed in the references.

Fig. 11.2.2.2. Phases present below 1800 K in a fully enriched ($^{235}\text{U}/\text{total U} \approx 0.93$) UO_2 - UC_2 kernel as a function of ^{235}U burnup and initial UC_2 content. The $\text{EuO}_{1.5}$ - EuC_2 system is not shown because it has a small ($<1\%$) yield. However, its chemical behavior is different from yttrium and the other lanthanides (RE), and it converts from the carbide to the oxide at about the same burnup as the strontium system (from Homan et al., 1977).

$$\alpha_h(t) = \alpha_c(t) + \alpha_o(t) , \quad (11.23.1)$$

$$\alpha_i(t) = 1 - e^{-\Delta_i^3} , \quad (11.23.2)$$

$$\Delta_i = \int_0^t k_i [p(\zeta), T(\zeta)] d\zeta , \quad (11.23.3)$$

$$k_i = k_{o,i} \left(1 - e^{-a p_{H_2O}}\right) e^{-Q/RT} \left\{ 1 + \frac{C_2 e^{Q'/RT}}{1 + e^{C_3(T - T_{ok})}} \right\} , \quad (11.23.4)$$

α_h	=	fractional hydrolysis of the UCO kernel,
α_i	=	fractional hydrolysis of component i , where $i = c$ (UC_2) or $i = o$ (UO_2),
t	=	time (s),
$k_{o,i}$	=	constant, for $i = c, o$ (s^{-1}),
p_{H_2O}	=	water vapor pressure at the kernel (Pa),
T	=	temperature (K),
T_{ok}	=	constant (K),
$Q/R, Q'/R$	=	temperature coefficients (K),
Q	=	activation energy ($J \text{ mol}^{-1}$),
R	=	ideal gas constant ($8.314 J \text{ mol}^{-1} K^{-1}$),
a	=	constant (Pa^{-1}),
C_2	=	constant (dimensionless),
C_3	=	constant (K^{-1}),
ζ	=	dummy variable.

These equations are also incorporated into the model for fission gas release from exposed kernels under hydrolyzing accident conditions, §4.5. The values for the model parameters are listed in Table 11.2.3.1. These values are the same as those listed in Table 4.5.1 of §4.5.

Range of validity

Limitations on the range of validity of the model are not specified by Myers (1986). Some of the experimental ranges are indicated by Table 11.2.3.2 (irradiation conditions; from Montgomery, 1981b), Fig. 11.2.3.1 (UC_2 hydrolysis; from Myers, 1986), and Table 11.2.3.3 (UCO and UO_2 hydrolysis; from Myers, 1986). As stated by Myers (1986), the "rate coefficient for hydrolysis has been measured for UC_2 over a range of temperatures [60 to

Table 11.2.3.1. Parameters in the reaction rate coefficient expression for kernel hydrolysis
(from Myers, 1986)

<u>Parameter</u>	<u>Values For</u>	
	<u>UC₂ (in UCO)</u>	<u>UO₂</u>
k_o (1/s)	6.55 (-2)	9.39 (-4)
a (1/Pa)	5.99 (-3)	3.65 (-3)
Q/R (K)	4371.	4371.
C_2	14.1	14.1
Q'/R (K)	1382.	1382
C_3 (1/K)	0.0443	0.0443
$T_{o,k}$ (K)	413.	413.

Table 11.2.3.2. Description of irradiated particles used in studies on kinetics of hydrolysis of LEU HTGR fuel
(from Montgomery, 1981b)

	SI-BISO UC_2 6449-00-0110-2(b)	TRISO $\text{UC}_{0.88}\text{O}_{1.12}$ 6157-08-032-1(b)	SI-BISO $\text{UC}_{0.36}\text{O}_{1.64}$ 6448-00-0110-2(b)	SI-BISO UO_2 6447-00-0110-1(b)
Irradiation parameters(a)				
Fluence, 10^{25} n/m ² (E > 29 f.) _{HTGR}	4.4	6.4	3.0	3.6
Burnup, % FIMA	23.4	26.2	20.0	19.1
Temperature, °C	915	905	915	860
Location	T15B	T74	T184	T4
Particle parameters				
Kernel				
Density, Mg/m ³	11.04	10.97	10.22	10.55
Diameter, μm	345	341	368	299
Std. dev., μm	14.99	15.74	11.25	8.11
Buffer				
Density, Mg/m ³	0.94	0.98	0.93	1.10
Thickness, μm	117	123	136	116
IPyC				
Density, Mg/m ³	1.86	1.84	1.92	1.95
Thickness, μm	37	47	43	32
SiC				
Thickness, μm	None	41	None	None
Density, Mg/m ³		3.18		
OPyC				
Density, Mg/m ³	2.17	1.84	2.07	2.14
Thickness, μm	117	44	116	120

(a) HRB-15B capsule.

(b) Heat treated at 1700°C for 1 h in Argon at 10 psig prior to irradiation.

Fig. 11.2.3.1. Reaction rate of UC_2 with water vapor vs reciprocal temperature (from Myers, 1986).

Table 11.2.3.3. Reaction rate coefficient data for hydrolysis of UCO and UO_2
(from Myers, 1986)

<u>Fuel Composition</u>	<u>Temp ($^{\circ}\text{C}$)</u>	<u>Pressure (Pa)</u>	<u>k (1/s)</u>
$\text{UC}_{0.36}\text{O}_{1.64}$	716	1200	8.12 (-4)
UO_2	720	1300	1.15 (-5)
$\text{UC}_{0.3}\text{O}_{1.7}$	800	18	1.14 (-4)

637°C] and partial water vapor pressures but only at a few temperatures for UO₂ and UCO."

Assumptions

1. The nucleation theory applied to the data assumes the reaction sites are spherical, which leads to the functional form of Eq. (11.2.3.2).
2. To represent the dependence of hydrolysis on temperature and water vapor pressure, the following general functional form is applied to the data:

$$\frac{d\alpha}{dt} = k'(T) f(\alpha) g(p) \quad , \quad (11.2.3.5)$$

- α = fraction of fuel hydrolyzed,
 t = time (s),
 T = temperature (K),
 p = water vapor pressure (Pa),
 $k'(T)$ = rate coefficient for hydrolysis (s⁻¹),
 $g(p)$ = some function of the water vapor pressure,
 $f(\alpha)$ = some function of α which reduces to $k = k'(T) g(p)$ for constant T and p .

3. To represent the dependence of hydrolysis on water vapor pressure, $g(p)$, the following functional form is assumed:

$$g(p) = 1 - \exp(-a p_{H_2O}) \quad , \quad (11.2.3.6)$$

a = constant (Pa⁻¹).

Additional details of the nucleation theory and associated assumptions applied to the analysis of the data may be available from the work of Montgomery (1980, 1981b). These documents have not been reviewed in detail by this writer.

Uncertainty

The uncertainty of the model has not been quantified.

MODEL CHRONOLOGY

The model is based on the experimental work of Montgomery (1981b) and presented in its current form by Myers (1986).

DISCUSSION

The model presented in this section forms an integral part of the model of §4.5 for AC release of fission gas from exposed kernels undergoing hydrolysis. The UC_2 portion of the UCO kernel undergoes hydrolysis significantly faster than the UO_2 portion. As a first approximation, the hydrolysis of the UC_2 portion can be considered complete before significant hydrolysis of the UO_2 portion occurs.

A summary of the nucleation mechanisms and phenomena are presented by Myers (1986): "The mechanisms of hydrolysis have been discussed by Montgomery [1981b]. For UO_2 and UCO where the amount of carbide is less than 20%, a nucleation and growth mechanism applies. In this mechanism, the limiting process is growth of the reactant sites. As the reactant sites become larger, their growth declines when they begin to merge. If the reaction sites are configurationally treated as spheres, the time dependence of the fraction of fuel hydrolyzed is given [in the form of Eq. (11.2.3.2), which is] formally identical to a Weibull distribution function; that such a distribution function can describe heterogeneous reactions is well known ...

"For UC_2 at high temperature, a phase boundary process controls the rate of hydrolysis and at low temperatures (approximately 200°C), the hydrolysis is controlled by diffusion. In the former mechanism, the rate of reaction is proportional to the unreacted fuel and in the latter to the rate at which reactants arrive at or leave the reaction site.

"The difference in reaction mechanisms between UCO and UC_2 needs to be clarified in view of the distinction made above between the UC_2 and UO_2 portions of the UCO kernel. In the experiments [Montgomery, 1981b] on the basis of which the reaction mechanisms were deduced, the UC_2 portion of the UCO kernel was that portion whose hydrolysis was measured; yet the mechanism deduced was different from that deduced from similar experiments with UC_2 kernels. The difference lies in the distribution of the carbide and oxide portion of the UCO kernel. The carbide portion is dispersed so that water has access to a large number of reaction sites. If the carbide were concentrated, say within a spherical volume, access to the interior would become difficult after the surface has been hydrolyzed and converted to oxide since water would have to diffuse through the effect of the oxide layer. With dispersal of the carbide portion, the oxide barrier to reaction is greatly mitigated, and the mechanism of reaction is changed ...

"... The relation between the rate [of UC_2 hydrolysis] and temperature is that described by an Arrhenius expression for temperatures above 300°C; below 300°C the rate rises to a maximum at 100°C and declines at lower temperatures [see Fig. 11.2.3.1]. At temperatures below 300°C the sorptivity of water on the fuel apparently increases significantly, resulting in a corresponding increase in the reaction rate. At temperatures below 100°C the availability of water is not limiting, and the reaction rate declines with further lowering of the temperature [Montgomery, 1981b]. To represent this behavior ... Eq. (11.2.3.5) is used, in which the "complex temperature dependence is abstracted into $k'(T)$."

"The reaction rate increases with increasing water vapor pressure until pressures above 1 kPa are reached [Montgomery, 1980]; independence of the reaction rate on water vapor pressure is observed ... at pressures of the order of 10 kPa. In the absence of acceptable

data on this dependence in the process of hydrolysis" the dependence of Eq. (11.2.3.6) is assumed. To evaluate the parameters k_{a_0} and a in Eq. (11.2.3.4), "singular data for UCO and UO_2 obtained in tests at GA ... and presented in Table [11.2.3.3] are used."

Additional details on the model derivation are provided by Myers (1986) and should be referred to for further information.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

As mentioned initially, the absence of a term in the governing equations related to UC_2/UO_2 composition within the UCO kernel should be considered.

In Fig. 11.2.3.2 Myers (1986) presents three data points obtained from the HRB-17/18 and related experiments. An analytical expression is also derived and presented in Fig. 11.2.3.2 to approximate the data points (f_m represents the maximum fraction of gas released based on the mechanism of nucleation and growth). Myers (1986) comments on this data: "The mechanism responsible for the limitation on the extent of hydrolysis of the carbide fraction remains to be established; however, one interpretation is as follows. The initial hydrolysis of the carbide portion of the UCO kernel proceeds according to a nucleation and growth mechanism ... In this mechanism reaction sites on the surfaces of the UC_2 grow until a merging results in covering the carbide particle surface with an oxide layer. At this point, water can no longer easily reach the carbide; the mechanism of reaction changes and the rate of reaction slows. This accounts for the decreased reaction rate observed ... After the slowing, a diffusion mechanism, as observed for UC_2 fuel ... probably governs the reaction. The nature of the diffusion is unknown; carbon could be diffusing through the oxide layer to react with water at the surface, water or oxygen could be diffusing into the layer to reach the carbon, or water, trapped in the oxide layer, could be diffusing to the carbide and reacting."

This information and related data from the HRB-17/18 and HFR-B1 capsules should be considered in future evaluation of this model.

DATABASE USED IN MODEL DEVELOPMENT

Much of the database relevant to this model is presented by Montgomery (1980, 1981b), some of which is presented in Tables 11.2.3.2 and 11.2.3.3 and Fig. 11.2.3.1. Another document by F. C. Montgomery ("Hydrolysis of Failed, Unirradiated UCO in HRB 17/18 Fuel Rods," GA Technologies Document No. 907258/0, ca. 1986) is referenced by Myers (1986) but has not been reviewed by this writer. Figures 11.2.3.3 and 11.2.3.4 are taken from Montgomery (1981b) and represent some of the work done in determining the dominant mechanism of kernel hydrolysis. Reference should be made to Montgomery (1980, 1981b) for additional details and related database.

Fig. 11.2.3.2. Extent of hydrolysis of the carbide portion of UCO as a function of the water vapor pressure and concentration by the mechanism of nucleation and growth at 800°C (from Myers, 1986).

Fig. 11.2.3.3. Comparison of reaction mechanisms with experimental data for low temperature hydrolysis of $UC_{0.36}O_{1.64}$ (from Montgomery, 1981b).

Fig. 11.2.3.4. Comparison of reaction mechanisms with experimental data for high temperature hydrolysis of irradiated UO₂ (from Montgomery, 1981b).

11.2.4 FRACTIONAL OXIDATION OF FISSILE FUEL KERNELS

function	This model calculates the time-dependent fractional oxidation of UCO for air ingress events as a function of temperature and oxygen vapor pressure.
present status	The model assumes comparable oxidation rates of the UC_2 and UO_2 portions of the UCO kernel, based on "very limited data" (Myers, 1986). No distinction is made between the UC_2 and UO_2 portions of the kernel. The model is based on first-order reaction kinetics.
model uncertainty	The model uncertainty has not been determined.
references	Myers (1986); Wood et al. (1985)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The fraction of UCO oxidized after the time t is given by Myers (1986):

$$\alpha_{ox}(t) = 1 - e^{-\Delta_{ox}} \quad , \quad (11.2.4.1)$$

$$\Delta_{ox} = \int_{t_i}^t k_{ox} [p(\zeta), T(\zeta)] d\zeta \quad , \quad (11.2.4.2)$$

$$k_{ox} = k_{ox,o} (1 - e^{-a_1 p_{O_2}}) e^{-Q''/RT} \quad , \quad (11.2.4.3)$$

$$t_i = \frac{t'_i e^{Q''/RT}}{1 - e^{-a_1 p_{O_2}}} \quad , \quad (11.2.4.4)$$

α_{ox}	= fractional oxidation of the UCO kernel,
t	= time (h),
$k_{ox,o}$	= constant (h^{-1}),
p_{O_2}	= oxygen vapor pressure at the kernel (Pa),
T	= temperature (K),
Q''/R	= temperature coefficient (K),

- Q'' = activation energy (J mol^{-1}),
 R = ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$),
 a_1, a_2 = constants (Pa^{-1}),
 t_1 = constant (h),
 ζ = dummy variable.

The values for the model parameters are listed in Table 11.2.4.1. These equations were also incorporated into the model for fission gas release from exposed kernels under oxidizing accident conditions, §4.7. The values listed in Table 11.2.4.1 are the same as those used in §4.7.

Range of validity

No limitation to the range of model applicability is explicitly stated by Myers (1986), therefore the model is assumed to be applicable over the range of expected MHTGR conditions. Apparently data has not been obtained for the oxidation of UC_2 ; data for UC is used to approximate the oxidation response of UC_2 . Data for the oxidation of UO_2 and UCO were reported for oxygen partial pressures of 0.2, 0.3, and 20 kPa and temperatures between approximately 200 and 500°C.

Assumptions

1. The rates of oxidation of UO_2 and UC are equal.
2. The rate of oxidation of UC can be used to represent that of UC_2 .
3. The same temperature dependence as determined from the time to completion of oxidation can be applied to the induction time for oxidation.
4. The pressure dependencies of the induction and reaction times take the functional form:

$$g(p) = 1 - \exp(-a_1 p_{\text{O}_2}) \quad , \quad (11.2.4.5)$$

$$a_1 = \text{constant } (\text{Pa}^{-1}).$$

5. A fractional oxidation value of 0.99 was assumed in the determination of values for k_{α_0} and a_2 .

Uncertainty

The uncertainty of the model has not been quantified.

MODEL CHRONOLOGY

This model was presented by Myers (1986) and based on data obtained from Wood et al. (1985) and Montgomery et al. (1983). This model is reproduced in FDDM/F.

Table 11.2.4.1. Values of the model parameters and constants for oxidation of UCO kernels
(from Myers, 1986)

<u>Parameter</u>	<u>Value</u>
$k_{ox,o}$ (1/h)	9.96 (6)
a_2 (1/Pa)	2.07 (-3)
$Q''/R(K)$	1.08 (4)
t'_I (h)	3.03 (-8)
a_1 (1/Pa)	9.51 (-5)

DISCUSSION

These model equations are used as the basis of the gas release model during AC oxidation (§4.7). As both UC_2 and UO_2 components of the UCO kernel are believed to oxidize at comparable rates, the kernel is treated as a single material unlike the case for hydrolysis. Myers (1986) comments that: "In determining rate coefficient expressions for oxidation, data from fuel initially containing carbon has been used. This can be justified on the basis of a comparison of data on the oxidation of UO_2 and of UC ... The value for UC is larger than for UO_2 and the use of data for fuel initially containing carbon ought to be conservative. Therefore, the assumption of equal rates of oxidation for UO_2 and UC, and by assumption for UC_2 , is adopted here."

Myers (1986) describes the derivation of the model. "The mechanism of air oxidation of UO_2 is determined from data [Wood et al., (1985)] recently reported. From the data ... given in Table [11.2.4.2], as plotted in Fig. [11.2.4.1], the mechanism is deduced to involve a first order reaction based on the linearity of the data in a semi-logarithmic plot. The mechanisms [Montgomery, 1981b] involving diffusion controlled reactions, phase boundary reactions, and nucleation and growth are not appropriate. Consequently, the time dependence of the fraction of fuel oxidized is given by [an equation in the form of Eq. (11.2.4.1)]. Comparable data on the oxidation of UC_2 are not available.

"To derive a rate expression for the oxidation of UO_2 , use is made of [Eq. (11.2.4.1)], the observation, evident in Fig. [11.2.4.1], that there is an induction period preceding the onset of the first order kinetic regime and measured times to complete oxidation [Wood et al., 1985; Montgomery et al., 1983]. Then

$$t_c = t_I + t_R, \quad (11.2.4.6)$$

where t_i = completion time ($i = c$), induction time ($i = I$) and reaction time ($i = R$). The completion times, t_c , determined experimentally are plotted in Fig. [11.2.4.2] for the data on the air oxidation of UO_2 at $p_{O_2} = 20$ kPa and on the oxidation of UCO at $p_{O_2} = 0.2$ to 0.3 kPa." Equations were then derived to approximate the experimental data, as given in Fig. 11.2.4.2. "With the information presented on completion and induction times, expressions for the induction time and the reaction rate coefficient can be derived, taking into account dependencies on temperature and the partial pressure of O_2 ." This induction time is incorporated into the model as the lower limit of the integral of Eq. (11.2.4.2).

Myers (1986) then discusses in detail the derivation of the model parameters of Table 11.2.4.1 and provides the results of the analyses of induction and completion times for oxidation in Table 11.2.4.3. Finally, comparison between the model and the experimental data for the "time dependence of weight gain upon oxidation of UO_2 at 500°C" is shown in Fig. 11.2.4.3. Reference should be made to Myers (1986) for additional details of the derivation of the model and parameters.

Table 11.2.4.2. The fractional oxidation of UO_2 by air at 500°C (from Wood et al., 1985; as reported by Myers, 1986)

<u>t(s)</u>	<u>Fraction Oxidized (α)</u>	<u>Complement of Fraction Oxidized</u>
200	0.0436	0.956
300	0.196	0.804
400	0.407	0.593
500	0.572	0.428
600	0.676	0.324
700	0.749	0.251
800	0.807	0.193
900	0.851	0.149
1000	0.887	0.113
1100	0.912	0.088
1200	0.935	0.065
1300	0.949	0.051
1400	0.964	0.036
1500	0.975	0.025
1600	0.983	0.017

Fig. 11.2.4.1. Test of mechanisms in the oxidation of UO_2 ; (○), nucleation and growth; (⊙), first order; (□), diffusion controlled; (△), phase boundary (from Myers, 1986).

Fig. 11.2.4.2. The temperature dependence of times to complete oxidation (from Myers, 1986).

Table 11.2.4.3. Completion and induction times in the oxidation of UO_2 and UCO
(from Myers, 1986)

Original Data			Temperature Corrected Data			
<u>t_c (h)</u>	<u>T_I (h)</u>	<u>T (°C)</u>	<u>t_c (h)</u>	<u>T_I (h)</u>	<u>T (°C)</u>	<u>p (kPa)</u>
5.83 (-1)	4.17 (-2)	500	64.78	4.63	305	20
270.	1.40 (2)	305	270.	140.	305	0.3

Fig. 11.2.4.3. Comparison between the calculated and observed fractional oxidation of UO_2 at 500°C in air (from Myers, 1986).

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Model revision would be difficult without additional data on the oxidation of UCO, UO_2 , or UC_2 . Specifically, any data on UC_2 oxidation would be very relevant to validation of this model. An additional consideration which was mentioned in §4.7 relates to German calculations which suggest that hydrogen gas generated by oxidation of graphite might retard the oxidation of UO_2 at temperatures above 700°C . However, this possibility is questioned for reasons given in "Additional Considerations" of §4.7 which will not be repeated here.

DATABASE USED IN MODEL DEVELOPMENT

Additional details on the database for oxidation of UO_2 can be obtained from Wood et al. (1985). Myers (1986) also presents data from Montgomery et al. (1983) and refers to data for the oxidation of UC attributed to K. A. Peakall and J. E. Antill (*Oxidation of Uranium Monocarbide*, Atomic Energy Research Establishment Report AERE-R3844, Harwell, UK, 1961). The last two references have not been reviewed by this writer.

11.2.5 HYDROLYSIS AND OXIDATION OF FERTILE FUEL KERNELS

function	This model calculates the time-dependent fractional hydrolysis and oxidation of ThO_2 only after it has undergone carbothermic reduction to ThC_2 as a function of temperature and water/oxygen vapor pressure.
present status	"In the case of ThO_2 fuel, hydrolysis and oxidation are only of interest if the exposed kernels have been subjected to high temperatures ($>1400^\circ\text{C}$) and conditions which promote carbothermic reduction. In this case, the now carbide kernels would be treated as UC_2 . (The detailed treatment of this case has not been developed.)" (Myers, 1986).
model uncertainty	The model uncertainty has not been determined.
references	Myers (1986)

ACCIDENT CONDITIONS

Model equations: oxidation

Oxidation of ThC_2 is treated identically to that of UC_2 . As the oxidation of UC_2 and UO_2 is believed to be similar, the fractional oxidation of ThC_2 can be modelled using

Eqs. (11.2.4.1) through (11.2.4.4) of §11.2.4, using the parameter values provided in Table 11.2.4.1.

Model equations: hydrolysis

Rates of hydrolysis for UC_2 and UO_2 are different, thus the fractional hydrolysis of ThC_2 is modelled using Eqs. (11.2.3.1) through (11.2.3.4) of §11.2.3, except that the oxide component $\alpha_o(t)$ of Eq. (11.2.3.1) is not included. The fractional hydrolysis of ThC_2 is then given by:

$$\alpha_h(t) = \alpha_c(t) = 1 - e^{-\Delta_c^3}, \quad (11.2.5.1)$$

$$\Delta_c = \int_0^t k_c [p(\zeta), T(\zeta)] d\zeta, \quad (11.2.5.2)$$

$$k_c = k_{ox} \left(1 - e^{-a_{PB_2O}} \right) e^{-Q/RT} \left\{ 1 + \frac{C_2 e^{Q'/RT}}{1 + e^{C_3(T - T_{\infty})}} \right\}, \quad (11.2.5.3)$$

with all terms as defined in §11.2.3 and the parameter values given in Table 11.2.3.1 for UC_2 .

Range of validity

The nature of the "conditions which promote carbothermic reduction" and the experimental data relevant to this process are unknown to this writer and therefore no statements related to the range of validity can be made. The statements of §11.2.3 and §11.2.4 regarding the experimental range of validity of the data for UC_2 are appropriate here.

Assumptions

1. Oxidation of ThO_2 is insignificant under reactor conditions.
2. The hydrolysis and oxidation of ThC_2 can be described by the same model as that used for UC_2 .
3. Under appropriate conditions of carbothermic reduction, the conversion of ThO_2 to ThC_2 can be considered complete.

Uncertainty

The uncertainty of this model has not been quantified.

MODEL CHRONOLOGY

This model was presented by Myers (1986) and reproduced in FDDM/F. Any statements relevant to this model prior to Myers (1986) are unknown.

DISCUSSION

The most detailed statement related to this model is that quoted above in "present status" from Myers (1986). No additional information on this model can be provided beyond that stated for the hydrolysis and oxidation of UC_2 kernels in §11.2.3 and §11.2.4.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

Additional information is required for the reaction of ThO_2 to ThC_2 and the related mechanisms. Any data for the oxidation or hydrolysis of ThC_2 would be important for comparison with UC_2 data.

DATABASE USED IN MODEL DEVELOPMENT

The database relevant to conversion of ThO_2 to ThC_2 is unknown. Reference should be made to §11.2.3 and §11.2.4 for discussion of the database relevant to hydrolysis and oxidation, respectively, of UC_2 .

11.3 HYDROLYSIS AND OXIDATION OF PARTICLE COATINGS

function	This model correlates the rate of hydrolysis and oxidation of the buffer layer with that of the fuel compact matrix material (§11.4) and the PyC layers with that of graphite (§11.6.3), using the same functional dependencies. The SiC layer is assumed not to react.
present status	In the absence of data for the hydrolysis and oxidation of buffer, PyC, and SiC coating layers, simple approximations are made for the reactions or lack of reaction.
model uncertainty	The model uncertainty cannot be quantified due to lack of data.
references	FDDM/F; Myers (1988)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations: buffer layer

In the presence of water or oxidant, the buffer layer is assumed to react at a rate equal to that of the fuel compact matrix material (FDDM/F):

$$R_b = R_c , \quad (11.3.1)$$

R_b = rate of hydrolysis or oxidation of the buffer layer (mass fraction reacting per unit time),

R_c = rate of hydrolysis or oxidation of the compact matrix material (mass fraction reacting per unit time).

The model equation for R_c is given in §11.4 below.

Model equations: PyC layers

In the presence of water or oxidant, the PyC layers are assumed to react at a multiple of the rate of H-451 graphite (FDDM/F):

$$R_{PyC} = 2.5 R_g , \quad (11.3.2)$$

R_{PyC} = rate of hydrolysis or oxidation of the PyC layers (mass fraction reacting per unit time),

R_g = rate of hydrolysis or oxidation of H-451 graphite (mass fraction reacting per unit time).

Model equations for R_g are given below in §11.6.3 (hydrolysis) and §11.6.4 (oxidation).

Model equations: SiC layer

In the presence of water or oxidant, the SiC layer is assumed to form a protective SiO_2 layer which prevents further reaction (FDDM/F):

$$R_{SiC} = 0 , \quad (11.3.3)$$

R_{SiC} = rate of hydrolysis or oxidation of the SiC layer (mass fraction reacting per unit time).

Range of validity

1. Lacking further information, the range of validity of the models for buffer and PyC layers must be based on the range of validity of the source models in §11.4, §11.6.3, and §11.6.4 below.

2. The SiO_2 surface layers protect the SiC over most core temperatures. As temperatures exceed 1500°C , the SiO_2 becomes more volatile (Martin, 1990). However, direct reaction of flowing water vapor with (nonreference) SiC samples is known to result in significant SiC weight loss at temperatures above 1200°C . A maximum temperature will not be specified here for the experimental range of validity of this model without further analysis, but one should realize that the rationale for this model for SiC hydrolysis becomes weaker at maximum AC temperatures under hydrolyzing conditions.

Assumptions

Each model represents an assumption. Apparently only Eq. (11.3.3) can be reliably based on pertinent data.

Uncertainty

No attempt has been made to quantify the level of uncertainty for each model.

MODEL CHRONOLOGY

The development of this model is unknown. The only source referenced by FDDM/F is a GA internal memorandum by R. D. Burnette.

DISCUSSION

Although the same model is used for both NOC and AC regimes, only during significant oxidant ingress to the reactor system during accident conditions would these reactions become a concern.

The ability of SiC to form a protective surface layer of SiO_2 under oxidizing conditions at elevated temperatures is well known, but if temperatures approach 1600°C that layer becomes more volatile and can decompose along with the SiC substrate, forming gaseous SiO. An introductory discussion of this decomposition mechanism is provided by Martin (1990). Data specific to the reaction of SiC with H_2O at elevated temperatures can be obtained from Antill et al. (1971). Additional information on the reaction of buffer and PyC layers with oxidants has not been obtained by this writer.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

If water ingress accidents could bring the SiC layers in contact with water for extended periods of time at maximum AC temperatures, the potential for destructive oxidation of the SiC increases. If the SiC is not exposed to flowing water vapor, the actual consequences of such a water ingress accident may not be significant. The potential effect of significant oxidation of the SiC on its subsequent high-temperature stability should be kept in mind (i.e., enhanced vaporization of SiO_2 as temperatures approach 1600°C).

Further development of the models for buffer and PyC reaction cannot be suggested without more background to the origin of these models and their assumptions. A review of the scientific literature may provide more relevant data than is apparent from the HTGR literature base.

DATABASE USED IN MODEL DEVELOPMENT

Data for the reaction of SiC with flowing water vapor at 1000 and 1200°C are presented in Figs. 11.3.1 and 11.3.2, respectively (Antill et al., 1971). The SiC samples used were those of nuclear fuel particles without the OPyC layers. These figures indicate that SiC weight loss can be significant at temperatures within the range of MHTGR conditions. However, these figures do not directly indicate a problem for MHTGR operation under accident conditions unless further analysis indicates the flow of the water vapor in the experiments has some analogy to conditions expected in the MHTGR.

Apparently no database exists for the reaction of buffer and PyC layers with water or oxidizing agents (Myers, 1988).

11.4 HYDROLYSIS AND OXIDATION OF FUEL COMPACT MATRIX MATERIAL

function	This model correlates the rate of hydrolysis and oxidation of the fuel compact matrix material with that of graphite (§11.6.3), using the same functional dependencies.
present status	The model for hydrolysis is based upon limited data, within a limited range of experimental conditions. According to Myers (1988), "our current modeling of the hydrolysis is incorrect ..." The model for oxidation is taken directly from that for hydrolysis due to lack of data.
model uncertainty	The uncertainty of the models has not been quantified, as the "uncertainty of the limited data on the hydrolysis of fuel compact matrix material is difficult to estimate" (Myers, 1988).
references	General Atomic (1974); FDDM/F; Myers (1988)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

According to General Atomic (1974), exposure to steam indicates "the matrix material is about 20 times more reactive than H-451 graphite at comparable burnoffs" which gives the model equation:

Fig. 11.3.1. Weight change vs time graph for 1000°C with a varying pressure of H_2O vapor (from Antill et al., 1971).

Fig. 11.3.2. Weight change vs time graph for 1200°C with a varying pressure of H_2O vapor (from Antill et al., 1971).

$$R_{c,h} = 20 R_{g,h} , \quad (11.4.1)$$

$R_{c,h}$ = rate of hydrolysis of the compact matrix material (mass fraction reacting per unit time),

$R_{g,h}$ = rate of hydrolysis of H-451 graphite (mass fraction reacting per unit time).

A comparable model is assumed to represent the rate of oxidation of the fuel compact matrix material (FDDM/F):

$$R_{c,ox} = 20 R_{g,ox} , \quad (11.4.2)$$

$R_{c,ox}$ = rate of oxidation of the compact matrix material (mass fraction reacting per unit time),

$R_{g,ox}$ = rate of oxidation of H-451 graphite (mass fraction reacting per unit time).

Model equations for $R_{g,h}$ and $R_{g,ox}$ are given below in §11.6.3 and 11.6.4, respectively.

Range of validity

The model is assumed to be valid over the entire range of reactor conditions. Experimentally, the range of validity is limited to a steam pressure of 0.03 atm at temperatures from 800 to 950°C, matrix material samples of size $0.75 \times 0.25 \times 0.125$ in., with the results "normalized to 1% burnoff" (no discussion is provided as to how this normalization was carried out, therefore the actual burnoff is unknown).

Assumptions

1. The relative rate of hydrolysis of graphite to compact matrix material at a single value of burnoff (normalized to 1%) provides a constant ratio which will not change over the entire range of potential burnoff fractions within the reactor.
2. The relative rate of hydrolysis of graphite to compact matrix between 800 and 950°C will not change significantly for reactor operating temperatures outside that range.
3. The relative rate of hydrolysis of graphite to compact matrix at a steam pressure of 0.03 atm will not change significantly for other pressures of steam.
4. The experimental conditions for the steam flow at the sample surface in this experiment is typical of that expected within the reactor under accident conditions; otherwise, the steam flow conditions must be assumed to be insignificant.
5. The rates of oxidation of graphite and compact matrix material over the entire range of reactor conditions occur in the same proportion as that of the hydrolysis experiment. Specifically, reaction rates are not a function of irradiation.

Uncertainty

The uncertainty of these models has not been quantified, but should be considered significant.

MODEL CHRONOLOGY

This model for hydrolysis of the compact matrix material as stated by General Atomic (1974) has remained unchanged to the present. The model for oxidation of the compact matrix material was added at some later date, in a form analogous to that of the hydrolysis model.

DISCUSSION

Although the same model is used for both NOC and AC regimes, only during significant oxidant ingress to the reactor system under accident conditions would these reactions become a concern.

The extent of knowledge related to this model can apparently be encompassed by two quotes. General Atomic (1974) provides the following discussion of experimental results. "A preliminary study was performed on fuel rod matrix material to measure steam oxidation reaction rates. Thin slab samples (0.125 in. thick) were machined from fired rods of matrix material. The results for a single sample exposed to 0.03-atm steam at temperatures between 800° and 950°C, normalized to 1% burnoff, are shown in Fig. [11.4.1]. The data show that the matrix material is about 20 times more reactive than H-451 graphite at comparable burnoffs ... It is felt that this relatively high reactivity is the result of the high impurity content and the high porosity of the matrix material. It is reasoned that the highly reactive matrix material would be sacrificially protective to PyC coated fuel particles, should water vapor diffuse or permeate graphite webs and contact fuel rod materials during normal reactor operation." The factor of 20 was determined by comparison to similar experiments performed on H-451 graphite which are represented by Fig. 11.4.2.

Myers (1988) comments: "The uncertainty of the limited data on the hydrolysis of fuel compact matrix material is difficult to estimate. Recent observations in experiment HFR-B1 indicate that for a reactor-relevant, fuel element configuration, the rate of hydrolysis decreases significantly after the exposed matrix material surface becomes saturated with adsorbed H₂O or its dissociation products. Clearly our current modeling of the hydrolysis is incorrect and after completion of the HFR-B1 experiment and analysis, a large reduction in uncertainty can be expected."

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The paucity of experimental data seriously hinders further model development. Myers' (1988) comment on data from the HFR-B1 experiment encourages review of this data and analysis as soon as it becomes available. In lieu of new data, model revision would be limited to review of the scientific literature for information on the oxidation and hydrolysis

Fig. 11.4.1. Reaction rate of fuel compact matrix material ($P_{\text{H}_2\text{O}} = 0.03$ atm, normalized to 1% burnoff, sample size = 0.75 in. by 0.25 in. by 0.125 in.) (from General Atomic, 1974).

Fig. 11.4.2. Reaction rate of H-451 graphite ($P_{\text{H}_2\text{O}} = 0.03$ atm, burnoff = 1%) (from General Atomic, 1974).

of porous materials and/or graphitic and carbonaceous materials, in an attempt to draw analogies with MHTGR conditions.

DATABASE USED IN MODEL DEVELOPMENT

Figures 11.4.1 and 11.4.2 apparently summarize the entire database used in the development of this model.

11.5 HYDROLYSIS AND OXIDATION OF FUEL COMPACTS

function	This model correlates the rate of hydrolysis and oxidation of the fuel compact to the rates for the compact components (matrix material, graphite shim, OPyC layers) as a function of the mass fraction of each component.
present status	This model is based on a summation of the rates of hydrolysis/oxidation for each component of the fuel compact.
model uncertainty	The uncertainty of this model is dependent on the uncertainty of the models for hydrolysis/oxidation of the compact components. As such, the uncertainty has not been quantified.
references	FDDM/F

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

This model is taken directly from FDDM/F. The mass fraction of the fuel compact which has reacted via hydrolysis or oxidation at time t is given by:

$$f_m = \sum_i X_i R_i t, \quad (11.5.1)$$

- f_m = mass fraction of fuel compact reacted,
 X_i = mass fraction of component i ,
 r_i = rate of fractional mass reaction of component i (s^{-1}),
 t = time (s),
 i = c (compact), m (compact matrix material), g (graphite shim), op (OPyC layer), or pi (region of the coated fuel particle interior to the OPyC layer).

Values for the parameters and expressions required for the calculation of the mass fractions of the compact components are given in Table 11.5.1, taken from FDDM/F. The quantities

Table 11.5.1. Values of the mass fractions of fuel compact components and their reaction rates under hydrolysis and oxidation conditions (from FDDM/F)

Fuel Rod Component	Mass Fraction (X_i)	Reaction Rate	
		Hydrolysis	Oxidation
Fuel rod matrix material	$0.42/S_{vp}$	$r_m = 20 r_g$	$r_m = 20 r_g$
H-451 graphite shim	$(1.003 \text{ to } 1.73 v_p)/S_{vp}$	r_g	r_g
OPyC			
Fissile particle	$0.508 v_p/S_{vp}$	$r_{op} = 2.5 r_g$	$r_{op} = 2.5 r_g$
Fertile particle	$0.465 v_p/S_{vp}$	$r_{op} = 2.5 r_g$	$r_{op} = 2.5 r_g$
Particle interior to OPyC			
Fissile particle	$2.13 v_p/S_{vp}$	$r_{pi} = 0$	$r_{pi} = 0$
Fertile particle	$2.90 v_p/S_{vp}$	$r_{pi} = 0$	$r_{pi} = 0$
S_{vp}			
Fissile particle	$1.423 + 0.91 v_p$		
Fertile particle	$1.423 + 1.63 v_p$		

X_i are stated to be given in terms of the volume fraction, v_p , of coated particles in the compact (apparently the volume fraction is represented by v_p in Table 11.5.1). The reaction rates listed in Table 11.5.1 are the same as those given in §11.3 and §11.4.

Range of validity

Equation (11.5.1) is valid only in the range:

$$r_i t \leq 1 \quad (11.5.2)$$

For the compact design current to FDDM/F, the volume fraction of particles plus graphite shim is given as 0.58 and that of the fuel compact matrix material given as 0.42. Although the particle/shim volume fraction of 0.58 remains constant throughout the core, the relative particle-to-shim volume fractions may vary. Application of Eq. (11.5.1) to fuel compacts with matrix material mass fractions other than 0.42 would require different calculations for X_i than those listed in Table 11.5.1.

Assumptions

1. The assumptions stated in §11.3 and §11.4 for the reaction rates of particle coatings and compact matrix material are applicable here.
2. The particle components interior to the OPyC layer do not react (see §11.3 with respect to SiC).
3. As the kernel material can also hydrolyze and oxidize, assumption 2 must imply that the reaction is assumed to terminate at the SiC layer (consistent with §11.3).
4. The fraction of fuel compact reacted can be accurately represented by a linear combination of the reactivities of its components.
5. The reactivity of each component of the compact does not change over the time of exposure to the water or oxidant until all the component material has reacted.

Uncertainty

Until the uncertainties of the models for hydrolysis and oxidation of the compact components have been quantified (§11.3 and §11.4), the uncertainty of this model cannot be quantified.

MODEL CHRONOLOGY

Discussion of this model other than in FDDM/F has not been observed. Reference is made by FDDM/F to what appears to be an internal GA memorandum which has not been reviewed by this writer.

DISCUSSION

Equation (11.5.1) assumes the reactivity of the compact is expressible as a linear combination of the reactivities and mass fractions of its components:

$$r_c = \sum_i X_i r_i, \quad (11.5.3)$$

with all terms defined previously. The reaction rates given in Table 11.5.1 are consistent with those stated in §11.3 and §11.4. Any variation of the mass fraction of the fuel compact matrix material from the reference value of 0.42 would require modification of the coefficients for X_m and S_{vp} in Table 11.5.1. The coefficients for X_i for the particle components in Table 11.5.1 are probably determined from the density and the fractional volume of the component within the particle.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

This writer has not confirmed that the NP-MHTGR reference value for the mass fraction of the compact matrix material is 0.42. If this value is different, the expressions for X_m and S_{vp} must be adjusted accordingly. The expression for X_i should also be confirmed by comparison with the planned particle-to-shim volume ratio in the NP-MHTGR design. The "Additional Considerations" listed in §11.3 and §11.4 are also relevant here.

DATABASE USED IN MODEL DEVELOPMENT

Refer to the database discussed in §11.3 and §11.4.

11.6 HYDROLYSIS AND OXIDATION OF GRAPHITE

11.6.1 INTRODUCTION

The state of modelling and related experimentation for graphite hydrolysis and oxidation is well stated by Myers (1988): "The rate of hydrolysis of graphite has been studied as a function of the partial pressures of H_2O and H_2 , the temperature, burnoff and the concentrations of the catalysts Ba and Sr. The uncertainty is small. The rate of oxidation of graphite has been studied as a function of the partial pressure of oxygen and the temperature; the uncertainty at 900°C is also small."

11.6.2 TRANSPORT OF WATER VAPOR

function	This model calculates the diffusion coefficient of water vapor (and other gas species) in helium as a function of temperature and total pressure, and the permeation coefficient in graphite without functional dependencies.
present status	"The parameters used to describe the transport of H ₂ O, H ₂ , CO and O ₂ through graphite are regarded as adequately known ..." (Myers, 1988).
model uncertainty	The uncertainties of gaseous transport through the graphite "are considered to be negligible" (Myers, 1988).
references	FDDM/F

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The effective diffusion coefficient through the graphite structure of water vapor in helium carrier gas is given by FDDM/F:

$$D_{H_2O, He} = \frac{10^{-5} T^{1.58}}{P} , \quad (11.6.2.1)$$

$D_{H_2O, He}$ = effective diffusion coefficient through graphite of water vapor in helium (m² s⁻¹),
 P = total pressure (Pa),
 T = temperature (K).

The corresponding effective diffusion coefficients for oxygen and carbon monoxide are reported (FDDM/F) to be the same as that for water vapor, while that for H₂ is reported to be twice that of water vapor.

A permeation model is applied to the transport of water vapor by convection, with the permeability coefficients in graphite given by FDDM/F:

$$K_I = 1.55 \times 10^{-13} , \quad (11.6.2.2)$$

$$K_P = 9.20 \times 10^{-14} , \quad (11.6.2.3)$$

K_i = permeability coefficient of water vapor in graphite, for $i = I$ or P (m²),
 I = "interior region consisting of a hexagonal block having an area in the plane of the hexagon one-seventh of the corresponding area of the entire block,"

P = "periphery region consisting of the entire hexagonal block minus the interior region."

Range of validity

Without additional information, the model equations must be assumed to apply to all reactor operating conditions. The only experimental range of validity known to this writer is that the data on which K_I and K_P are based were obtained using H-327 graphite. The model is assumed to apply to both H-327 and H-451 graphite.

Assumptions

The only assumptions in the derivation of this model that are known to this writer are the following.

1. Transport of gaseous species is the same in H-451 graphite as that in H-327 graphite.
2. Apparently the transport of O_2 and CO is assumed to be the same as that for water vapor under identical conditions of temperature and pressure, and the transport of H_2 assumed to be twice that of water vapor.

Uncertainty

The uncertainties are "considered to be negligible" (Myers, 1988). According to FDDM/F, uncertainty analysis has been performed only for the graphite permeability, with the uncertainty in the permeability coefficient given by:

$$\sigma(\ln K_i) = 1.1, \quad (11.6.2.4)$$

$\sigma(\ln K_i)$ = standard deviation of $\ln K_i$, for $i = I$ or P (defined above).

MODEL CHRONOLOGY

These model equations are taken directly from FDDM/F. Reference is made in FDDM/F to an internal GA memorandum and to a GA document by R. J. Price ("Graphite Design Data Manual," GA Document No. 906374/A, September 1984), neither of which have been reviewed by this writer. The chronology of this model is therefore unknown.

DISCUSSION

As stated above, the contents of the source references indicated in FDDM/F are unknown to this writer and cannot be commented upon here. No other information on these model equations has been located.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

According to Myers (1988), the uncertainties of this model are small; therefore, significant effort in further model development is not warranted. To be thorough, the above-mentioned document by R. J. Price could be reviewed for additional information.

DATABASE USED IN MODEL DEVELOPMENT

The database used in the development of this model is unknown to this writer.

11.6.3 HYDROLYSIS OF GRAPHITE

function	This model calculates the equilibrium rate of hydrolysis of H-451 graphite by steam as a function of temperature, partial vapor pressure of water and hydrogen, fraction of graphite burnoff, and concentration of impurity catalysts.
present status	The experimental rate of graphite hydrolysis has been determined as a function of the significant experimental variables. The model is considered adequate in its present form, although greater uncertainty exists for transient conditions.
model uncertainty	According to Myers (1988), the uncertainty of the model is small.
references	Velasquez et al. (1978); General Atomic (1976c)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The rate of hydrolysis of H-451 graphite by steam is given by (Velasquez et al., 1978; FDDM/F):

$$R_{g,h} = \frac{K_1 P_{H_2O} F_b F_c}{1 + K_2 P_{H_2} + K_3 P_{H_2O}}, \quad (11.6.3.1)$$

$$K_i = K_i^0 e^{-Q_i/RT}, \quad i = 1, 2, 3, \quad (11.6.3.2)$$

$$F_b = \sum_{t=1}^8 c_t b^{t-1} , \quad (11.6.3.3)$$

$$F_c = 1 + (C_{Ba} + 0.2 C_{Sr}) e^{a-dT} , \quad (11.6.3.4)$$

- $R_{g,h}$ = rate of graphite hydrolysis (mass fraction of graphite s^{-1}),
 K_i = rate constant, for $i = 1, 2, 3$ (see footnote to Table 11.6.3.1 for units),
 K_i^o = pre-exponential factor, for $i = 1, 2, 3$ (see footnote to Table 11.6.3.1 for units),
 P_j = partial vapor pressure of species j , for $j = H_2O$ or H_2 (Pa),
 F_k = parameters to correct for the effects of burnoff ($j = b$) and catalysis by inorganic impurities ($j = c$) (dimensionless),
 Q_i = activation energy, for $i = 1, 2, 3$ ($J\ mol^{-1}$),
 T = temperature (K),
 b = graphite burnoff (weight %),
 C_m = concentration of impurity catalysts, for $i = Ba$ or Sr [$mg\ (g\ graphite)^{-1}$],
 R = ideal gas constant ($8.314\ J\ mol^{-1}\ K^{-1}$),
 a, n = constants (dimensionless),
 d = constant (K^{-1}),
 c_ℓ = coefficients, for $\ell = 1$ to 8 .

Values for the model parameters are given in Table 11.6.3.1, taken from FDDM/F and Velasquez et al. (1978).

Range of validity

The model is apparently applied over all reactor conditions; although for water vapor pressures above 3000 Pa, the model may be used but "with less confidence" (Velasquez et al., 1978). Application of this model to transient conditions increases the uncertainty of the model because "hydrogen sorption on graphite is relatively slow and has a profound effect on the apparent oxidation rate" (Velasquez et al., 1978).

The experimental range reported by General Atomic (1976c) for the reaction of water vapor with H-451 graphite includes water partial pressures from 45 to 3000 Pa, hydrogen partial pressures from 0 to 1000 Pa, and temperatures from 820 to 980°C. The experiments of Velasquez et al. (1978) covered the temperature range of 820 to 980°C, water vapor pressures from approximately 45 to 3550 Pa, hydrogen pressures from 0 to 3000 Pa, graphite burnoffs from approximately 0.8 to 9.7%, and a linear flow velocity of carrier gas and water vapor of $1.6\ cm\ s^{-1}$ at 1173 K.

Table 11.6.3.1. Parameters for the model for hydrolysis of H-451 graphite, Eqs. (11.6.3.1) through (11.6.3.4)

Index i	$K_i^{\circ(a)}$	Q_i (J mol ⁻¹)	c_i	n	a	d (K ⁻¹)
1	900	274,000	0.447	0.75	12.2	0.00426
2	110	747,000 ^(b)	0.809	-	-	-
3	30	959,000 ^(c)	0.322	-	-	-
4	-	-	0.0681	-	-	-
5	-	-	0.00613	-	-	-
6	-	-	1.23×10^{-5}	-	-	-
7	-	-	2.89×10^{-5}	-	-	-
8	-	-	1.15×10^{-6}	-	-	-

- (a) Units for $K_1^{\circ} = \text{Pa}^{-1} \text{s}^{-1}$;
units for $K_2^{\circ} = \text{Pa}^{-0.75}$; and
units for $K_3^{\circ} = \text{Pa}^{-1}$.
- (b) Value from FDDM/F; Velasquez et al. (1978) state a value of 74,660 J mol⁻¹.
- (c) Value from FDDM/F; Velasquez et al. (1978) state a value of 95,850 J mol⁻¹.

Assumptions

The derivation of the model is discussed in detail in Velasquez et al. (1978). This document should be reviewed for the assumptions required for derivation of the model. The model assumes no effect of irradiation on hydrolysis rate.

Uncertainty

According to FDDM/F, the uncertainty in the rate of hydrolysis is given by:

$$\sigma(\ln R_{g,h}) = 0.45 \quad , \quad (11.6.3.5)$$

$\sigma(\ln R_{g,h})$ = standard deviation of $\ln R_{g,h}$ as defined above.

MODEL CHRONOLOGY

Preliminary data on the hydrolysis of H-451 graphite was presented by General Atomic (1974) and more detailed data by General Atomic (1976c). Much of the data presented by General Atomic (1976c) is included in the report by Velasquez (1978). All model parameters for Eqs. (11.6.3.1) and (11.6.3.2) were derived by Velasquez et al. (1978) and incorporated into FDDM/F. The source of the model parameters for Eqs. (11.6.3.3) and (11.6.3.4) are not known to this writer, but may originate in a reference mentioned in FDDM/F (R. J. Price, "Graphite Design Data Manual," General Atomic Document No. 906374/A, 1984).

DISCUSSION

FDDM/F comments that $F_b = 1.0$ at 1 w/o burnoff and that $F_{b>13} = F_{b=13}$. The hydrolysis of graphite will not be significant under NOC (in the presence of water vapor impurity in helium). Myers (1988) comments that the "rate of hydrolysis of graphite has been studied as a function of the partial pressures of H_2O and H_2 , the temperature, burnoff and the concentrations of the catalysts Ba and Sr. The uncertainty is small."

Complete details of the experimental data and theory used in derivation of this model are contained in Velasquez et al. (1978) and will not be discussed in detail here. The effect of the catalysts Ba and Sr are not discussed by Velasquez et al. (1978). As stated by Velasquez et al. (1978), the rate of reaction of graphite with water vapor is typically described by the Langmuir-Hinshelwood equation which takes the form of Eq. (11.6.3.1), and that the "theoretical basis for a Langmuir-Hinshelwood equation of this type is that the chemical reaction of water vapor with graphite is dependent on three distinct processes: (a) sorption of water molecules on active carbon sites, (b) chemical reaction of the sorbed water to form H_2 and CO , and (c) inhibition of water sorption by competitive sorption of H_2 molecules." Velasquez et al. then go on to describe the derivation of Eq. (11.6.3.1).

Velasquez et al. (1978) summarize their work as follows: "It was found that an apparent transition in the reaction mechanism occurred at about 300 Pa (3000 μ atm) H_2O . This was analyzed by calculating two unique sets of rate constants for two regimes of water vapor pressure. A third, composite set of constants is also submitted which approximately describes the oxidation rate over the entire range of P_{H_2O} . The composite set is recommended for computer (or other) calculations should the use of two separate sets prove cumbersome. The three sets of reaction rate constants are listed" in Table 11.6.3.2. Comparison of Tables 11.6.3.1 and 11.6.3.2 indicates that FDDM/F recommends the use of this composite model, although a factor of 10 difference in stated values for Q_2 and Q_3 exists between FDDM/F and Velasquez et al. (1978). The reason for this discrepancy has not been determined.

Velasquez et al. (1978) also comment that: "It is hypothesized that the transition in apparent rate ... is due to a change in mechanism of the rate determining step. At low water vapor concentrations, adsorption of water on active sites is rate determining, whereas at high water vapor concentrations desorption of product becomes the rate-determining step. As

Table 11.6.3.2. Rate constants for Langmuir-Hinshelwood equation for hydrolysis of H-451 graphite (from Velasquez et al., 1978)

Use	K_1	K_2	K_3
Low water regime $0 < P_{H_2O}(\text{Pa}) \leq 300$	2.0×10^3 $\exp(-274000/RT)$	1.1×10^2 $\exp(-74660/RT)$	2.0×10^2 $\exp(-95850/RT)$
High water regime $300 < P_{H_2O}(\text{Pa}) \leq 3500$	1.1×10^{-1} $\exp(-19500/RT)$	7.9×10^{-8} $\exp(119700/RT)$	1.3×10^{-9} $\exp(131400/RT)$
Composite regime (a) $0 < P_{H_2O}(\text{Pa}) \leq 3500$	9.0×10^2 $\exp(-274000/RT)$	1.1×10^2 $\exp(-74660/RT)$	3.0×10^1 $\exp(-95850/RT)$
Units	Pa/s^{-1}	$\text{Pa}^{-0.75}$	Pa^{-1}

(a) The pooled standard deviation on reaction rates using the composite constants is a factor of 2.4, for 2 sigma or 95% confidence. To obtain the upper bound, the mean rate is multiplied by 2.4. The lower bound is obtained by dividing the mean rate by 2.4.

a consequence, it is noted that the reactivity of the specimen per unit water concentration decreased at concentrations greater than 300 Pa H_2O ...

"The second important factor discovered in this study is that hydrogen sorption on graphite is relatively slow and has a profound effect on the apparent oxidation rate ... In the case of normal reactor operation, water vapor concentrations up to 10 Pa and hydrogen concentrations up to 500 Pa are anticipated, and, because of the long times involved, equilibration of hydrogen sorption is expected. Under these conditions, one would expect relatively low oxidation rates as described by the low water or composite rate constants in Table [11.6.3.2]. In the case of transient steam-leak accident, the core is rapidly subjected to high water concentrations. Under these conditions, one would expect the rate of graphite oxidation to start off relatively low and then slowly increase as hydrogen desorption and water adsorption occurs. Accurate assessment of the oxidation rate may be difficult because the rate continuously increases as H_2 is desorbed. During large water ingress events, however, the reactor is automatically shut down, and graphite temperatures drop several hundred degrees in less than 10 min. Under such transient conditions, the long term effects of H_2 equilibration observed in this study would have considerable effect on the overall oxidation rates due to the inhibiting effect of hydrogen in long term equilibrium with the core graphite." Although the transient reactor conditions described above may be quantitatively representative of LHTGRs rather than MHTGRs, the point that hydrolysis rates may change with time is pertinent to MHTGR transient conditions. The model equations as presented represent a constant rate of hydrolysis and do not take into account the transient effects described above.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

The reason for the discrepancy in the values of Q_2 and Q_3 stated by FDDM/F and Velasquez et al. (1978) should be determined. Sufficient experimental data has been evaluated such that significant effort in further model development does not appear to be warranted without additional relevant data. A recent report by Fuller et al. (1990) presents data on the reaction of water with H-451 graphite at 800°C. This report has not been evaluated by this writer but should be compared to the existing model equations for consistency.

One conclusion stated by Velasquez et al. (1978) should be kept in mind for transient simulations: "Long times (>48 hours) are required to achieve equilibrium in a hydrogen-steam-graphite system at one atmosphere and reactor temperatures." The significance of these transient effects on the rate of graphite hydrolysis were discussed above. The validity of applying equilibrium models to transient conditions should be considered if sufficient data exist for analysis.

DATABASE USED IN MODEL DEVELOPMENT

Most of the database relevant to this model can be obtained from Velasquez et al. (1978). Representative figures from this reference are presented here. Figure 11.6.3.1 shows the data for the rate of oxidation of H-451 graphite as a function of water vapor

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Fig. 11.6.3.1. Isothermal oxidation of H-451 graphite exposed to helium-steam gaseous mixtures at one atmosphere at 1253 K (from Velasquez et al., 1978).

pressure at 980°C with no hydrogen present; additional figures provide similar information at temperatures of 900 and 820°C. Figure 11.6.3.2 indicates the data used in the determination of the value of Q_1 and Fig. 11.6.3.3 shows the same for Q_2 and Q_3 . Figures 11.6.3.4 through 11.6.3.6 indicate the effect of varying the hydrogen partial pressure from 0 to 507 Pa on the rate of graphite hydrolysis at 980°C; additional figures provide similar information at temperatures of 930, 900, and 880°C. Figure 11.6.3.7 shows the effect of graphite burnoff on the relative reaction rate at 820°C; additional figures provide similar information at temperatures of 900 and 980°C. Figure 11.6.3.8 shows the data used in the determination of the value of the exponent n . Refer to Velasquez et al. (1978) for additional information.

11.6.4 OXIDATION OF GRAPHITE

function	This model calculates the rate of H-451 graphite oxidation as a function of temperature and oxygen partial pressure.
present status	Although the uncertainty of the existing model at 900°C is stated to be small, the model parameters were derived from experiments on H-327 graphite rather than the reference H-451 graphite. Ongoing experiments will permit more detailed evaluation of model accuracy.
model uncertainty	According to Myers (1988), the model uncertainty is small at 900°C.
references	Jensen et al. (1973); FDDM/F; Hagrman et al. (1991)

NORMAL OPERATING CONDITIONS AND ACCIDENT CONDITIONS

Model equations

The rate of oxidation of H-451 graphite is given by (Jensen et al., 1973; FDDM/F):

$$R_{g,ox} = K P_{O_2} e^{-Q/RT} \quad , \quad (11.6.4.1)$$

- $R_{g,ox}$ = rate of graphite oxidation (mass fraction of graphite s^{-1}),
 K = constant ($s^{-1} Pa^{-1}$),
 P_{O_2} = partial pressure of oxygen (Pa),
 Q = activation energy ($J mol^{-1}$),
 T = temperature (K),
 R = ideal gas constant ($8.314 J mol^{-1} K^{-1}$).

Values for K and Q are given as (FDDM/F):

Fig. 11.6.3.2. Arrhenius plot of Langmuir-Hinshelwood rate constant (from Velasquez et al., 1978).

Fig. 11.6.3.3. Arrhenius plot of Langmuir-Hinshelwood rate constants K_2 and K_3 (from Velasquez et al., 1978).

Fig. 11.6.3.4. H-451 graphite isothermal rate of oxidation vs P_{H_2O} in helium-steam mixtures at one atmosphere at 1253 K (from Velasquez et al., 1978).

Fig. 11.6.3.5. H-451 graphite isothermal rate of oxidation vs $P_{\text{H}_2\text{O}}$ in helium-hydrogen-steam mixtures at one atmosphere at 1253 K, $P_{\text{H}_2} = 101 \text{ Pa}$ (from Velasquez et al., 1978).

Fig. 11.6.3.6. H-451 graphite isothermal rate of oxidation vs P_{H_2O} in helium-hydrogen-steam mixtures at one atmosphere at 1253 K, $P_{H_2} = 507 \text{ Pa}$ (from Velasquez et al., 1978).

Fig. 11.6.3.7. Effect of burnoff on relative reaction rate (or burnoff factor F_b) at 1093 K (from Velasquez et al., 1978).

Fig. 11.6.3.8. Plot of $\ln(1/R - 1/R_0)$ vs $\ln P_{H_2}$ for the purpose of determining the coefficient of hydrogen sorption, n (from Velasquez et al., 1978).

Values for K and Q are given as (FDDM/F):

$$K = 0.79 \text{ s}^{-1} \text{ Pa}^{-1} , \quad (11.6.4.2)$$

$$Q = 1.7 \times 10^5 \text{ J mol}^{-1} . \quad (11.6.4.3)$$

Range of validity

The model range of validity is apparently assumed to apply for all reactor conditions. However, Hagerman et al. (1991) comment that the model equation recommended by Jensen et al. (1973) "is valid only for the case in which the carbon-oxygen reaction at a microscopic graphite surface is rate limiting (low temperature, high surface/volume)."

For the experimental range of validity (Jensen et al., 1973), the oxidation of H-327 graphite by air was measured from 385 to 566°C for both irradiated and unirradiated graphite and in the presence of a gamma flux of 10^6 rad h^{-1} .

Assumptions

1. The oxidation behavior of H-451 graphite is comparable to that of H-327 graphite.
2. The only significant variables affecting the rate of graphite oxidation are the oxygen partial pressure and the temperature.

Uncertainty

The uncertainty in the oxidation of H-451 graphite is given by FDDM/F:

$$\sigma(\ln R_{\infty}) = 0.551 - 0.0722 \left(\frac{10^4}{T} \right) + 0.00258 \left(\frac{10^4}{T} \right)^2 , \quad (11.6.4.4)$$

$\sigma(\ln R_{\infty})$ = standard deviation of $\ln R_{\infty}$
 T = temperature (K).

MODEL CHRONOLOGY

This model is based on the experiments of Jensen et al. (1973) for the oxidation of H-327 graphite by air. The value of Q [Eq. (11.6.4.3)] reported by Jensen et al. (1973) is the same as that of FDDM/F; however, the value of K [Eq. (11.6.4.2)] reported by Jensen et al. (1973) appears to vary by a factor of 100 from that of FDDM/F. FDDM/F also references a document by R. J. Price ("Graphite Design Data Manual," General Atomic Document No. 906374/A, 1984) which has not been reviewed by this writer but which might shed light on this difference.

DISCUSSION

For an oxygen partial pressure of 0.21 atm (21,300 Pa), Jensen et al. (1973) give a value of $K = 77 \text{ s}^{-1} \text{ Pa}^{-1}$ which varies from that given in Eq. (11.6.4.3) by two orders of magnitude. As stated above, the reason for this variation is not clear. Jensen et al. (1973) also state the standard error (in terms of $\log R_{\text{ox}}$) to be 0.266.

Oxidation of the graphite structure should not be significant under NOC in the presence of background levels of oxidizing impurities in the helium coolant. Myers (1988) comments that: "The rate of oxidation of graphite has been studied as a function of the partial pressure of oxygen and the temperature; the uncertainty at 900°C is also small." As the data of Jensen et al. (1973) do not extend to the temperature range of 900°C, one again wonders whether the above-mentioned reference of Price (1984) contains additional data or information not presented elsewhere.

The results of the reaction of air with graphite at elevated temperatures is summarized by Jensen et al. (1973), with "the reaction rate increasing from $2.5 \times 10^{-4}\%$ graphite oxidized per hour at 385° to 0.22% graphite oxidized per hour at 566°C. Gamma fluxes of 10^6 rad/hr did not bring about any significant change in the reaction rate within the temperature range studied. In addition, variation of surface-to-volume ratios for the graphite samples had no measureable effect on the reaction rate in the temperature range investigated."

Additional experiments on graphite oxidation are currently in progress (Hagrman et al., 1991). The draft document by Hagrman et al. (1991) presents much more detailed theoretical background than that presented by Jensen et al. (1973) and comments that Jensen et al. "employ an equation which is valid only for the case in which the carbon-oxygen reaction at a microscopic graphite surface is rate limiting (low temperature, high surface/volume) ... The[ir] oxidation rate information ... has several limitations. [Their equation is not] based on data from H-451 graphite. This limitation is most important at temperatures where porosity variations between grades may affect the in-pore diffusion and this step may be rate controlling. Second, [their model cannot] be used to find the depth of the reaction zone. The low temperature equation assumes oxygen diffuses into the entire sample, a fact that is true only up to some maximum graphite thickness, even at the temperatures of the correlation's data base ..." Hagrman et al. (1991) continue with a discussion of German data and model equations for graphite oxidation.

ADDITIONAL CONSIDERATIONS FOR MODEL DEVELOPMENT

With ongoing experiments on the oxidation of H-451 graphite (Hagrman et al., 1991), these data should be evaluated as they become available and compared to the model equations. Such a comparison should provide information on the need for model revision.

DATABASE USED IN MODEL DEVELOPMENT

The database reported by Jensen et al. (1973) is tabulated in Table 11.6.4.1 and plotted in Figure 11.6.4.1. Whether additional relevant data is available from, for example, the 1984 document by Price mentioned above is unknown to this writer.

11.7 UPDATE

The significant variation in UCO kernel stoichiometry (from UO_2 to UC_2) observed recently must be considered by models of hydrolysis and oxidation of kernel material. The assumption of an average stoichiometry to describe the fuel is not realistic.

In addition to the mentioned report by Fuller et al. (1990) on the reaction of water with H-451 graphite, Fuller et al. recently issued a report on H-451 graphite corrosion by coolant impurities:

Fuller, E. L., Jr., O. C. Kopp, T. D. Burchell, and A. D. Underwood (1992), "Microgravimetric Analysis of Corrosion of H-451 Graphite by Coolant Impurities: Preliminary Report of Kinetics and Mechanisms," USDOE Report DOE-HTGR-88526, ORNL/GCR-90/3, Oak Ridge National Laboratory.

These two reports should be reviewed for their relevance to the models listed herein.

This writer is not aware of data reported from the work mentioned previously on the oxidation of H-451 graphite by Hargman et al. (1991), and does not know whether this work was completed. The analysis of the HRB-17/18 moisture ingress tests (Myers, 1991a) and the ongoing analysis and upcoming PIE of the HFR-B1 moisture ingress tests will provide important data relevant to the models presented in this chapter.

Table 11.6.4.1. Measured oxidation rates for reaction of air with H-327 graphite (from Jensen et al., 1973)

Laboratory		TRIGA			Linac	
Av Temp (°F)	Graphite Weight Loss (Z/hr)	Av Temp (°F)	Graphite Weight Loss (Z/hr)		Av Temp (°F)	Graphite Weight Loss in γ-Flux (Z/hr)
			Without γ-Flux	With γ-Flux (a)		
		100		2.0×10^{-4} 1.3×10^{-5} 8.0×10^{-6}		
720	1.7×10^{-4}	745		9.7×10^{-4}	901	1.3×10^{-2}
750	$5.2 \times 10^{-4}(b)$			1.2×10^{-3}		1.1×10^{-2}
	$5.9 \times 10^{-4}(b)$			5.0×10^{-4}		$3.8 \times 10^{-3}(b)$
830	1.6×10^{-3}	853		9.1×10^{-3}		$7.7 \times 10^{-3}(b)$
	2.5×10^{-3}			$8.4 \times 10^{-3}(b)$	952	5.2×10^{-2}
850	$3.8 \times 10^{-3}(b)$	875	1.6×10^{-2}			4.9×10^{-2}
	5.0×10^{-3}		1.4×10^{-2}			1.7×10^{-1}
	4.3×10^{-3}		2.0×10^{-2}			$1.9 \times 10^{-1}(b)$
	9.5×10^{-3}	880		3.1×10^{-2}	1040	2.6×10^{-1}
	4.2×10^{-3}			$4.9 \times 10^{-2}(b)$		2.8×10^{-1}
	$4.5 \times 10^{-3}(b)$			2.1×10^{-2}		$1.8 \times 10^{-1}(b)$
900	$5.9 \times 10^{-3}(b)$	903		4.7×10^{-3}		$2.1 \times 10^{-1}(b)$
	1.0×10^{-2}			$9.9 \times 10^{-3}(b)$		
	1.6×10^{-2}	950		3.2×10^{-2}		
950	2.8×10^{-2}			$5.0 \times 10^{-2}(b)$		
	2.5×10^{-2}	955	6.4×10^{-2}			
	4.1×10^{-2}		5.4×10^{-2}			
975	5.3×10^{-2}		8.1×10^{-2}			
	9.4×10^{-2}	1050	2.8×10^{-1}			
1000	8.4×10^{-2}		1.6×10^{-1}			
	1.2×10^{-1}		2.7×10^{-1}			
	$4.0 \times 10^{-2}(c)$					
	$8.0 \times 10^{-2}(c)$					
1050	1.8×10^{-1}					
	2.3×10^{-1}					
	2.9×10^{-1}					
	$1.3 \times 10^{-1}(b)$					

(a) γ-flux of ~ 6 rad/hr.

(b) Previously irradiated samples ($\sim 6 \times 10^{21}$ n/cm²).

(c) Large graphite block.

Fig. 11.6.4.1. Least-squares plot of log percent weight loss of H-327 graphite vs inverse temperature (from Jensen et al., 1973).

12. ADVANCED MATERIALS

12.1 INTRODUCTION

Some materials have been considered for advanced MHTGR applications but which are not discussed in existing model compilations. For example, zirconium carbide has been considered as a high-temperature replacement for SiC in the MHTGR program in Japan. The possible use of neptunium oxide as a kernel material for special applications of the NP-MHTGR has been discussed. As MHTGR-specific models for such materials have not been presented, development of such models is premature at this time. However, some literature references related to these advanced topics have been located and these references will be briefly presented and suggested as a source for those interested in pursuing analysis of these materials.

12.2 ZrC PARTICLE COATING LAYER

Zirconium carbide has been considered as a particle coating material since at least the mid-1970s because of its refractory character and its potential as a diffusion barrier. Presently, the MHTGR program in Japan is actively considering ZrC as a coating layer (Shiozawa, 1990). Zirconium carbide layers were tested for early TRISO particle designs during the 1970s in the U.S. program (Homan et al., 1985), and a serious effort was devoted to exploring the potential of kernel doping with ZrC to act as an oxygen getter (Bullock et al., 1982). Experimental data has also been obtained on the performance and FP retention characteristics of ZrC layers in the Japanese and Soviet programs.

Homan and Kania (1985) summarize the irradiation experience with ZrC-containing particles within the U.S. program during the 1970s and 1980s. They provide a listing of all U.S. irradiation tests on ZrC-coated and ZrC-gettered particles. The results are summarized as follows. "The testing done to date on HTGR fuel particles with ZrC coatings has been very limited compared with the testing done on the Triso particle design ... Fission product retentiveness of particles with ZrC coatings has generally been inferior to that of similar particles with the Triso design, but it is emphasized that the fabrication of ZrC coatings has not been optimized to nearly the extent of that of SiC coatings."

Bullock and Kaae (1982) considered the performance of particles with ZrC addition to the kernel to act as an oxygen getter and thus reduce kernel migration of UO_2 kernels. The kernel was either doped with ZrC or overcoated with an intact ZrC layer. They analyzed both the irradiation performance and the FP retention characteristics during heating and found that during postirradiation annealing "no fission products were released during testing for ... 10,000 h at 1500°C". Specifically, no release of Ag or Eu was detected, thus the Ag retention is apparently superior to that of SiC.

Ogawa and Ikawa (1982) analyzed the diffusion of several FP species through ZrC (Sr, Ba, Nb, Ru), calculated approximate diffusion coefficients, and found that their diffusion coefficients for Ba and Sr in ZrC were lower than reported diffusion coefficients in SiC.

"Though further experiments are needed before making conclusive remarks, the present results on $\text{ZrC}_{1.0}$ could be considered promising." References are provided for other diffusion data for ZrC. In an earlier paper Fukuda et al. (1979) studied the diffusion of Cs, Sr, and Ce in ZrC-coated particles.

Ogawa and Ikawa (1981b) heated UO_2 TRISO particles with a ZrC coating layer in place of the SiC layer at temperatures between 1900 and 2500°C and observed pressure-vessel-type failure of some particles at high temperatures. They also discuss the internal CO pressure buildup and the thermodynamics of ZrC and metallic FP. "The high-temperature durability of the advanced Triso-coated UO_2 particles with ZrC as the third layer has been demonstrated. The particles in unirradiated conditions could withstand the heating at 2723 K for 1 h." Ogawa and Ikawa (1981a) also compared the crushing strengths of SiC- and ZrC-coated TRISO particles.

In the Soviet HTGR program, Chernikov et al. (1985) reported diffusion coefficients for Ag, Ba, Ce, and Pm in ZrC.

12.3 NpO_2 KERNELS

The possible use of neptunium oxide as a kernel material in the NP-MHTGR has been discussed. A quick review of the scientific literature provided several references which might prove useful should models of NpO_2 and Np physical properties and transport behavior within the MHTGR be required. None of these references were reviewed in detail, but the previous work on these topics will be briefly mentioned here and a few references provided for further analysis.

As a product of neutron capture by uranium, the chemical properties of Np are well-studied in relation to fuel reprocessing. Because of its radiological hazard, studies of Np with respect to nuclear waste and management are common. Several reviews of the chemical and physical properties of Np and its compounds are available. C. Keller (*The Chemistry of the Transuranium Elements*, Verlag Chemie GmbH, Weinheim/Bergstr., Germany, 1971) discusses the properties of Np and its compounds, with emphasis on fuel reprocessing considerations. In 1979 R. E. Mosley ("Neptunium: A Bibliographic Reference," Environmental Monitoring Support Laboratory Report EMSL-LV-0539-29, EPA, Las Vegas, Nev.) presented a comprehensive bibliography of the literature on Np through 1975. In 1978 O. L. Keller, Jr. ("The Chemistry of Protactinium, Neptunium, Americium, and Curium in the Nuclear Fuel Cycle," *Radiochim. Acta* 25, 211-223) presented a review of the chemistry of Np and other actinides with emphasis on the nuclear fuel cycle.

Previous HTGR-specific analyses have concentrated on Np as a byproduct of the fuel cycle and its effect on fuel burnup and management. Investigations into the production and transmutation of actinides in pebble-bed HTGRs was reported by H. Schaal et al. of KFA Jülich in 1980. Detailed core calculations for the HTR-2000 pebble bed reactor were reported in 1989 by F. Thomas of KFA Jülich. In 1978 P. Wydler et al. of Switzerland considered Np recycling in the gas-cooled fast breeder reactor with respect to reactivity coefficients during steam penetration. In the U.S. the isothermal, fuel, and moderator

temperature coefficients for the LHTGR were calculated in 1977 by P. G. Bailey of Los Alamos National Laboratory.

The use of Np as a target material was discussed in the U.S. by G. F. O'Neill in 1982 ("Additional Plutonium-238 Production," Du Pont de Nemours Report DPST-82-839, Aiken, S.C.) and in the USSR by V. S. Valyavkin et al. in 1981 ("Some Methods for Preparing and Calibrating Targets of Fissionable Radionuclides," *Prikl. Yad. Spektrosk.* 10, 102-108, in Russian).

The release of Np from nuclear fuel has been primarily studied in relation to light water reactors. For example, studies of release by annealing and melting of LWR fuel pins in air and steam was reported in Germany in 1981, and studies of release from defective fuel elements and radionuclide deposition within the heat-transport system and on piping surfaces was reported in Canada in 1986.

Several publications are reported on the interaction of Np with metallic surfaces. In 1986 B. L. Zhuikov et al. ("Sublimation and Thermochromatography of Lower Actinide and Lanthanide Oxides," *Radiokhimiya* 28, 246-252, in Russian) studied the high-temperature sublimation of Np oxides from the surfaces of several metals into streams of helium and hydrogen. In 1970 R. Haulet et al. ["Plate-out of Radioactive Products in (Turbulent Flow) Pipes. Theoretical Aspects and Experimental Verifications," *Congr. Int. Diffus. Prod. Fission, Actes 1969*, 159-189, in French] published their experimental and modelling work on the plateout of Np and several FP on steel and graphite in an out-of-pile loop cooled by CO₂. An empirical model was reported by B. Eichler et al. of Germany in 1985 for the adsorption of actinides on metallic surfaces, and D. H. Smith reported on an experimental investigation of the desorption of Np and other actinides from hot tungsten in his 1970 dissertation.

Literature references for the physical properties of Np and NpO₂ are numerous. Information is readily available on such topics as the evaporation behavior, thermal expansion, and heat capacity of NpO₂, and the vapor pressure of Np, among others. Other reported references discuss the radiation chemistry and fuel chemistry of Np, the sorption of Np in concrete, the transport of Np by aerosols during accident conditions, and the leachability of Np from coated-particle fuels by brines.

This cursory review of the literature indicates that sufficient information exists for some model development related to the use of NpO₂ in coated fuel particles. Although more detailed literature review and appropriate experiments would be required for refinement of the models, at first glance such a modelling effort appears feasible.

12.4 UPDATE

The Japanese work on ZrC coating layers continues with some recent publications. The use of NpO₂ kernels has not been recently discussed, but greater interest in the use of PuO₂ kernels has recently surfaced. A draft report on irradiation data of PuO₂ TRISO particles was written several years back by T. N. Tiegs at ORNL. Other irradiation data on PuO₂ fuels should be readily available in the literature.

13. CONCLUSIONS

This chapter first addresses specific issues relevant to model content and revision, then critically addresses the present state of the MHTGR modelling effort in relation to recent experimental results.

This compilation should provide a good foundation for model development and for analysis of experimental results obtained from the MHTGR program. Incorporation of model revisions into a future revision of this compilation can provide an up-to-date working document for the MHTGR program. The utility of this document can be enhanced by integration of the operating conditions and design basis events predicted for the MHTGR into the analysis of the models and their general applicability to the specifics of the MHTGR design. Incorporation of future suggestions and comments on this document should also enhance the content of this compilation.

This compilation is based on documents available to the author and does not represent a complete or independent review of the models and their derivation. Any future revision of this document would be improved by greater accessibility to source documents which discuss the derivation of specific models.

General revision of models should not be pursued apart from the ongoing experimental efforts of the MHTGR program and recently completed NP-MHTGR work. The evaluation of new data in relation to existing models should be considered a priority effort, as such data provides the best opportunity for validation of the existing MHTGR models relative to current MHTGR design and fuel. The general evaluation of existing models using new hypotheses or consideration of non-MHTGR scientific literature can be pursued as a secondary priority relative to the analysis of MHTGR data.

Some of the experiments from which significant new data relevant to the MHTGR program have or will become available in the near future include the capsule experiments HRB-17/18 and HFR-B1, the graphite oxidation tests discussed by Hagrman et al. (1991), the COMEDIE liftoff experiments, and the fuel particle performance and FP release tests using the Core Conduction Cooldown Test Facility (CCCTF) at Oak Ridge National Laboratory.

In the course of assembling this document, several modelling topics appeared to this writer to be potentially fruitful for further analysis. These topics will be briefly presented below. Analysis of these models is not suggested as a programmatic outline, but as interim suggestions of areas which might prove fruitful with some investment of effort.

The tritium transport models will likely take on greater significance for the NP-MHTGR program and justify further analysis than has been undertaken by the general MHTGR program. As mentioned in §9, significant information on tritium transport has not been incorporated into MHTGR modelling efforts. Specifically, a great deal of information has become available from the fusion energy program on tritium transport; and as mentioned in §9.7, much information has been compiled on tritium permeation through metallic structures that has apparently not been considered by the MHTGR model. This information can be evaluated with respect to revision of the existing models for tritium transport. Design Data Need 11.49 is relevant to this suggestion.

As discussed in §2.3, the pressure-vessel model now predicts insignificant failure levels of standard particles such that the validation of this model becomes impractical. However, pressure-vessel effects could be expected to have much greater significance in the performance of the target particles for the NP-MHTGR. If data on the performance of the target particles were provided to the MHTGR fuel program, the results might provide a useful quantitative test of the validity of the pressure-vessel model. Such a quantitative test has been difficult with the variable and non-reference fuel particle designs over past years, and the availability of experimental results from high-quality coatings and particles with significant internal pressures could be quite fortuitous. The fuel failure observed in recent U.S. irradiation capsules presently leaves the PV model in a state of unknown validity or applicability.

With the SiC failure mechanisms of kernel migration and FP corrosion predicted to have minor or insignificant effects on the performance of the SiC layer, more detailed modelling effort on the high-temperature behavior of the SiC layer and its microstructural evolution during thermal decomposition may prove beneficial. The limitations of our phenomenological understanding of the high-temperature evolution of the SiC layer under accident conditions were mentioned in §2.4.4. Significant information is presently available in the non-MHTGR scientific literature which might permit formulation of more refined models of SiC behavior at AC temperatures rather than the existing model which is limited to the dichotomy of intact vs failed SiC layers, with no transitional regime or consideration of an increase in permeability due to the development of internal porosity as the silicon is vaporized. The observation by Myers (1986) that the rate equation for hydrolytic reaction of the kernel material is "formally identical to a Weibull distribution function" and that "such a distribution function can describe heterogeneous reactions" is interesting in this regard. The Weibull distribution has been successfully used to approximate FP release from fuel particles but under the assumption that the relevance of the distribution function is limited to the strength of the SiC layer. The possibility that a Weibull-like formulation might also be applied to the decomposition of the SiC layer at high temperatures may permit a more mechanistic hypothesis of SiC decomposition to be developed, rather than relying on the unproven assumption of sudden SiC failure.

A related issue is the debate over the transport or nontransport of metallic FP through an intact SiC layer. Although diffusion data has been obtained from numerous experiments, the variability in the results has encouraged some to deny the existence of transport through intact SiC. Some effort at more detailed analysis of the existing diffusion data and particularly its relation to irradiation conditions would be fruitful if some consistency in the interpretation of the experimental results could be achieved. However, any consideration of the transport of metallic FP through the SiC layer cannot be divorced from considerations of the microstructural evolution of the SiC layer at high temperatures because of the synergism between the two phenomena. Design Data Need 11.47 is directly pertinent to these considerations of SiC model analysis. The recently observed microstructural differences of SiC from the U.S. and German programs and their relation to the superior fuel performance and FP retention of the German program requires serious consideration in this regard.

Accident analyses and fuel performance modelling are usually tied to specific accidents. As a result, fuel performance in the temperature range of 1250° to 1600°C is ambiguously covered by existing models whose applicability or accuracy is uncertain. Other examples are the neglect of accidents during reactor operation (e.g., overpower transients) and synergistic effects such as might be induced by limited moisture ingress during reactor operation.

In §6 it was noted that Cs release from the core is sometimes significantly underpredicted. This nonconservatism in prediction of FP release raises concerns for the reliability of the models used. The application of Fickian models of diffusion to the transport of some metallic FP species is known to be an oversimplification. The existing data on diffusion and sorption of metallic FP in graphite might be reconsidered with respect to non-Fickian models of diffusion or the coupling of the phenomena of diffusion and sorption in graphite. Such an analysis would be directly pertinent to DDN 11.48.

The effects of surface oxidation and the presence of surface oxide layers on the sorption and transport of FP appear to be relevant for several core components (primary circuit alloys, graphite, and perhaps the particle coating layers). Although analogies exist between the effects of oxidation on FP transport for several reactor components, this writer has not seen a good discussion on the general theory and available data on the effects of surface oxidation on FP transport and the interaction of FP with surface oxide layers. Such a general evaluation may provide qualitative insight into the effects of water and air ingress on the transient transport and release of FP under accident conditions and subsequent modification of the transport processes through oxidized materials.

The availability of non-MHTGR-specific information relevant to these models within the scientific literature should be considered. In many cases literature reviews have apparently not been conducted since the models were proposed years ago. In situations where few data exist or the data are contradictory, reference to the scientific literature may provide more certainty as to dominant phenomena or in some cases may provide relevant quantitative information. Models such as SiC microstructural evolution, tritium transport, interaction of FP with metallic structures and oxidized surfaces, and possibly liftoff and washoff models and others might benefit from such an analysis. For those models which may require revision and for which no new data are forthcoming, the scientific literature may provide the best opportunity for improvement of such models.

Summation

Fuel design and fabrication, quality control, specifications, and performance are closely linked. Models and model parameters derived for earlier fuel designs are not necessarily applicable to the specific MHTGR fuel designs recently irradiated. Existing U.S. models for MHTGR fuel and FP analysis is based on the performance of fuel with significantly lower as-manufactured fuel quality than recently fabricated. Conceivably the important phenomena governing the performance of high-quality fuel may not be significant in modelling lower-quality fuel performance, and the use of questionable or erroneous models may be acceptable for poorer fuel but unacceptable for higher-quality fuel. Models which are based on curve fits to existing data rather than understanding the underlying phenomena cannot adapt to unexpected fuel performance results resulting from changes in design.

Specific models can be singled out which require further analysis or revision: PV model of fuel performance, SiC and OPyC layer performance, metallic FP transport in graphite, and plateout/liftoff models. The derivation of these models and assumptions used range from questionable to wrong.

The recently observed manufacturing "surprises" such as SiC gold spots, extreme variation in UCO stoichiometry, and concave surfaces on HRB-21 fertile particles bode ill for the accuracy of fuel performance models. Such defects have been observed on the percent level, and even if they do not affect NOC fuel performance, the relevance of AC models to particles with these anomalies is unexplored.

The failure of the MHTGR program to devise single-effects tests to confirm the appropriateness of important models leaves many unanswered questions. The uncertainty in the relation of gas to metal release from SiC layers as a measure of SiC failure, and the lack of definitive evaluation of this question by coupling IMGA and particle gas analysis measurements, is unacceptable. The reliance on the PV model because it provides a warm and cozy semblance of understanding could only recently be evaluated from the HRB-21 piggyback samples which contained missing coating layers. Those samples remain unanalyzed to date. The MHTGR modelling philosophy is too often not whether a model is based on a sound phenomenological or theoretical framework but simply whether the calculations come close enough to experimental data, and if they are off by orders of magnitude they should at least be "conservative."

The fundamental model for in-reactor fuel performance, PV failure, has been demonstrated to be wrong in four recent irradiation capsules. The fundamental assumption that U.S. SiC will be as retentive for FP as German SiC appears to be significantly in error based on recent CCCTF tests. The fundamental assumption that high-quality U.S. MHTGR fuel can be produced because the Germans produced it appears groundless.

Existing approaches to MHTGR fuel performance and FP analysis have not been the beneficiary of independent analysis in recent times. As observed by Martin (1990), the independent assessment by Tokar (1976) of deficiencies in HTGR fuel performance models remains as valid today as when it was written nearly twenty years ago. As of 1993, the MHTGR fuel performance and FP modelling effort is sorely in need of independent assessment.

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