Gulf General Atomic Incorporated

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AEC RESEARCH AND
DEVELOPMENT REPORT

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HTGR BASE PROGRAM QUARTERLY PROGRESS REPORT FOR THE PERIOD ENDING MAY 31, 1968

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GA-7981-March, 1967, through May, 1967
GA-8200-June, 1967, through August, 1967
GA-8356-September, 1967, through November, 1967
GA-8530-December, 1967, through February, 1968

INTRODUCTION

This report covers the work performed by Gulf General Atomic Incorporated under U.S. Atomic Energy Commission Contract AT(04-3)-167, Project Agreement No. 17. This Project Agreement calls for preliminary design and related exploratory development of a 1000-Mw(e), gas-cooled, nuclear power reactor incorporating advanced technology, and a 150-300 Mw(e) prototype. This program is based on the concept of the High-temperature Gas-cooled Reactor (HTGR) system developed by Gulf General Atomic.

The related exploratory development effort is aimed at a 1000-Mw(e) gas-cooled reactor plant that could be placed in operation in the 1970's, with operation of the prototype at an earlier date. The plant would demonstrate such new design features as:

1. Breeding or near breeding of fuel in a high-temperature, gas-cooled, thermal reactor using a Th-U²³³ fuel cycle.
2. Advanced reactor fuel elements, which may include new and simpler configurations and new methods of processing and fabricating to extend fuel lifetime and reduce fuel costs.
3. Alternative plant arrangements to reduce plant capital costs, including such possibilities as alternative materials (e.g., concrete pressure vessels) and the assembly of the reactor and steam-generating equipment in a single containment.
4. A supercritical-pressure steam cycle that is particularly adaptable to a 1000-Mw(e) plant and to the inherent high-temperature capabilities of the HTGR system.

CONTENTS

INTRODUCTION	1
TASK I. UPDATED 1000-MW(E) HTGR CONCEPTUAL DESIGN	1
Refueling Studies	1
TASK III. ANALYTICAL METHODS DEVELOPMENT	2
Three-dimensional Heat-transfer Code	2
Gamma Buildup in Heterogeneous Media	2
TASK IV. FISSION-PRODUCT MECHANISMS	11
Mathematical Treatment of Fission-product Transport	11
SLIDER Code	11
FIPER Code	18
Fission-product Vaporization Studies	18
Strontium-Graphite System	18
Cesium-Graphite Sorption Studies	20
Cesium Sorption Characteristics of Irradiated Graphite	22
Strontium Sorption Characteristics of Irradiated Graphite	26
Fission-product Diffusion Studies	28
Diffusion of Metallic Fission Products in Graphite	28
Transport of Strontium in Graphite	28
Diffusion of Metallic Fission Products in Pyrolytic Carbon	30
Diffusion of Metallic Fission Products in Silicon Carbide	41
Mixed Fission-product Deposition Studies	43
TASK V. RECYCLE FUEL STUDIES	48
Central HTGR Fuel Reprocessing Plant Studies	48
Fuel Refabrication Studies	49
Survey of Mechanical Considerations for Removing Fuel Particles from HTGR Spent Fuel	50
Ocean Shipping of Spent HTGR Fuels	50
Criticality	50
Retention of Uranium in Alumina Fluidized Beds	50
Head-end Reprocessing	51
Gaseous Debonding Process	51
Thermogravimetric Analysis Studies	56
Methods for Destroying Coatings on Fuel Particles	57
Stability of Irradiated (Th,U)O ₂ - ThO ₂ Fuel Kernels Under Oxidizing Conditions	62

TASK VI. PHYSICS METHODS	63
Kinetics	63
Status of Kinetics Codes at Gulf General Atomic	63
Cross-section Evaluations	72
Scattering Kernels for Graphite	72
Doppler Broadened Cross Sections	72
The 1.056 ev Resonance in Pu ²⁴⁰	72
Cross-section Evaluation Working Group Activities	73
Flux Spectrum Code Development	74
TASK VII. EXPERIMENTAL PHYSICS	87
Lattice Assembly No. 2	87
Experimental Results	90
Analytical Results	91
TASK VIII. PHYSICS AND FUEL MANAGEMENT	101
Parametric Studies	101
Code Development	101
HTGR Off-site Program Surveillance	102
TASK IX. ADVANCED COATED PARTICLE FUELS	103
Barrier Coating Development	103
Deposition of SiC from Methyldichlorosilane	103
Microstructure of Coatings on Fuel Particles	103
Mechanical Properties of SiC Coatings	104
Thermal Stability Studies	104
Thermal Expansion of Vapor-deposited Silicon Carbide	105
Irradiation Effects in Vapor-deposited Silicon Carbide	105
Irradiation Effects in Vapor-deposited Zirconium Carbide	110
Coating Contamination Studies	114
Coated Particle Irradiations	118
Gulf General Atomic Capsules	118
Cooperative Irradiation Programs	119
TASK XI. GRAPHITE RESEARCH	120
Graphite Irradiations	120
Graphite Irradiations in Dragon	120
Graphite Irradiations in Dounreay	120
Gulf General Atomic-BNWL Joint Irradiations	121
Postirradiation Examination of Specimens from ETR Capsules	121
Carbon Irradiations	177
Boronated Graphite Irradiation Studies	184
Irradiation Experiment BG-1	184
Irradiation of Spherical B ₄ C	184

Task I

UPDATED 1000-MW(E) HTGR CONCEPTUAL DESIGN

REFUELING STUDIES

An extensive shielding reappraisal has indicated that the saving in concrete vessel wall thickness anticipated in the quarterly report for the period ending November 30, 1967 (GA-8356) was indeed possible. The required thickness of concrete for neutron shielding is 4-1/2 ft. The required thickness of local shielding at a density assumed to be that of steel has been reduced from 12 in. to 8 in. Bulk shielding material procurement studies, while not complete, have indicated that bulk densities as high as steel are not obtainable at the optimum price, so the actual thickness will be greater than 8 in with the weight only slightly increased.

A brief appraisal of the vessel indicated that 4-1/2 ft of concrete would be more than adequate structurally.

The structural and shielding studies and other relevant material are being consolidated into the third topical report mentioned in the previous quarterly report (GA-8530). The major portion of this topical report, designated GA-8639, has been written. This, in conjunction with GA-8075 (Ref. 1) and GA-8471 (Ref. 2), will fully report the work done on through-the-head handling equipment which has been designated as Case 1.

Work was begun on the Case 2 study, which deals with on-power refueling of the reference core design with in-vessel fuel handling equipment. Detailed information on the French Euratom in-vessel refueling system was obtained, and two reactor arrangement drawings showing the effect of incorporating it in the 1000-Mw(e) HTGR were produced. These drawings will form a basis for an evaluation of in-vessel fuel handling equipment.

The Case 3 study, which deals with on-power refueling of a new core that has been designed to simplify the on-power refueling problem, was also begun during this period. A drawing of the fuel element and structural graphite block was produced. This drawing will form the basis for an evaluation of this alternative.

References

1. Paget, J. A., A Survey of Technical Considerations Applicable to an On-line Refueling System for Large HTGR's, USAEC report GA-8075, General Dynamics, General Atomic Division, June 30, 1967.
2. Paget, J. A., A Technical Description of Study "A": A Base Case Design of On-line Refueling Machine for a Multiple Reactor HTGR Power Station, USAEC report GA-8471, Gulf General Atomic, to be published.

Task III
ANALYTICAL METHODS DEVELOPMENT

THREE-DIMENSIONAL HEAT-TRANSFER CODE

Work is continuing on developing the steady-state option for the RAT-3D heat-transfer program. The algorithm has been programmed and several cases run as part of the debugging procedure. In these cases it was found that the steady-state option is faster by at least a factor of five than the original method used to obtain steady-state temperatures. So far the test problems have not included flowing coolants. Work is now proceeding along the lines of debugging with a complex problem having flowing coolants. In addition to the debugging of the steady-state option, a revised version of the code document (Ref. 1) is being prepared to describe the additions included and changes made during this fiscal year.

Following extensive debugging, the two-dimensional version of the, TAC, heat-transfer program has been released for production use. A user's report is in preparation and is expected to be completed during the next quarter.

It has been demonstrated that the TACPLT plotting routine for the heat-transfer codes is operational. When the user's report has been completed, the program will be released for production use.

GAMMA BUILDUP IN HETEROGENEOUS MEDIA

Gamma buildup factors were calculated for 0.5, 1.0, and 2.0 Mev isotropic point sources in beryllium, lithium hydride, and carbon/thorium using the 1DF transport code and the NAGE conversion code, described in earlier quarterly progress reports.

The gamma dose, energy, and energy-absorption buildup factors for beryllium are plotted in Figs. 3.1, 3.2, and 3.3. This is believed to represent the first detailed calculation of gamma buildup in an element of such low Z number ($Z = 4$). The only comparisons available in the literature comprise mere extrapolations of Goldstein's moments method data (Ref. 2) for a minimum atomic number of 13 (aluminum). In the referenced report, the authors carried out extrapolation of B_r versus Z down to $Z = 8$. In their plots for $E_0 = 0.5$ Mev, it is implied that B_r approaches infinity for $Z < 9$ and $\mu_{0r} = 20$, whereas a value of $B_r = 1400$ for $Z = 4$ was calculated in the present study. Goldstein's curve for $E_0 = 2$ Mev, $\mu_{0r} = 20$ can be extrapolated to a value of $B_r = 27$ at $Z = 4$, compared with the calculated value of $B_r = 43$.

Another comparison can be drawn from Table 5 of Ref. 3. Inserting the tabulated parameters into the equation

Fig. 3.1--Gamma dose buildup factors (isotropic point source in beryllium)

Fig. 3.2--Gamma energy buildup factors (isotropic point source in beryllium)

Fig. 3.3--Gamma energy absorption buildup factors (isotropic point source in beryllium)

$$B_a = 1 + a(\mu_0 r) + b(\mu_0 r)^2 + c(\mu_0 r)^3$$

for $Z = 4$, one obtains $B = 210$ for 0.5-Mev source energy, $B_a = 70$ for 1 Mev and $B_a = 37$ for 2 Mev, all at $\mu_0 = 20$. From Fig. 3.3, it can be seen that at 0.5-Mev source energy, the disagreement is almost 50%.

As shown in Figs. 3.4, 3.5, and 3.6, buildup in LiH reaches some very high levels, particularly in the case of the 0.5-Mev source energy. Here there is no feasible way of comparing the results with the literature, because it is not clear what equivalent Z number should be assigned to LiH.

Buildup for a 2-Mev source energy was computed in a homogeneous graphite-thorium mixture with an atom ratio of 165/1. The comparison plots in Fig. 3.7 suggest that this particular mixture of carbon and thorium can be simulated by the buildup factors for tin, which are readily available in the literature. It is reasonable to assume that this substitution will hold equally well for other source energies.

References

1. Clark, S. S., and M. Troost, RAT-3D, A General Three-dimensional Heat Transfer Code, USAEC report GAMD-7346, General Dynamics, General Atomic Division, October 10, 1966.
2. Goldstein, H., and J. E. Wilkins, Jr., Calculations of the Penetration of Gamma Rays, report NYO-3075, June 30, 1954, pp. 188-192.
3. Claiborne, H. C., Survey of Methods for Calculating Gamma Ray Heating, report ORNL-RSIC-8, June 1965.

Fig. 3.4--Gamma dose buildup factors (point isotropic source in lithium hydride)

Fig. 3.5--Gamma energy buildup factors (point isotropic source in lithium hydride)

Fig. 3.6--Gamma energy absorption buildup factors (point isotropic source in lithium hydride)

Fig. 3.7—Gamma dose buildup factors (2-Mev isotropic point source)

Task IV
FISSION-PRODUCT MECHANISMS

MATHEMATICAL TREATMENT OF FISSION-PRODUCT TRANSPORT

SLIDER Code

An important parameter in evaluating the safety of an HTGR reactor system is the release of fission products from coated fuel particles. Estimation of the release of fission products from these particles under reactor conditions has been attempted using the SLIDER code (Ref. 1). This code consists of a numerical solution of Fick's law in spherical coordinates, continuity equations, a representation of fission-product decay and birth rates as a function of position, and a thermodynamic description of fission-product behavior at interfaces. These relations are presented as

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

$$C^-(r_i,t) = \phi_i C^+(r_i,t) \quad , \text{ and} \quad (2)$$

$$J^-(r_i,t) = J^+(r_i,t) \quad , \quad (3)$$

where $C(r,t)$ is the concentration of the fission product as a function of radial position in the sphere, r , and time t ; $D(t)$ is the concentration-independent diffusion coefficient of the fission product in the particular medium; λ is its decay constant; $S(r,t)$ is its source function; ϕ_i is the distribution coefficient at the interface of r_i ; and J is the flux of the fission product (+ and - superscripts refer to either side of the interface). A condition providing for $C(r,t) = 0$ for all time greater than 0 at the outermost border is generally added to these equations.

To evaluate fission-product release in a reactor, it is necessary to supply the appropriate particle geometry, diffusion coefficients, and distribution coefficients. This is a formidable task. In order to approach this problem, studies have been made of postirradiation fission-product release as a function of temperature. The results of these studies are complex and require considerable interpretation. The SLIDER code without a source term has proved to be of considerable value in this interpretation. Parametric studies have been made of the integrated release of fission products, initially wholly in the fueled region, as a function of the diffusion coefficients and the distribution coefficients. These studies have led to observations of critical features in describing integrated fission-product releases. From

experimental values associated with these critical features, it is possible to at least partially evaluate diffusion coefficients and distribution coefficients. These experimental values may then be put back into SLIDER with appropriate birth and decay rates to evaluate in-reactor particle fission-product releases. Figure 4.1 is a representation of SLIDER simulation of a simplified postirradiation fission-product release experiment. Calculations have been made with the following pertinent input data:

1. A 0.01-cm radius kernel initially uniformly loaded with a stable fission product.
2. A coating 0.007-cm thick initially free of this fission product.
3. Diffusion coefficients of 1.4×10^{-12} cm²/sec and 4.8×10^{-9} cm²/sec in the kernel and coating, respectively, a distribution coefficient of unity, and a perfect sink outside the coating.

It has been found convenient to express the integrated release as a function of the square root of time, as in Fig. 4.1. The critical features apparent in this curve are a delayed initial release and a later release which, with increasing time, approaches the release this kernel would have shown if it had not been coated. This asymptote is represented by the dotted line passing through the origin. In this particular system, the quantity of fission product in the coating is approximated by the difference between the two curves; that is, the release from the fueled kernel is hardly altered by the coating and the release from the particle soon becomes rate-limited by the release from the kernel. If the particle release curve is extrapolated linearly from the straight portion of the release curve to a zero release point on the time axis, one obtains a $t_d^{1/2}$ where t_d can be called a delay time for release. A delay time for release from a membrane of thickness ℓ , where the membrane is initially free of a diffusing species and has a constant source on one side and a perfect sink on the other, can be given by

$$6Dt_d = \ell^2 \quad . \quad (4)$$

This particular formula predicts the delayed release from the coated particle reasonably well. In this case, the delay time predicted by the formula was somewhat longer than the extrapolated value. The main reason for this deviation appears to be that the kernel source is far from constant. If it were constant, the release curve would exhibit a much higher slope, and the calculated release curve would thus extrapolate to a longer delay time.

The calculated releases shown in Fig. 4.2 were obtained in parametric variations of the values used in deriving Fig. 4.1. These curves illustrate changes (1) the diffusion coefficient in the coating ($D_2 \times 2$), characterized by an appropriate change in $t_d (\times 1/2)$ and a faster approach to the bare kernel release line; (2) the diffusion coefficient in the kernel ($D_1 \times 2$), characterized by an approach to a steeper bare kernel release with an unchanged delay time; and (3) the distribution coefficient ϕ ($\phi = 1, 10^2, 10^{-2}$). Where the distribution coefficient has been changed to provide a greater driving force for transfer of fission product from the fueled region to the coating ($\phi = 10^2$), the fission-product release curve is almost identical to the one

Fig. 4.1--Calculated fractional release from a two-zone particle

Fig. 4.2--Calculated fractional release in a two-zone particle

for unit ϕ , which has been repeated in this figure ($\phi = 1$). Where the driving force has been decreased, the release curve shows quite a different character. The release is decreased considerably and the nearly linear character of releases versus $t^{1/2}$ following the delay time is not apparent. This suggests transfer from kernel control of release to coating control. Apparently, this change has greatly lengthened the time period during which the release can be considered to be characterized by membrane diffusion.

Release behaviors in the region of parameters described by these figures are useful in determining experimental values of these parameters. In particular, the diffusion coefficient in the coating can be approximated from delay times and coating thicknesses, and the diffusion coefficient in the kernel can be derived from later behavior. Distribution coefficients may be revealed in some cases by permeabilities and diffusion coefficients.

A study was also made of release with equal diffusion coefficients in the coating and the kernel. The description of delay time is much the same as in the previous case. Figure 4.3 illustrates this similarity in delay time, as well as later release behavior. In this case also, the $t^{1/2}$ plot shows a long linear region. The reason is probably that depletion effects are reasonably followed by this function and not that there is kernel control. This release has a much greater tendency to be coating-controlled. Since kernel control occurs late, if at all, a kernel diffusion coefficient is generally not well defined by the releases. However, the effect of the distribution coefficient as described in this figure is generally more important, and release data can be used in evaluating this quantity within the ranges of the illustrated parametric changes.

An attempt to investigate more realistic fuel particles and fission-product loadings has been made. A buffer carbon layer for absorbing recoil fission products has been included in the particle, and tests and releases with recoil into this layer have been considered. Another factor that may pertain is the dependence of the diffusion coefficient on radiation flux. A study of this effect is planned.

Calculations for Fig. 4.4 illustrate a recoil source with the same parameters as those used in the study depicted by Fig. 4.1, except that a buffer carbon layer 0.0006 cm thick with a diffusion coefficient of 10^{-6} cm²/sec was placed between the coating and the kernel. Distribution coefficients were taken as unity, and a recoil range of 0.0006 cm was assumed in both the kernel and coating materials. Results of this calculation differ considerably from those for experiments with no recoil. These differences are consistent with about 4.5% release from the kernel during irradiation. After release of this quantity of fission product from the particle, the releases approach those of the bare kernel. The recoil effects become trivial after releases of 7% to 8%.

An attempt has been made to describe distribution coefficient control (ϕ) of release of fission products from a particle. A ϕ control layer can be added to a particle between the fuel and the outer coating. This layer with, for instance, even a somewhat larger diffusion coefficient than the

Fig. 4.3--Calculated fractional releases with equivalent diffusion coefficients in the two zones

Fig. 4.4--Calculated fractional release from a three-zone particle with recoil from the fuel region

normal coating layer may have the property of either strongly rejecting or strongly absorbing a particular fission product and thus limiting the release of this fission product. In the case of small ϕ , the layer can act as a permeation barrier to the fission product. In the case of large ϕ , the layer may act as a sink, thus greatly reducing the concentration of fission product available to be diffused through an outer coating. One advantage the highly absorptive layer may have over the rejecting layer is that it would function independently of the continuity of this layer. It may be more difficult, however, to find an appropriate material for this layer. When selecting the fuel material itself, this absorptive effect might be considered.

FIPER Code

The study of the diffusion and release of metallic isotopes from HTGR fuel elements using the FIPER code has continued. A number of different calculations have been performed to investigate the dependence of the release on the various parameters that determine the diffusion and adsorption processes of metallic isotopes.

First, the release of Sr^{90} has been calculated using various values for the diffusion coefficient inside the uranium-thorium dicarbide kernel at 1300°K . It is found that using a value of $10^{-13} \text{ cm}^2/\text{sec}$ rather than $10^{-12} \text{ cm}^2/\text{sec}$ results in a release that is smaller only by a factor of two. Even using the value of $10^{-13} \text{ cm}^2/\text{sec}$, the stationary state is reached within three years as compared with the six-year life of a fuel element. A drastic reduction of the release can be expected if the diffusion coefficient is substantially smaller than $10^{-13} \text{ cm}^2/\text{sec}$.

Second, the effect of other isotopes on the release of Sr^{90} has been evaluated. There is a large effect on fractional release if one assumes that the Freundlich adsorption isotherm holds at low concentrations. For the concentrations of interest in the reference design of a 300-Mw(e) reactor, the Sr^{90} concentration is so small that the Langmuir adsorption isotherm probably holds in the graphite region near the coolant hole, and therefore no significant cross effects have been calculated. However, all of these calculations have been made under the assumption that the diffusion coefficient of a particular metal isotope does not depend on the concentration of that or of other isotopes. For more correct calculations, the concentration dependence of the diffusion coefficients should be known.

Third, the FIPER code has been applied to calculate the Sr^{90} release from segment 16 and segment 18 of the British PLUTO 3 experiment. The calculated release is smaller than the measured release by several orders of magnitude. The origin of this discrepancy is not clear at present.

FISSION-PRODUCT VAPORIZATION STUDIES

Strontium-Graphite System

Knudsen Cell Tracer Method. Studies of the strontium-graphite system using the Knudsen cell tracer technique have been delayed due to mechanical problems in the apparatus. An experiment will soon be conducted to determine

if the vapor pressure within the cell is kinetically- or equilibrium-established. This test will employ a molybdenum crucible with a tight-fitting graphite sleeve covering the periphery of the crucible. After the initial run, in which the only opening will be the target-directed orifice, the graphite sleeve will be removed, and additional openings will be made on the side of the crucible. The graphite sleeve will then be replaced and will serve as a getter for the strontium that has been directed through the new openings. With the addition of new orifices, if the cell pressure has been established kinetically, a reduction in pressure will be observed, whereas if the cell pressure corresponds to equilibrium conditions, the pressure will be maintained.

Knudsen Cell Mass Spectrometric Method. Studies of the vaporization of strontium from graphite using the Knudsen cell mass spectrometric method have continued. A different Knudsen cell with a tungsten liner was constructed to allow easy loading and unloading of the sample. The cell, which is made of tantalum, has a press-fitted cover. In previous experiments the cells had been welded shut, which led to difficulties in sample introduction and removal.

Two nearly identical experiments were conducted using the newly constructed cell. A sample of graphite was impregnated with strontium nitrate and then decomposed in a graphite crucible at about 1000 C for 1/2 hr in vacuo. The sample was then divided into four portions, of which two were used to determine the initial strontium concentration and the other two were used in successive vaporization studies. The plots of $\log P_{Sr}$ versus $\log C_{Sr}$ for these two experiments are essentially identical and are in fair agreement with the data presented in the previous quarterly report (GA-8530).

The heats of vaporization obtained during these two experiments show a much different dependence on the concentration than has been obtained previously, and they do not show the consistency that would be expected from "identical" samples. The difference between these and past experiments is probably due to the nature of the pretreatment. This has been previously noted for H_2 , O_2 , CO , and CO_2 chemisorption on a variety of metal oxides (Ref. 2). The difference between the two "identical" experiments may be due to the initial starting temperatures and/or the time-temperature profile of the experiments, since there appears to be a strong dependence of the heats of vaporization on sample treatment.

Further experiments on the effect of sample treatment and the various experimentally determined parameters are in progress.

Pseudoisopiestic Method. Studies of the vapor pressure of strontium sorbed on graphite using the pseudoisopiestic method have continued. Twenty sorption runs have been conducted at 1000°C using tantalum tubing liners to replace the molybdenum liners used in earlier runs. Preliminary runs using the tantalum liners indicated that the length of the runs should be at least 21 days to ensure equilibrium conditions in the system. Shorter runs yielded very erratic data, and no reliable estimate of the rate of sorption of strontium could be made. Consequently, the more recent runs have varied in length from 21 to 32 days, with the longer runs occurring in systems with strontium pressures of less than 10^{-8} atm.

The data from these runs, presented in Fig. 4.5, show a deviation from a Freundlich isotherm at strontium pressures above about 10^{-7} atm. This behavior (in which the curve bends over) may be caused by an approach of the strontium concentration to monolayer level or by beginning of the formation of strontium carbide. The behavior is not unexpected, however, and has been observed in earlier studies of the cesium-graphite system (Ref. 3) as the equilibrium cesium concentration approached the monolayer level.

It has been shown (Ref. 4) that the vapor pressure of SrC_2 at 1000°C is 3×10^{-6} atm, and that the pressure of barium over a substrate with $\text{C/Ba} = 2500$ is only a factor of four less than that over BaC_2 , a reduction which was attributed to diffusion effects. Assuming that SrC_2 behaves in the same manner, a substrate with $\text{C/Sr} = 2500$ (2.9 mg Sr/g C) would also be expected to yield a strontium pressure of about 3×10^{-6} atm. Thus, the agreement between these data and that of Flowers and Rauh (Ref. 4) is quite good. Since a sharp break in the isotherm as this limiting pressure is approached would not be expected, it is reasonable to assume that a slow transition would be observed with increasing concentration as a SrC_2 phase begins to form.

The slope of the isotherm at the lower pressures is very steep and therefore of questionable validity. The strontium loadings obtained at low pressures are high in comparison with data obtained using the mass spectrometric method. Since the strontium loadings obtained at these low pressures appear high, there is no question about insufficient time for transport of strontium to the specimens. One possible explanation for the high loadings, and the resultant steep slope, would be the presence of residual oxygen in the graphite. This would favor the formation of sorbed SrO , which should be relatively stable at 1000°C ; thus the measured concentrations would reflect the presence of the SrO in addition to the sorbed strontium. If this is the case, the quantity of SrO present in the graphite should be independent of strontium pressure.

Two experimental approaches are being investigated in an attempt to determine if the presence of SrO in the graphite is detrimental to the equilibrium sorption measurements. First, two runs are in progress at 1000°C using graphite that was outgassed in situ for 4 hr at 1150°C instead of at the normal outgassing temperature of 1050°C . The increase of 100°C should have some effect on reducing the amount of residual oxygen in the graphite. Second, two additional runs are in progress at 1000°C using specimens from earlier runs that were loaded with strontium to 0.441 and 0.313 mg Sr/g C. Since these specimens have been exposed to air for nearly two months, a large fraction of the sorbed strontium should have been converted to SrO . If sorption data on these four specimens are in reasonable agreement with previously obtained data in the 10^{-9} to 10^{-10} pressure range, this would indicate that the presence of oxygen in the graphite has no effect on equilibrium sorption measurements.

Cesium-Graphite Sorption Studies

Cesium sorption measurements have been completed on 9567 and RC-4 graphites at 900° to 1100°C using the pseudoisopiestic method described in an earlier report (Ref. 5). Table 4.1 gives the values of the constants (a,b,c,d) used

Fig. 4.5--Sorption of strontium on graphite at 1000°C

in the general equation for expressing the equilibrium pressure-composition-temperature data for these graphites,

$$\log P = \left[a + b \left(\frac{10^3}{T} \right) \right] \log C + \left[c + d \left(\frac{10^3}{T} \right) \right], \quad (5)$$

where P is in atm, C is in mg Cs/g C, and T is in °K.

Table 4.1 also includes values previously obtained for H-327, HLM-85, and TS-688 graphites. (Cesium concentrations in the equations for HLM-85 and TS-688 graphite were previously expressed as $\mu\text{moles Cs/m}^2$ graphite.) These results compare the cesium sorption characteristics of the various types of graphite.

Table 4.1
SUMMARY OF CESIUM-GRAPHITE SORPTION DATA

Graphite	a	b	c	d
HLM-85	-14.2	23.1	-5.64	4.40
TS-688	-13.2	22.5	0.05	4.11
H-327	-19.0	31.7	-2.24	0.0
9567	-19.0	33.0	-2.48	0.0
RC-4	-21.1	35.0	5.42	-12.0

These studies were conducted on samples of the various graphites using granules of about 2 to 3.3 mm. Cesium concentrations calculated from these data are estimated to be 25% higher than predicted loadings in bulk graphite.

Cesium Sorption Characteristics of Irradiated Graphite

Equilibrium cesium sorption measurements have been conducted on 16 specimens of graphite that had been irradiated in the G12 capsule to fast neutron exposures of from 2.0×10^{21} to 6.0×10^{21} nvt at temperatures ranging from 610° to 1130°C. The irradiation temperatures and fast-neutron exposures for the specimens examined in this study are shown in Table 4.2.

Sorption measurements were conducted using the pseudoisopiestic method (Ref. 5), and a common reference cesium pressure of $P_{\text{Cs}} = 1.0 \times 10^{-5}$ atm (Cs supply = 140°C) and a specimen temperature of 1000°C were selected. Three specimens of the irradiated graphite and one unirradiated specimen, to serve as a control sample, were used in each sorption run. Comparison of the cesium loading in the control samples among several runs showed an average deviation of about $\pm 2\%$. The length of each sorption run was six days to ensure equilibrium of the system. The results of these measurements are shown in Fig. 4.6, where the cesium loadings are plotted against the fast-neutron exposure ($E > 0.18$ Mev). Duplicate measurements were conducted on several of the specimens and are shown by connecting lines between the data points.

Fig. 4.6--Sorption of cesium on irradiated graphite at 1000°C; $P_{Cs} = 1 \times 10^{-5}$ atm

Table 4.2
DESCRIPTION OF GRAPHITE SPECIMENS IRRADIATED
IN THE G12 CAPSULE

Specimen No.	Irradiation Temp (°C)	Exposure E > 0.18 Mev (10 ²¹ nvt)
293	880	4.85
292	965	5.00
302	910	5.20
245	1105	5.60
278	1105	5.60
270	1130	5.85
239	1005	6.00
240	1005	5.95
276	1005	5.95
252	950	5.05
254	950	4.80
260	950	4.35
261	950	4.00
266	720	3.75
268	695	2.90
256	610	2.00

NOTE: The order of listing of the specimens roughly shows the temperature and flux profile in the capsule (top to bottom).

These data show a continuing increase in the cesium sorption capacity of the graphite with increasing exposure to 6×10^{21} nvt; however, no evidence of a plateau is indicated, suggesting that additional neutron exposure may result in a further increase in the sorption capacity. Specimen 239 (irradiated at 1005°C to 6.0×10^{21} nvt) shows an increase of a factor of 12.2 over the unirradiated materials.

The conditions of the capsule irradiation experiment were such that it is not possible to delineate between the effect of the irradiation temperature and the effect of the neutron dose on these observed increases in sorption capacity. It is apparent, however, that the specimens irradiated at 1105° and 1130°C show a marked reduction in their cesium sorption capacity, indicating a thermal effect. Because of the uncertainty in the measured irradiation temperatures, it is difficult to ascertain the temperature at which this reduction in loading begins to occur. The data indicate that this effect is probably small for specimens irradiated at temperatures up to 1000°C and becomes quite apparent at some temperature between 1000° and 1100°C.

To further investigate this possible annealing effect, three irradiated specimens, as well as a control specimen, were annealed in vacuo at 1100°C for 204 hr. The temperature was then lowered to 1000°C and the specimens

were exposed to cesium vapor ($P_{\text{Cs}} = 1.0 \times 10^{-5}$ atm) for a normal six-day sorption run. The results of this run are shown in Table 4.3.

Table 4.3

EFFECT OF ANNEALING AT 1100°C ON THE CESIUM SORPTION CAPACITY OF IRRADIATED GRAPHITE AT 1000°C , $P_{\text{Cs}} = 1.0 \times 10^{-5}$ ATM

Specimen No.	Irradiation Temp ($^{\circ}\text{C}$)	Exposure (10^{21} nvt)	Concentration (mg Cs/g C)		Change (%)
			Before Anneal	After Anneal	
278	1105	5.60	1.26	1.28	+1.6
276	1005	5.95	3.66	3.35	-8.5
260	950	4.35	2.29	1.92	-16.1
Control	---	---	0.320 ± 0.007	0.324	---

Examination of the results of this run indicate that the sorption sites for cesium were not annealed out of either the control specimen or the specimen irradiated at 1105°C , since the cesium loadings observed were within the limits of experimental error. However, the annealing effect is pronounced for the specimens irradiated at 1005° and 950°C , with the largest decrease occurring in the specimen irradiated at the lower temperature.

An attempt was made to obtain a cesium sorption isotherm at 1000°C using specimen 252 (irradiated at 950°C to 5.05×10^{21} nvt) in order to observe whether the slope of the isotherm differed from the slope measured with unirradiated graphite. No significant change in the slope of the isotherm could be detected over a cesium pressure range of 3×10^{-7} to 1×10^{-4} atm during this 17-day run. However, the isotherm appeared to be shifting slightly during this period; i.e., cesium loadings obtained during the early stages of the run could not be duplicated later. The concentration corresponding to a cesium pressure of 1×10^{-4} atm was reduced by 22% between the fourth and sixteenth day of the run. This reduction is compared to -16.1% of specimen 260 (Table 4.3) after about 8-1/2 days at 1100°C and six days at 1000°C .

It is believed that this apparent reduction was not due entirely to the removal of active sorption sites by the 1000°C anneal, but may be due in part to the movement of cesium in and out of the graphite as the cesium pressure, and thus the concentration, was raised and lowered during the run. It should also be mentioned that the data from the isotherm run are somewhat uncertain as a result of inaccuracies in the in situ monitoring of the Cs^{137} gamma activity because of the residual gamma activity of activation products in the graphite.

One additional sorption run was conducted to investigate the effect of particle size on the cesium sorption capacity of the irradiated graphite.

Earlier studies using unirradiated graphite specimens had indicated that the amount of cesium sorbed on a particular graphite is a function of the particle size of the specimen. For example, at a given temperature and cesium pressure the equilibrium cesium loading on a 3-mm-diameter particle was increased by approximately a factor of two by reducing the particle size to about 125 μ and by a factor of three by reduction to about 50 μ . Thus, it is of interest to determine whether the sorption capacity of irradiated graphite could be increased by reducing the particle size of the specimen.

Three specimens of the irradiated graphite and one control specimen were pulverized in an agate mortar to a particle size less than 150 μ . (No accurate measure of the range of particle size could be made since only 200 mg of sample was available.) Weighed portions, 75 to 100 mg, of each of the specimens were transferred to a stainless steel boat designed to accommodate four separate specimens. The boat was covered with a 25- μ stainless steel screen and fitted with a perforated lid to hold the screen in place. The boat was placed in the cesium sorption apparatus, and a normal sorption run at 1000°C with a cesium pressure of 1×10^{-5} atm was conducted.

The results of this run were quite unexpected. The control specimen and a specimen irradiated at 1105°C showed predictable behavior; i.e., the sorption capacity increased by 60% to 80%. Specimens irradiated at 610° and 1005°C showed decreases in cesium loading by 15% to 35%. This apparent reduction in sorption capacity of the specimens irradiated at the lower temperatures suggests that a large fraction of the additional sorption sites produced by the irradiation could be removed by the mechanical action of pulverizing the graphite. This observation needs to be confirmed.

A systematic study of the various parameters affecting the production and stability of sorption sites is necessary before more than general observations of this system can be made. Such a study would require irradiation of graphite specimens to various neutron exposures at a constant temperature and also at various temperatures to a constant exposure. Earlier studies using other grades of graphite irradiated to about 2.5×10^{21} nvt have shown that the increase in cesium sorption capacity as a function of irradiation varies with the graphite, thus introducing another variable for investigation.

A more detailed discussion of this investigation is presented in a recent topical report (Ref. 6).

Strontium Sorption Characteristics of Irradiated Graphite

A sorption run has been completed to examine the effect of irradiation on the strontium sorption characteristics of three of the irradiated specimens (261, 252, and 239) listed in Table 4.2. The pseudoisopiestic method was used. The run lasted 21 days and was conducted at 1000°C with a strontium pressure of 1.2×10^{-6} atm.

Figure 4.7 shows the measured strontium loadings plotted as a function of fast-neutron exposure. The shape of the curve differs considerably from that observed in the cesium sorption measurements. The largest increase observed in the strontium loading is a factor of 6.7, compared to a factor of

Fig. 4.7--Sorption of strontium on irradiated graphite at 1000°C; $P_{Sr} = 1.2 \times 10^{-6}$ atm

12.2 for cesium in a duplicate specimen. Since the irradiation temperatures of 950° to 1000°C approximate the conditions of this sorption run, it is not believed that the significantly lower sorption capacity is a result of the additional period of annealing, 21 days for strontium compared to six days for cesium.

FISSION-PRODUCT DIFFUSION STUDIES

Diffusion of Metallic Fission Products in Graphite

Experimental studies of the diffusion of fission-product metals in graphite have continued. Work is under way to study the diffusivity of strontium in graphite prepared in a manner to simulate the graphite that will exist in an HTGR reactor. A possible method of fabricating HTGR fuel elements involves carbonizing the fuel rods in place in the fuel elements at 900° to 1000°C. This treatment might alter the number of sorption sites in the graphite and thus change the diffusion behavior of metals in the graphite matrix. Therefore, experiments are being carried out to clarify this matter. Compacts are prepared by inserting green fuel rods (1/2-in. in diameter by 1/2-in. long) into graphite crucibles and annealing at 900°C. The fuel rods are then removed from the compacts.

Two diffusion anneal experiments were carried out at 1000°C using graphite crucibles prepared in this manner. One crucible was used without further preparation. The other was heated to 1800°C in vacuum for about 5 hr before the diffusion anneal. Prior to the diffusion anneal, a source of tagged strontium was introduced into each crucible. The samples were kept at 1000°C for 1 hr.

The results, although preliminary, are very interesting. They show a marked difference in the strontium uptake. The amount of source strontium diffused into the graphite was about 80% for the 1800°C vacuum-prepared sample and about 5% for the sample not treated in this manner, indicating that the latter sample had either a lower diffusion coefficient or lower solubility for strontium. This suggests that annealing the graphite with the green fuel rod in place might lead to a lower rate of transport for metals in graphite and thus might have a beneficial effect. More experiments are under way.

Transport of Strontium in Graphite

An experiment to measure the rate of permeation and diffusion of strontium through graphite is presently under way. The experimental procedure consists of annealing strontium-impregnated materials (tagged with Sr^{85}) in a graphite crucible and then (1) measuring the evaporation rate of strontium from the crucible and (2) determining strontium concentration profiles across the crucible wall. Knowing the evaporation rate (i.e., the flux) and the concentration profile, one can calculate an effective diffusion coefficient.

A schematic diagram of the apparatus is shown in Fig. 4.8. The dimensions of the graphite crucible simulate those of the average fuel hole (0.5-in. ID) and the graphite web thickness (0.18 in.) of a typical HTGR fuel element.

1. TANTALUM LINER
2. MULLITE HEATER TUBE
3. He PURGE CHANNEL
4. GRAPHITE BASE
5. GRAPHITE PEDESTAL
6. MULLITE STRONTIUM COLLECTOR TUBE
7. GRAPHITE CRUCIBLE
8. STRONTIUM SOURCE MATERIAL

SCALE 1:1

Fig. 4.8--Strontium permeation apparatus

Strontium evaporating from the graphite surface is collected by a mullite tube surrounding the test crucible. (Previous work at Gulf General Atomic has shown that hot mullite could be an effective collector for strontium vapor.) Strontium permeation (rate of evaporation) is measured by removing the collector tube at frequent intervals, measuring the Sr^{85} activity, and comparing the activity to that of known standards of identical geometry.

Concentration profiles are determined at the end of a particular experiment by machining increments from the crucible wall and radioassaying the machined dust collected from each increment.

Helium purified by passage through activated carbon at -196°C is purged through the furnace tube at $200\text{ cm}^3/\text{min}$. This slow helium purge ensures that the concentration of oxidizing impurities is minimized. Oxidizing impurities such as O_2 or CO could arise from either graphite outgassing or dissociation of oxygen from the ceramic furnace tube (with subsequent reaction with the graphite samples to form CO).

The strontium source was prepared by adding strontium nitrate solution (tagged with Sr^{85}) to charcoal matrix material similar to that used to bind fuel particles in HTGR fuel elements. The mixture was evaporated to dryness and then heated to about 1000°C in graphite to decompose the nitrate. The material was next transferred to a tantalum crucible and fired to about 1400°C for 3 hr to complete the conversion of SrO to a SrC_2 phase. The final strontium loading after these procedures was $50\text{ }\mu\text{g Sr/g charcoal}$. Each crucible contained 2.4 g of the source material, or $120\text{ }\mu\text{g strontium}$.

Two experiments are presently under way. Strontium permeation through graphite at 975°C has been measured for times up to 1350 hr. Strontium permeation rates of 0.5 to $3.6\text{ }\mu\text{g Sr/cm}^2\text{-hr}$ have been observed. Figure 4.9 shows the fraction of strontium lost from the crucibles versus time for both experiments. The apparent delay time for both runs is about 40 hr. Using the relation $D \approx X^2/6t$, where D = the strontium diffusion coefficient (cm^2/sec), X = the graphite thickness (cm), and t = delay time (sec), a diffusion coefficient of approximately $3 \times 10^{-7}\text{ cm}^2/\text{sec}$ was calculated.

Figure 4.10 shows the strontium concentration profile across the 0.18-in. crucible wall for experiments 13-1 (after 520 hr). It can be seen that no concentration gradient exists; thus, calculation of an effective diffusion coefficient is not permitted. The essentially flat profile may indicate that the hot mullite tube is an imperfect collector for strontium, perhaps because of saturation effects. A saturated collector surface would (1) result in a significant back pressure of strontium, (2) limit evaporation from the graphite surface, and (3) result in apparent strontium permeation rates that are too low.

A new experimental apparatus and procedure are presently being devised in which a cooled surface will be employed as the strontium collector.

Diffusion of Metallic Fission Products in Pyrolytic Carbon

Diffusion data for cesium, strontium, barium, and europium in pyrolytic carbon measured at Gulf General Atomic have been reviewed. The diffusion

Fig. 4.9--Permeation of strontium through graphite

Fig. 4.10--Strontium concentration profile in graphite (Exp 13-1)

coefficients for the different metals are given in Tables 4.4 through 4.7 and are plotted versus $1/T$ in Figs. 4.11 through 4.14.

Table 4.4
DIFFUSION OF CESIUM IN PYROLYTIC CARBON

Source Concentration (g Cs/g C)	Temp (°K)	Diffusion Coefficient (cm ² /sec)	Arrhenius Equation (cm ² /sec)	Source
1.0×10^{-7}	1273	5.8×10^{-14}	$D = 9.7 \times 10^{-7} \exp \left(- \frac{42,000}{RT} \right)$	CsCl
	1473	5.8×10^{-13}		
	1673	8.6×10^{-12}		
	1973	1.4×10^{-11}		
1.5×10^{-3}	1673	3.6×10^{-12}	$D = 1.2 \times 10^{-3} \exp \left(- \frac{57,000}{RT} \right)$	Cs ₂ O
	1973	8.2×10^{-11}		
1.2×10^{-3}	1323	2.9×10^{-13}		
	1473	3.8×10^{-12}		
	1573	5.9×10^{-11}		
	1673	1.6×10^{-11}		
	1738	1.2×10^{-10}		
	1973	4.3×10^{-10}		

Table 4.5
DIFFUSION OF STRONTIUM IN PYROLYTIC CARBON

Source Concentration (g Sr/g C)	Temp (°K)	Diffusion Coefficient (cm ² /sec)	Arrhenius Equation (cm ² /sec)	Source
1×10^{-4}		<u>Chemical Diffusion</u>	$D = 4.4 \times 10^{-2} \exp \left(- \frac{48,000}{RT} \right)$	SrCl ₂
	1373	8.0×10^{-10}		
	1473	3.7×10^{-9}		
	1573	1.0×10^{-8}		
	1673	2.6×10^{-8}		
	1773	4.4×10^{-8}		
2×10^{-3}		<u>Self-Diffusion</u>		SrCl ₂
	1273	8.5×10^{-11}		
	1373	1.5×10^{-9}		
	1573	7.8×10^{-9}		
	1773	4.4×10^{-8}		
	1973	3.5×10^{-7}		

Table 4.6
DIFFUSION OF BARIUM IN PYROLTYIC CARBON

Source Concentration (g Ba/g C)	Temp (°K)	Diffusion Coefficient (cm ² /sec)	Arrhenius Equation (cm ² /sec)	Source
1x10 ⁻⁵	1273	<u>Chemical Diffusion</u> 1.5x10 ⁻¹⁰	$D=2.3 \times 10^{-4} \exp \left(-\frac{35,500}{RT} \right)$	BaCl ₂
	1273	2.3x10 ⁻¹⁰		
	1523	1.6x10 ⁻⁹		
	1673	3.3x10 ⁻⁹		
	1823	1.4x10 ⁻⁸		
	1973	2.9x10 ⁻⁸		
	1973	2.7x10 ⁻⁸		
1x10 ⁻⁵		<u>Self-Diffusion</u>	$D=1 \times 10^{-1} \exp \left(-\frac{56,000}{RT} \right)$	BaCl ₂
	1273	2.7x10 ⁻¹¹		
	1473	4.2x10 ⁻¹⁰		
	1673	4.3x10 ⁻⁹		
	1873	2.7x10 ⁻⁸		
1x10 ⁻²		<u>Chemical Diffusion</u>	Including all four points, $D=1.1 \times 10^6 \exp \left(-\frac{84,700}{RT} \right)$. Without point 1073°C, $D=41.4 \exp \left(-\frac{57,300}{RT} \right)$.	BaCl ₂
	1073	1.6x10 ⁻¹²		
	1173	5.7x10 ⁻¹⁰		
	1273	1.1x10 ⁻⁸		
1x10 ⁻²	1473	9.9x10 ⁻⁸		
		<u>Self-Diffusion</u>		
1x10 ⁻²	1273	1.2x10 ⁻⁸		BaCl ₂

Table 4.7
DIFFUSION OF EUROPIUM IN PYROLYTIC CARBON

Source Concentration (g Eu/g C)	Temp (°K)	Diffusion Coefficient (cm ² /sec)	Arrhenius Equation (cm ² /sec)	Source
1.9x10 ⁻³		<u>Chemical Diffusion</u>	$D = 1.64 \exp \left(- \frac{49,200}{RT} \right)$	EuCl ₃ + NH ₃ → Eu ₂ O ₃
	1073	1.6x10 ⁻¹⁰		
	1273	5.4x10 ⁻⁹		
	1373	4.4x10 ⁻⁸		
	1373	1.2x10 ⁻⁸		
	1473	6.6x10 ⁻⁸		
	1473	1.1x10 ⁻⁷		
1.9x10 ⁻³		<u>Self-Diffusion</u>	$D = 0.73 \exp \left(- \frac{45,900}{RT} \right)$	EuCl ₃ + NH ₃ → Eu ₂ O ₃
	1273	6.7x10 ⁻⁹		
	1373	6.7x10 ⁻⁸		
	1373	3.8x10 ⁻⁸		
	1473	7.5x10 ⁻⁸		
6.0x10 ⁻⁷	1523	<u>Chemical Diffusion</u>		EuCl ₃ + NH ₃ → Eu ₂ O ₃
		6.0x10 ⁻⁹		
6.0x10 ⁻⁷	1273	<u>Self-Diffusion</u>		
		2.1x10 ⁻⁹		

It is difficult to correlate the diffusion behavior of the different elements in graphite. Self-diffusion coefficients and chemical diffusion coefficients seem to vary little in the case of europium and strontium but significantly for barium. The concentration dependence of the diffusion coefficients is pronounced for barium where there is a large difference in the concentration (approximately three orders of magnitude). A change of one order of magnitude in concentration does not affect the diffusion coefficient for strontium. The few points for europium and cesium do not allow a comparison at the different concentration levels.

A correlation seems to exist between the diffusion coefficients for the different metals and their atomic radii. It has been found that diffusion coefficients show a linear relation when plotted versus the reciprocal atomic radii of the respective elements. Figure 4.15 is a plot of this correlation,

Fig. 4.11--Diffusion of cesium in pyrolytic carbon

Fig. 4.12--Diffusion of strontium in pyrolytic carbon

Fig. 4.13--Diffusion of barium in pyrolytic carbon

Fig. 4.14--Diffusion of europium in pyrolytic carbon

Fig. 4.15--Comparison of calculated and experimental diffusion coefficients for transport in isotropic pyrocarbon

which allows the prediction of diffusion coefficients for different metals in isotropic PyC.

A comparison of the diffusion coefficients for strontium and barium at 1400°C with values calculated from release measurements shows good agreement in the barium data but a difference of one order of magnitude in the strontium data.

It is of significance that some of the measurements were carried out using metal chloride sources, since a change in diffusion behavior for the different sources would be expected. It has been demonstrated that the use of Cs_2O as a source leads to higher diffusion coefficients for the diffusion of cesium in pyrolytic carbon than does the use of CsCl as a source. Similar effects for strontium and barium are expected.

Since all experiments were carried out using either metal chloride or oxide sources, it is not clear how well the data are applicable to reactor calculations. In the reactor one would expect to have the metals or metal carbides as the diffusion source.

Diffusion of Metallic Fission Products in Silicon Carbide

Studies of the diffusion of metals in SiC have continued. The experimental procedure is similar to that used in the studies of diffusion of metals in PyC and has been described earlier (Ref. 5). In this case, however, diamond-impregnated abrasive paper was used for lapping the wafers.

Diffusion coefficients for strontium and cesium in SiC have been determined. The measurements for strontium were carried out using a constant chemical potential source of 1×10^{-3} g Sr/g C. The diffusion coefficients are given in Table 4.8 and plotted versus $1/T$ in Fig. 4.16. From the temperature dependence of the diffusion coefficients, a diffusion equation was calculated:

$$D_{\text{Sr}} = 0.25 \exp \left(- \frac{68,700}{RT} \right), \text{ cm}^2/\text{sec} \quad . \quad (6)$$

A comparison of the migration of strontium in PyC and in SiC shows that the diffusion coefficients for strontium in SiC are only about two orders of magnitude lower than in PyC. Therefore, the effectiveness of SiC as a diffusion barrier for strontium is probably the result of relatively low solubility of strontium in SiC rather than the result of a very low diffusion coefficient for strontium in SiC.

Experiments on the diffusion of cesium in SiC show a very wide scatter in the data. Therefore, it seems unwarranted to calculate an Arrhenius equation from the given points. The diffusion coefficient data for cesium are reported in Table 4.9 to show lower and upper limits.

Fig. 4.16--Diffusion of strontium in silicon carbide

Table 4.8
DIFFUSION COEFFICIENTS OF STRONTIUM IN SILICON CARBIDE

Temp (°K)	Source Concentration (g Sr/g C)	D_{Sr} (cm ² /sec)
1273	1.0×10^{-3}	2.0×10^{-13}
1473	1.0×10^{-3}	5.0×10^{-11}
1686	1.0×10^{-3}	2.5×10^{-10}
1963	1.0×10^{-3}	4.0×10^{-9}

Table 4.9
DIFFUSION COEFFICIENTS OF CESIUM IN SILICON CARBIDE

Temp (°K)	Source Concentration (g Cs/g C)	D_{Cs} (cm ² /sec)
1323	7.0×10^{-4}	3.0×10^{-14}
1573	1.2×10^{-3}	4.0×10^{-12}
1738	9.2×10^{-4}	3.1×10^{-10}
1973	1.2×10^{-3}	2.4×10^{-10}

Mixed Fission-product Deposition Studies

Previous studies (Refs. 7,8) of the deposition of fission products (cesium, strontium, and iodine) on metal surfaces have indicated that they may be retained to a high degree on metal components of the coolant circuit of an HTGR reactor. In the case of cesium and strontium deposition, the earlier studies were conducted primarily using Type 304 stainless steel at temperatures greater than 900°F and with metal partial pressures greater than 10^{-8} atm. Iodine plateout studies have been conducted using low chrome alloy, mild steel, and Incoloy 800 at temperatures less than 900°F with I_2 source pressures of 10^{-9} to 10^{-5} atm. In each of these earlier experiments, however, only the deposition of a single species was studied, and thus no information was obtained regarding the level of deposition of these fission products when combined at low partial pressures. Consequently, a long-term mixed fission-product deposition experiment was conducted to investigate the deposition of cesium, strontium, and iodine on low chrome alloy over a temperature range of 300° to 500°C (570° to 930°F).

The apparatus used in this experiment was a closed loop, in which cesium, strontium, and I_2 were simultaneously carried by three separate helium streams to a low-chrome-alloy tubing specimen (1/2 in. in diameter, 15 in. long),

where the vapors were allowed to mix and pass through the tubing to a charcoal trap. The inlet helium was initially purified by passing through a zirconium getter, a cesium getter, and finally a dry ice-acetone trap (to remove residual cesium) before it was divided into three streams, one to each of the source tubes. The source tubes were maintained at temperatures that would yield partial pressures of about 10^{-9} atm for each of the elements (i.e., strontium about 300°C , cesium about 25°C , and I_2 about -78°C). The connecting lines between the source tubes and the specimen tube were designed to minimize sorption of the elements before they reached the specimen tube. Stainless steel tubing was used for the strontium and cesium, but Pyrex tubing was necessary for iodine to prevent reaction and the formation of iron iodide. Only the cesium was tagged, because of the short half life of iodine nuclides and the difficulty in tagging strontium metal. The 1% Cr - 1/4% Mo tubing was initially cleaned in a 20% Vertan 690 solution for 2 hr at 95°C , rinsed with water, and finally rinsed with acetone.

After assembly, the system was evacuated and cesium metal was distilled into the cesium getter tube. Cesium metal, tagged with Cs^{137} , and iodine were distilled into the respective supply tubes and trapped in liquid nitrogen. The vacuum was broken to helium and a slow purge (about $10\text{ cm}^3/\text{min}$) was maintained while heating the system to the desired temperatures. The iodine supply tube was placed in a dry ice-acetone bath (-78°C) and helium was recirculated through the system at $300\text{ cm}^3/\text{min}$ while maintaining a positive pressure of 12 cm Hg. (Because of the uniform diameter of the connecting tubing in the apparatus, it was assumed that the helium stream divided uniformly and a flow of $100\text{ cm}^3/\text{min}$ passed through each of the three fission-product supply tubes.)

The experiment was terminated after 3000 hr operation. The 15-in.-long specimen tube was cut into 1-in.-long sections, and each section was acid-etched to remove the deposition material. The etching solutions were counted to determine the Cs^{137} activity and were submitted for analyses of strontium and iodine by activation. Other sections of the system were etched and analyzed to obtain a material balance for calculating the average partial pressures of the cesium, strontium, and iodine during the run.

Figure 4.17 shows the deposition of these three species as a function of temperature and distance along the specimen tube. Appreciable fractions of the cesium and strontium were found in the stainless steel mixing chamber, where the three gas streams were combined prior to actual entry of the specimen tube. Presumably this was the result of either the formation of SrI_2 and CsI or the retention of these metals by the oxide film on the metal surface.

Average partial pressures of the three elements as determined by the amount of each species found in the system were: cesium = 8.1×10^{-12} atm; strontium = 1.5×10^{-9} atm; and I_2 = 7.5×10^{-8} atm. These pressures were based on the amount of each entering the mixing chamber. The calculated strontium pressure agrees very well with the predicted pressure (1.0×10^{-9} atm) based on the temperature of the strontium source. The calculated cesium pressure is about a factor of 100 too low, presumably because of excessive deposition of cesium on the walls of the Pyrex source tube. The calculated

iodine pressure is about a factor of 75 higher than expected, apparently due to fluctuations in the level of the dry ice-acetone bath over the 3000-hr experiment.

Examination of the plateout profiles of each of the three elements shows:

1. Cesium deposition was uniformly low (less than 10^{-3} $\mu\text{g Cs/cm}^2$) along the specimen tube in the range 483° to 312°C . Only 38% of the cesium was found in this area. The remainder passed through the system and condensed in cooler areas. No cesium was detected downstream of the rear connection to the specimen tube (see Fig. 4.17).
2. The deposition of strontium was initially high in the front section of the specimen tube, decreasing uniformly over the next 8 in., and finally reaching an approximate constant level at temperatures below about 430°C . No distinct effect of temperature on the deposition is discernible. Below about 300°C , 21% of the strontium was found in the cooler regions.
3. Like strontium, iodine deposition occurred on the first metal surfaces contacted at temperatures above 450°C , decreased slightly until the metal temperature dropped below 300°C , and finally occurred in heavy amounts in the cooler region of the system. Seventy-seven percent of the iodine entering the system was found in the temperature range 100° to 200°C . Only 0.7% was found at temperatures above 312°C . Essentially no iodine was found downstream of the specimen tube. This deposition profile indicates that all of the iodine reacted with the metal surface to form FeI_2 , which was subsequently evaporated from the surface and transported downstream to condense in an area where the partial pressure of FeI_2 was extremely low ($P_{\text{FeI}_2} \approx 3 \times 10^{-13}$ atm at 200°C). This observation agrees with earlier studies of the deposition of iodine on metal surfaces (Ref. 8).

Although the calculated partial pressures of the cesium, strontium, and iodine differed considerably in this experiment, the results show that the deposition of cesium and strontium on low-chrome alloy is relatively independent of the temperature of the metal, with the heaviest strontium deposition occurring on the first surface contacted. There is no way to verify whether these two species were transported as iodides, but examination of the first 3 in. of the specimen tube shows a deficiency in the amount of iodine necessary for SrI_2 to be the deposited species. In all other areas there is a sufficient amount of iodine deposited to combine with the cesium and strontium.

The observed iodine deposition of $1.1 \mu\text{g I/cm}^2$ at 400°C (750°F) is about a factor of six lower than previously measured levels on low-chrome alloy. This observation may be due to differences in surface condition of the two specimens used, the presence of strontium and cesium in this experiment, or the added length of the current experiment (3000 hr) as compared to the earlier study (366 hr).

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Task V
RECYCLE FUEL STUDIES

CENTRAL HTGR FUEL REPROCESSING PLANT STUDIES

The base case study (designated Case III A) on reprocessing HTGR fuel in a central plant considered a hexagonal-block HTGR fuel element containing silicon carbide-coated uranium oxide fissile particles and pyrocarbon-coated thorium oxide fertile particles (Ref. 1)*. This study assumes that the fissile particles are packaged for disposal rather than processed for recovery of the residual uranium. The conceptual central plant is sized to serve a 15,000 Mw(e) HTGR economy. Based on the Case III A plant, studies were undertaken to derive the incremental costs for the recovery of the fissile particle uranium and the costs of reprocessing HTGR fuels having silicon carbide coatings on both the fissile and fertile fuel particles.

In these new studies, (Case III A3), a burn-leach head-end process is also used, but additional process steps are included to penetrate the silicon carbide coating and/or to prepare the fissile particles for solvent extraction. The fissile particles from fuels with pyrocarbon-coated fertile particles are processed, and the initial head-end process steps of fuel block burning, leaching, and screening are the same as in the Case III A study. The additional process operations are performed on the fissile particle fraction from the screening step. A roll mill grinder is used to fracture the silicon carbide coatings, and the ground particles are then fed to a small fluidized bed burner where the buffer carbon coatings are oxidized to CO_2 and the fissile particle kernels to U_3O_8 . The burner ash is then leached with nitric acid to dissolve the U_3O_8 to form the solvent extraction feed solution. After rinsing and drying, the leached ash is screened to separate the burner bed material from the silicon carbide hulls. The bed material is recycled to the burner, and the hulls are packaged for disposal as high-level radioactive waste. Decontamination of the fissile particle uranium is achieved by two cycles of solvent extraction followed by a silica gel tail-end treatment. The radioactive waste solutions arising from the solvent extraction process are combined with those from the fertile particle processing for solidification and disposal.

In the study of reprocessing HTGR fuel elements with silicon carbide coatings on both fuel particle types, the same head-end processing steps described above are used but the sequence differs. The burner ash from the first (fuel block) burner is separated by tabling and screening into three fractions, fertile particles, fissile particles, and burner bed material. The fertile particles are ground, burned, and leached yielding a solvent extraction feed solution. The fissile particles are packaged for disposal as a high-level radioactive waste (Case III B) or processed for uranium recovery as described above (Case III B1).

*References will be listed at the end of each section.

The Case III A3 study report has been completed and is being prepared for publication (Ref. 2). Both the Case III B and the Case III B1 studies are contained in a report currently in preparation.

Estimated costs associated with the various study alternatives are given in Table 5.1. The incremental cost of processing the fissile particles is about \$0.50/g of contained uranium for both the III A3 and III B1 cases.

Table 5.1
ESTIMATED REPROCESSING COSTS

	Case Number			
	III A	III A3	III B	III B1
Capital cost, millions of dollars	30.8	33.7	32.2	34.7
Annual reprocessing cost, millions of dollars per year	10.3	11.4	11.1	12.0
Reprocessing charge dollars per kg (Th + U)	62	69	67	73

Fuel Refabrication Studies

Utilization of uranium bred from thorium in the HTGR system requires reprocessing to recover U^{233} and U^{235} mixtures from spent fuel and refabrication of the recovered uranium into fuel elements to complete the fuel cycle. The refabrication step is complicated by the fact that daughters of U^{232} found in the bred U^{233} are radioactive to a degree requiring special handling techniques.

The current study of refabrication of HTGR fuels examines one plan for solving this problem. The study refabrication plant has been defined as one capable of refabricating HTGR fuel elements containing U^{233} , U^{235} , and Th at a rate of 500 kg/day (about 50 fuel elements/day). This volume is sufficient to support a 15,000 Mw(e) HTGR economy. In the study, U^{233} fuel particles are prepared by a Sol-Gel process employing amine extraction of a reduced uranyl nitrate solution to form the sol. Sol drops are then formed and the water extracted from them to form a gel microsphere. The microspheres are fired, carbon coated, formed into fuel rods, and loaded into fuel elements.

Since the scope of this study does not include preparation of U^{235} and thorium particles, it is assumed these components are purchased in the fabricated form from an outside source. Partial segregation of U^{233} and U^{235} in the core has been assumed; that is, some elements contain U^{233} and U^{235} and some only U^{235} . Two separate assembly lines for fuel elements are employed. Segregating will permit a smaller facility for remote assembly than if all elements contained a mixture of U^{233} and U^{235} . This will permit some saving in shipping costs in that only about 60% of plant production will need to be

shipped in shielded shipping casks. The remaining fuel elements, containing only U^{235} , may be shipped without shielding.

A block flow diagram, material balances, and equipment criteria drawings have been completed and equipment space layout studies have begun. Development of manpower and material costs has been initiated. About 360 men will be required to operate the facility on a 24-hr/day basis. Metallurgical and chemical laboratory requirements are being estimated. Contaminated laundry services are assumed to be supplied by outside contractors, and costs have been secured for such services.

On-line computer control of refabrication facilities is being studied. Informal estimates indicate capital expenditures at about \$500,000 plus \$50,000 to \$100,000 to write the software, and about \$20,000 to \$30,000 per year maintenance expense. About five operators are required to run the computer equipment on a 24-hr/day basis.

Survey of Mechanical Considerations for Removing Fuel Particles from HTGR Spent Fuel

A survey of mechanical considerations for removing fuel particles from spent HTGR fuel blocks for further processing was completed. A possible arrangement for a gaseous debonding machine was developed. This machine uses a stream of hot gas to selectively burn away the carbon binder of a fuel element thereby releasing undamaged particles from the graphite block for further processing. This method appears to be quite complicated and expensive for use in a commercial reprocessing plant as a head-end step, but may have merit for use at a reactor site to permit separation of graphite block from fuel. This may result in reduced spent fuel shipping and storage costs, and may be especially desirable for those reactors discharging fuel before HTGR fuel reprocessing services are available.

Ocean Shipping of Spent HTGR Fuels

In preparation for future studies on spent HTGR fuel shipping, data on water shipping are being assembled from the literature and by a survey of shipping concerns.

Criticality

A survey has been initiated to define the criticality problems for fuel recycling. The criticality parameters for design of the reprocessing burner and the shipping cask are being studied first. A literature survey to determine the progress in these particular areas is under way.

RETENTION OF URANIUM IN ALUMINA FLUIDIZED BEDS

The retention of uranium and thorium in the Al_2O_3 used as a fluidizing medium in the head-end oxidation step for HTGR fuels was mentioned in the previous quarterly report, GA-8530, and similar results have been reported by other workers (Ref. 3).

Studies are now under way to determine whether saturation of uranium and thorium occurs in the aluminum oxide fluidizing material used in the oxidation. If the alumina is to be reused for several fluidizing cycles, it is necessary to know if the uranium retention on the alumina reaches a saturation value, or if it continues to build up in such a manner as to cause criticality problems or unacceptable losses. Recent studies have used (Th,U)O₂ particles with a Th:U ratio of 10:1. The alumina has been recycled five times with the retentions noted in Table 5.2. A marked decrease in the pickup is noted by the fifth recycle. However, since the uranium concentration in these particles is low, an attempt will be made to obtain better analytical precision by using pyrolytic carbon-coated UO₂ particles.

Table 5.2
RETENTION OF URANIUM AND THORIUM
BY ALUMINUM OXIDE

Time (hr)	Uranium (%)	Thorium (%)
9	0.57	0.031
15	0.62	0.038
23	1.07	0.084
29	1.24	0.120
34	1.25	0.127

HEAD-END REPROCESSING

Gaseous Debonding Process

One of the most promising methods for recovering coated particles from a bonded bed in a graphite fuel element is a gaseous process employing O₂, air, or steam. Selective oxidation of the carbonaceous bonding material allows the coated particles to be separated from the fuel element without damage to the particle coatings.

In this process the gas is introduced into a bonded bed by means of a follower nozzle or into a general reaction chamber where no attempt to localize the gas flow is made. The sample, positioned open-end down, is heated by an external heater so that the particles fall into a cooled area as they are loosened. The nozzle, which is made of Inconel 600, follows the receding surface of the bonded bed during debonding by means of an air piston drive. The tip of the follower nozzle is held 3/8 in. from the bed surface by three vertical standoffs. One of the standoffs is hollow and contains a Chromel-Alumel thermocouple that is used to record sample temperature. The susceptor is also instrumented with a Chromel-Alumel thermocouple, which is used for furnace control. Completion of an induction-heated debonder for 30-in.-long samples was reported last quarter.

The thermocouple in the follower nozzle was used with an empty sample tube to determine the temperature profile of the assembly. A difference of about 30°C along the 30-in. sample tube was observed at a control setting of 850°C (see Fig. 5.1).

Four 30-in.-long fuel rods were inserted into graphite tubes in the cured stage. The rods contained BISO-coated ThC_2 in only the fertile size. The matrix of two of the rods contained R72S phenolic resin with 30 wt-% GP-38 graphite flour. The matrix of the other two rods contained 5023-SP phenolic resin mixed with a small amount of furfuryl alcohol/maleic anhydride and 30 wt-% GP-38. After end caps were bonded on the samples, they were carbonized to 900°C. The end caps were drilled out and the samples were subjected to a variety of debonding conditions. The gap between the sample tube and the furnace susceptor was purged with 10 l/min of nitrogen. The resulting debonding rates are summarized in Table 5.3.

It was observed that coated particle breakage occurred more frequently as the probe approached the end of the tube. This was probably due to a longer exposure of the particles to the hot excess O_2 or air as they fell from the bed surface to the bottom of the sample tube. Samples with an R72S matrix debonded more rapidly than those with a 5023-SP matrix. This is in accordance with earlier results from 1-in.-long samples (Ref. 4). Due to the time lag between controller and probe thermocouples, adjusting air or O_2 flow rate was a more sensitive and controllable method of adjusting probe temperature than adjusting controller set point. In an attempt to improve the debonding rate, the probe was vibrated with a pneumatic vibrator. When vibration was reduced to the point where broken particles were not observed, the debonding rate was about twice that for the case with no vibration.

Several graphite fuel blocks designed to hold twelve 6-in.-long fuel rods were prepared. The blocks, hexagonal in cross section, are 10-in. long with a large, central coolant hole and a ring of six smaller coolant holes. The coolant holes were drilled through the entire length of the blocks. These blocks, which are similar to the fuel elements used in the Fort St. Vrain proof test elements, will be used in an evaluation of debonding by crushing.

Three blocks were loaded with fuel rods, and the elements were carbonized to 900°C. In two of the elements, each web between fuel hole and coolant hole was broached part way through by a drift studded with a pointed tool, as shown in Fig. 5.2. The broaching was done to cause preferential cracking of the webs during subsequent crushing, thus exposing the entire length of the fuel rod. Exposing the fuel rods could lead either to separation of loose fuel rods from the graphite followed by debonding by mechanical or gaseous oxidation processes, or, when fuel remains lodged in large graphite pieces, to further separation treatment such as tumbling or selective oxidation of matrix carbon.

One of the elements was inserted into a thin aluminum sleeve to contain it, and was then crushed in a universal testing machine. A compressive load to 6500 lb was applied across flats of the hexagonal block at which load the element cracked. The element was turned in 60° increments so that cracking

7

Fig. 5.1--Single-rod debonding apparatus. Thermocouple A remained at $845^{\circ}\text{C} \pm 2^{\circ}$ throughout the scan. Thermocouple B (probe):

First 10 in.	830°C
Second 10 in.	850°C
Third 10 in.	860°C

Table 5.3
RESULTS OF GASEOUS DEBONDING OF FOUR 30-IN. FUEL RODS

Rod Type	Probe Temp (°C)	Gas		Calculated Debonding Rate ^a		Comments
		Type	Flow Rate (l/min)	Time to Debond 1 in. of Rod Length (min)	Corresponding Time to Debond 30 in. of Rod Length (min)	
5023-SP	660	Air	3	145	4350	Clean particles
5023-SP	750	Air	1 to 3	64	1920	Clean particles
5023-SP	540	O ₂	1/2	58	1740	Broken particles above 540°C
5023-SP	540	O ₂	1	74	2220	Some residue
5023-SP	540	O ₂	1	145	4350	Coating damage more severe at end of 30-in. run
5023-SP	625	Air	4	97	2910	New sample
5023-SP	650	Air	5	51.5	1545	Clean particles
5023-SP	650	Air	5	55	1650	Clean particles
R72S	600	Air	5	45	1350	New sample; entire sample debonded with these conditions; clean particles
R72S	625	O ₂	3	39	1170	New sample
R72S	875	Air	2 to 4	19	570	Temperature was controlled by adjusting gas flow
R72S	850	Air	2 to 4	10	300	Probe vibrated
R72S	825	Air	2	13	390	Probe vibrated
R72S	825	Air	3 to 4	10	300	Probe vibrated

^a Actual length of debonded rod varied for each set of conditions.

3-1/2 in.

Fig. 5.2--Top view of a loaded and broached fuel element

Fig. 5.3--Fuel element disassembled by broaching and crushing

was achieved by compressing across each of three sets of flats. The last compressive failure occurred at a load of 2100 lb. The block was still in one piece after the sleeve was removed since only a portion of the webs had failed. Another drift was used to complete disassembly of the element but the drift was studded with a round pin instead of a pointed tool. The pin diameter was slightly larger than the broached grooves so that as the pin was forced down the groove, the groove was opened, thus cracking the web along its entire length. The disassembled element is shown in Fig. 5.3. Approximately half of the 12 fuel rods were separated from the block by this method, and almost all of the remaining half were exposed. No hydrolyzed or broken fuel particles were observed. It is anticipated that further developments will simplify the process and improve the separation of the fuel rods from the graphite.

Thermogravimetric Analysis Studies

Thermogravimetric analysis (TGA) is being used to characterize the oxidation of the bonding matrix, fuel element graphite, and pyrocarbon in air and O_2 . A TGA experiment consists of measuring sample weight versus temperature at a constant rate of temperature rise ($2.5^\circ C/min$ in most of these studies). Weight is measured by an automatic electrobalance. Temperature measurements are made using a Chromel-Alumel thermocouple located in the gas stream adjacent to the sample pan. Weight versus temperature is continuously recorded during a run on an X-Y recorder. The sample is held in a shallow platinum pan at the center of a Nichrome wire-wound tube furnace. The samples, in the form of large granules, and the balance are contained in a quartz envelope. Gas flow was $57\text{ cm}^3/min$ in all tests. During this reporting period, only oxygen was used.

Studies of matrix carbon containing graphite and charcoal filler were reported in the previous quarterly report (GA-8530). It was concluded that in the temperature range of about 450° to $600^\circ C$ the oxidation rate of matrix carbon without prior heat treatment above the carbonization temperature of $900^\circ C$ is reasonably high and significantly higher than the corresponding rates for LTI and HTI pyrocarbons. The thermograms for matrix samples that were heat treated to $1300^\circ C$ or above, however, indicated that the distinct and reasonably rapid debonding action that has been observed in gaseous debonding tests may be somewhat degraded by the effects of heat aging.

This quarter efforts were concentrated on studying (1) unfilled matrix carbon in order to separate the effects of the filler and (2) fuel element graphite in order to compare oxidation of the fuel element graphite with that of matrix carbon.

Unfilled matrix carbon was prepared by carbonizing 5023-SP phenolic resin to $900^\circ C$. Samples of carbon were then outgassed for 24 hr at 1300° , 1600° , and $2000^\circ C$. The thermograms for these samples (typically approximately 100 mg) are shown in Fig. 5.4. As noted last quarter, the heat treatment even at $1300^\circ C$ causes a considerable delay in oxidation, and a compound curve is observed for samples that are not outgassed.

Several TGA runs were made for graphite. Some of the thermograms are shown in Fig. 5.5. These curves are similar to those for pyrocarbon reported in the last quarterly report. When Figs. 5.4 and 5.5 are compared, it may be noted that outgassed matrix carbon does not appear to oxidize rapidly relative to graphite.

An experiment was performed to evaluate the effects of an accelerated carbonization cycle on the thermogram. Grade 5023-SP phenolic resin was carbonized using a 14-hr cycle instead of the normal 37-hr cycle. The two carbonization cycles are compared in Table 5.4. The thermograms for the 5023-SP for the accelerated cycle are shown in Fig. 5.6. The oxidation rate is seen to increase discontinuously at 460°C. This is characteristic of sample ignition and was absent when the normal cycle was used.

Several TGA runs with 10-mg samples of matrix carbon and graphite were made to evaluate the effects of sample size and heating rate. No significant difference was observed between thermograms for the 10-mg samples and the 100-mg samples. Reducing the rate of temperature rise during the TGA run to 0.96°C/min resulted in an increased negative slope, but the incremental ratio of weight loss to time remained essentially unchanged.

An experiment was performed to compare the oxidation of graphite and pyrolytic SiC since reference fuel particle coatings now contain SiC. A graphite disk with an SiC coating deposited in a fluidized bed was cut in half parallel to the flats of the disk. The resulting wafer was about 200 μ thick and 3/8 in. in diameter. It was placed into the sample pan with the graphite surface facing upward to allow a better exposure of the graphite to the O₂ stream. A TGA run was made using a 0.96°C/min heating rate. The results are shown in Fig. 5.7. From these data it is apparent that the disk contained 71 wt-% SiC and 29 wt-% graphite. The graphite was apparently burned away at 700°C since sample weight was constant above 700°C. The constant weight also indicates that oxidation of the SiC is undetectable (less than 0.5 mg SiO₂). This result lends support to debonding schemes that involve combustion of the outer pyrocarbon coating and retention of an integral SiC coating to allow size separation of fissile and fertile material.

METHODS FOR DESTROYING COATINGS ON FUEL PARTICLES

Studies have continued on the use of dissociated gases (created by allowing the tank gas to flow through an RF discharge) for the destruction of pyrolytic carbon coatings on fuel particles. As discussed in the previous quarterly report, the pyrolytic carbon coatings were successfully removed using partially dissociated oxygen. The rate of 1% to 2%/min compared favorably with coating removal in molecular O₂ at about 1100°C. As expected, SiC coatings subjected to partially dissociated oxygen rapidly formed SiO₂ surface coatings, and the reaction subsided.

It was found that SiC powder reacts readily with partially dissociated chlorine. On the other hand, partially dissociated chlorine was found to have no appreciable effect on the SiC coatings.

Fig. 5.4--Thermograms of carbonized phenolic resin with various heat treatments prior to TGA

Fig. 5.5--Thermograms of graphite

Fig. 5.6--Thermograms for phenolic resin with an accelerated carbonization cycle (see Table 5.4)

Fig. 5.7--Thermogram of a pyrolytic SiC-coated graphite disk

Table 5.4
NORMAL AND ACCELERATED CARBONIZATION CYCLES

Sample Temp (°C)	Rate of Temperature Rise (°C/hr)	
	Normal Cycle (37 hr total)	Accelerated Cycle (14 hr total)
150-250	33.3	100
250-500	10.0	30
500-900	50.0	150
900	(a)	(b)

^aHeld for 1 hr at 900°C.

^bHeld for 2 hr at 900°C.

STABILITY OF IRRADIATED (Th,U)O₂ - ThO₂ FUEL KERNELS UNDER OXIDIZING CONDITIONS

Studies of the stability of irradiated BISO-coated (Th,U)O₂ and ThO₂ Sol-Gel kernels under oxidizing conditions are under way. The particle samples used in this study are from lot GA-323 (portion containing (Th,U)O₂ kernels) and lot OR-205-OR-206 ThO₂ - (Th,U)O₂. Both sets of particles were irradiated at ORNL. The burnups were 1.3% FIMA for GA-323 (irradiated in loop 1-15) and 2.7% FIMA for OR-205-OR-206 (irradiated in loop 1-14). Experiments were conducted at 800° to 850°C using an O₂ flow of about 2 l/min in an alumina fluidized bed. The runs were continued for 24-hr periods. Rapid coating disintegration was observed, but the kernels of the microspheres were stable and no breakage or cleavage was noted. Additional irradiated particles have been received from ORNL and will be tested soon.

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Task VI
PHYSICS METHODS

KINETICS

Status of Kinetics Codes at Gulf General Atomic

There are a variety of point and one-dimensional kinetics codes available with different heat-transfer treatments. These codes and their kinetics and heat-transfer characteristics are compared in Table 6.1. All codes, with the exception of WIGL2, were developed at Gulf General Atomic. The comparison shows that GAKIT (Ref. 1), a combination of the one-dimensional multigroup kinetics code GAKIN (Ref. 2) and a quasi-two-dimensional heat-transfer code RZTEMP, is in several respects the most advanced of the codes listed. Some of its most remarkable features are:

1. A one-dimensional kinetics calculation.
2. A general multigroup neutron energy treatment.
3. An arbitrary scattering matrix capability.
4. A stable and swift time integration procedure.
5. A two-dimensional heat transfer option, allowing heterogeneous structure with coolant channels.

Significant improvements were recently made in the kinetics-thermodynamic iteration strategy. The code has also been used in additional test calculations, most recently to solve a rod withdrawal accident modeled by a 100-sec ramp change of reactivity.

A new strategy for the time integration in GAKIT has been developed resulting in a computer running time reduction of about a factor of three. The strategy requires a heat-transfer calculation after each kinetics time step and a constant time step for appropriate time zones. Although the temperature calculation requires slightly more time than the neutron calculation for one time step, a net saving in computer running time is realized for reasons described below.

The time integration method utilized in GAKIT requires the fulfillment of the following inequality for each time step:

$$\left| e^{\omega \Delta t_j} - \frac{\phi_j}{\phi_{j-1}} \right| < \epsilon \quad , \quad (1)$$

where ϵ is an input number and ω is a space-dependent instantaneous period. By using the ω of the last time step as an initial guess, a predictor-corrector procedure is applied to find an acceptable ω for the current time step.

Table 6.1
GULF GENERAL ATOMIC REACTOR DYNAMICS CODES

	BLOOST-5 (Ref. 3)	BLOOST-6 (Ref. 4)	GAPOTKIN (Ref. 5)	WIGL2 (Ref. 6)	GAKIN (Ref. 2)	GAKIT (Ref. 1)
<u>KINETICS PORTION OF CODE</u>						
Dimension for kinetics model	0-D	0-D	0-D	1-D	1-D	1-D
Maximum number of neutron energy groups	1	1	1	2	10	10
Maximum number of delayed neutron groups	6	6	6	6	6	6
Scattering matrix	-	-	-	Downscattering only	Arbitrary	Arbitrary
Geometry for kinetics model	-	-	-	Slab, cylinder, sphere	Slab, cylinder, sphere	Slab, cylinder, sphere
Boundary conditions	-	-	-	$\phi=0$ or $\nabla\phi=0$	$\phi=0$ or $\nabla\phi=0$	$\phi=0$ or $\nabla\phi=0$
Time step	Variable	Variable	Variable	Constant in each time zone	Variable	Variable
Time dependence of cross sections or reactivity due to external change	Table	Table	Linear or quadratic	Linear	Linear or quadratic	Linear or quadratic
Numerical method	Runge-Kutta	Runge-Kutta	Semi-implicit	Implicit	Semi-implicit	Semi-implicit
Stability	Stable for small time-steps	Stable for small time-steps	Stable	Stable	Stable	Stable
Xenon feedback	No	No	No	Yes	Yes	Yes
<u>HEAT TRANSFER PORTION OF CODE</u>						
Temperature feedback	Yes	Yes	Yes	Yes	No	Yes
Dimension of heat transfer model	2-D	2-D and 1-D	0-D	1-D	-	2-D
Geometry for heat transfer model	(r,z)	(r,z) and sphere	-	Plane, cylinder, sphere	-	(r,z)
Limitations	-	-	-	Nonboiling heat transfer	-	No axial conductivity
Numerical method	Difference equations, Peaceman-Rachford, alternating direction	Difference equations, Peaceman-Rachford, alternating direction	-	Analytic	-	Difference equations, for r-dependent difference equations, Gauss-elimination
Physical problem solved	General, but coolant channels only at inner and outer boundaries	Same as BLOOST-5 and heat transfer for spherical coated fuel particles	-	Nonboiling heat transfer. Axial or radial type problems	-	General, but coolant channels only at inner and outer boundaries
Typical running times for HTGR problems	<1 min	5-10 min	<1 min	5-10 min	5 min	5-20 min
Steady-state calculation	Yes	Yes	No	No	Yes	Yes

For example, ϕ_j is calculated by using the (space-dependent) initial guess for ω , and then improved space-dependent ω values are calculated from

$$\omega = \frac{1}{\Delta t_j} \ln \frac{\phi_j}{\phi_{j-1}} \quad (2)$$

If a heat-transfer calculation were done, for example, after every fifth kinetics time step, unsatisfactory convergence would be observed and the time step would have to be reduced. Then, because of prompt-jump-like conditions, the new value of ω required by Eq. (1) would have to be substantially larger, so that again the procedure would converge poorly. However, by performing a heat-transfer calculation after each kinetics time step and by keeping the time step constant in appropriate time zones, the first time step estimated is usually acceptable. If this strategy is used in GAKIT, large time steps (0.05 to 0.1 sec) compared to the prompt neutron lifetime (4×10^{-4} sec) can be utilized. The accuracy is satisfactory and no instabilities have been observed. Data on these points are presented in the next section.

A rod withdrawal accident has been studied in a two-group reactor model. The rod withdrawal time was assumed to be 100 sec and the total amount of reactivity removed was approximately \$2.00. The problem was treated with six delayed-neutron groups in cylindrical geometry (outer radius 360 cm) with a core and a reflector region. The core was divided into three channels. The problem parameters and the geometrical configurations used in the kinetics and heat-transfer parts are given in Tables 6.2 and 6.3 and Figs. 6.1 and 6.2, respectively. Initial conditions for the fluid flow and heat-transfer calculation are shown on Table 6.4. The conditions are typical of an HTGR-type element.

The calculation covered a total time of 250 sec. In Fig. 6.3 the time-dependent power densities for the three channels are plotted (the rod withdrawn from the first channel). In Fig. 6.4 the time-dependent averaged fuel and moderator temperatures are plotted for each channel. Finally, Fig. 6.5 shows the thermal flux shape for $t = 0, 100$, and 200 sec, respectively.

The results shown in Figs. 6.3, 6.4, and 6.5 are very interesting. Channel 1 shows the largest increase in power density and also the largest asymptotic value. The averaged fuel and moderator temperatures always stay relatively close together. Channel 1 has the largest temperature increase from 600° to about 1300°F after 250 sec.

The computer running times for different time step sizes are listed below for a 250-sec transient:

Time step (sec)	0.025	0.05	0.1	0.2
Running time (min)	33	18	10	6

The GAKIT code will be useful for many types of reactor dynamics studies. It should be emphasized, however, that modeling problems (for example, in the case of rod withdrawal accidents) are sometimes very serious. The development of a two-dimensional kinetics code is highly desirable.

Table 6.2
PARAMETERS USED IN ROD-WITHDRAWAL ACCIDENT TEST PROBLEM

	Group	Channel No. 1 ^a	Channel No. 2 ^a	Channel No. 3 ^a	Reflector ^a
Average neutron speed, cm/sec	1	4.56x10 ⁸	4.56x10 ⁸	4.56x10 ⁸	4.56x10 ⁸
	2	5.75x10 ⁵	5.75x10 ⁵	5.75x10 ⁵	5.75x10 ⁵
Neutrons per fission	1	2.5555	2.5555	2.5555	0.0
	2	2.5555	2.5555	2.5555	0.0
Fission yield	1	1.0	1.0	1.0	0.0
	2	0.0	0.0	0.0	0.0
Capture cross section	1	1.9x10 ⁻³	1.1639x10 ⁻³	1.1586x10 ⁻³	4.9708x10 ⁻⁶
	2	3.7594x10 ⁻³	2.1219x10 ⁻³	2.1514x10 ⁻³	1.5616x10 ⁻⁴
Fission cross section	1	1.8688x10 ⁻⁴	1.8632x10 ⁻⁴	1.8646x10 ⁻⁴	0.0
	2	2.8715x10 ⁻³	2.7374x10 ⁻³	2.7699x10 ⁻³	0.0
Diffusion coefficient	1	1.4157	1.416	1.4159	1.0706
	2	1.0531	1.0572	1.0559	0.86124
Transfer cross section	1→2	2.2408x10 ⁻³	2.22759x10 ⁻³	2.2308x10 ⁻³	4.8845x10 ⁻³
Average fuel temp, °C		594.4	757.45	715.24	---
Average moderator temp, °C		588.45	746.46	705.55	---

NOTE: Cross sections apply to the initial steady-state conditions.

^a See Figs. 6.1 and 6.2 for a geometrical definition of these channels.

$$\Delta \rho (\text{ROD}) = \$2.00$$

ROD WITHDRAWAL TIME: 100 SEC

Fig. 6.1--Kinetics model: rod withdrawal accident test problem

Fig. 6.2--Fluid flow and heat-transfer model: rod withdrawal accident test problem

Fig. 6.3--Power density for each channel of a 100-sec rod removal problem (GAKIT results)

Fig. 6.4--Average temperatures for each channel of a 100-sec rod removal problem (GAKIT results)

Fig. 6.5--Thermal flux distribution for a 100-sec rod removal problem (GAKIT results)

Table 6.3

DELAYED NEUTRON DATA: ROD WITHDRAWAL ACCIDENT TEST PROBLEM

I	Fractional Yield from Delayed Group I into Fission Group G		Neutron Yield for Each Delayed Group (β)
	<u>Group 1</u>	<u>Group 2</u>	
1	0.01251	0	2.22×10^{-4}
2	0.03155	0	1.115×10^{-3}
3	0.11938	0	9.775×10^{-4}
4	0.30632	0	1.667×10^{-3}
5	1.13500	0	4.46×10^{-4}
6	2.87620	0	1.831×10^{-4}
Total			4.6106×10^{-3}

The sensitivity of the time-dependent fluxes to time step size was investigated in connection with the code improvements noted in the previous sections. The results are shown on Table 6.5. A thermal-hydraulic calculation for each kinetics time step permits time step sizes of about 0.1 sec to be used.

CROSS-SECTION EVALUATIONS

Scattering Kernels for Graphite

New scattering kernels have been generated for graphite at 600°, 900°, 1050°, 1200°, and 1500°K. The scattering law, $S(\alpha, \beta)$, for these kernels was obtained using the GASKET (Ref. 7) code. The scattering properties of the carbon atoms were considered to be characteristic of harmonic anisotropic vibrations with a continuous frequency spectrum, the particular frequency spectrum being taken from Ref. 7. The coherent elastic scattering cross sections used in these kernels were obtained using the HEXSCAT (Ref. 8) code.

Doppler Broadened Cross Sections

Doppler broadened neutron cross sections for Rh^{103} , Sm^{149} , Sm^{151} , Eu^{153} , Pu^{239} , Pu^{240} , and Pu^{241} have been generated at various temperatures between 300° and 1200°K. These data sets have been prepared in a format suitable for the Gulf General Atomic thermal neutron cross-section library and they will be used to investigate the Doppler effects of these materials on reactivity coefficients in HTGR reactors.

The 1.056 ev Resonance in Pu^{240}

The very strong 1.056 ev resonance in Pu^{240} complicates the analysis of systems containing significant quantities of Pu^{240} . One of the problems, especially in graphite systems, concerns the importance of upscattering into or

Table 6.4

INITIAL CONDITIONS: ROD WITHDRAWAL ACCIDENT TEST PROBLEM

	Bottom Reflector	Top Reflector	Moderator Region	Fueled Region
Density, lb/ft ³	106	106	106	128
Specific heat constant ^a				
A	0.54	0.54	0.54	0.54
B	-0.000743	-0.000743	-0.000743	-0.000743
C	150	150	150	150
Thermal conductivity, Btu/hr-ft-°F	1.6	1.6	1.6	1.6

NOTE:

Initial inlet temperature, °F 756.0

Initial average flow rate,
lb/hr-element 127.95Initial inlet heat-transfer
coefficient, Btu/hr-ft²-°F 275.0

Specific heat, Btu/lb-°F 1.24

^a For a given temperature (T) the specific heat (C_p) is calculated from the specific heat constants as:

$$C_p = A \left[1 - e^{B(T-C)} \right], \quad \left[\text{Btu/lb-°F} \right]$$

above this resonance. In a very simple study, upscattering at temperatures of 300° and 800°K was studied using thermal scattering kernels generated by the GASKET and HEXSCAT codes. For 1.0 ev incident energy neutrons at 300°K, it was found that about 5% of the total scattering cross section consisted of upscattering events, while at an 800°K moderator temperature it was about 15%. It was concluded that upscattering into the 1.056 ev resonance of Pu²⁴⁰ may indeed be a significant factor.

Cross-section Evaluation Working Group Activities

During the current reporting period contributions to the Cross-section Evaluation Working Group (CSEWG) continued. Under a data-testing program designed to review and evaluate the data sets on the ENDF/B file, comments by CSEWG members on data sets were collected, and those comments relevant to errors and deficiencies in the existing data sets were forwarded to the National Neutron Cross Section Center at Brookhaven National Laboratory.

Neutron reaction Q values that are contained in the existing ENDF/B data sets were reviewed. Several errors were found, many due to a misunderstanding of the recommended procedures for use in specifying Q values, while other errors

Table 6.5

SENSITIVITY OF TIME-DEPENDENT FLUXES TO TIME STEP SIZE:
ROD WITHDRAWAL ACCIDENT TEST PROBLEM

Time Interval (sec)	$\Delta t = 0.05$			$\Delta t = 0.1$			$\Delta t = 0.2$		
	Channel			Channel			Channel		
	1	2	3	1	2	3	1	2	3
0-50	0.39	0.39	0.39	1.16	1.21	1.22	2.9	2.9	3.0
50-100	0.35	0.35	0.35	1.6	1.72	1.73	3.9	4.0	4.0
100-150	2.60	2.46	1.80	10.2	9.2	8.6	8.3	8.3	8.3
150-200	0.61	0.61	0.61	3.1	3.4	3.6	3.9	4.0	4.0

NOTE: Percent difference in the channel averaged flux from case with $\Delta t = 0.025$ sec.

were due to poor information or typographical errors. A summary of this review has been prepared and includes new recommended Q values for those data sets that were in error. This summary will be sent to the National Neutron Cross Section Center so that the existing data sets can be revised.

To assist the National Neutron Cross Section Center in developing a revised system for storage and retrieval of experimentally measured neutron cross sections, a comprehensive review was made of the SCISRS-II proposal. Suggestions relevant to modifications and expansions of the proposed system were summarized and forwarded to Brookhaven National Laboratory.

FLUX SPECTRUM CODE DEVELOPMENT

Since the documentation of GGC-3 was completed, some code modifications have been made and some new options have been added. This newer version is known as GGC-4. Another version, which is on the same level as GGC-4 but which has the capability of performing a doubly heterogeneous resonance calculation (using GAROL), is called GGC-5. The additional options, which are now available in the newer GGC versions, are summarized below. These have been described in prior quarterly reports.

1. Negative Buckling. The transport equation in both the FAST and THERMAL sections can now be solved for a system with either a positive, zero, or negative buckling. This buckling (a single input parameter) is used to describe the spatial dependence of the angular neutron flux.
2. Resonance Treatment. In addition to the existing resonance treatment (GANIT), a second resonance treatment is now available. A new link (GAROL) has been added to the code, which permits a resonance calculation in a unit cell composed of two regions (which may have grain structure) taking into account resonance overlap.

3. Plot Routines. A general purpose plot routine has been adopted to plot selected sets of GGC data. This routine is external, and is not yet permanently incorporated into the GGC package.
4. Resonance Integrals. In the resolved resonance region of the FAST section, fine group capture cross sections and effective capture integrals are now calculated and printed.
5. Convergence Acceleration. Proper normalization, and a better first-flux guess have been introduced into the method of solving the B_1 transport equation in the THERMAL section. This change improves the convergence of the flux and current expansions.
6. Definitions for the Microscopic Transport Cross Section. An identical set of definitions for a microscopic transport cross section are now available in both the FAST and THERMAL sections.
7. Auxiliary Codes. A new code has been written to handle and edit existing results tapes.

A major undertaking to rewrite GGC-5 in the form of a single code covering the entire fast and thermal energy range is planned. At the same time, programs will be written to prepare fine-group cross sections for the code directly from ENDF/B data files. The new program will carry out a GAROL-type (P-0 two-region, 8000-energy-point) resonance calculation over the entire energy range in which there are resolved resonances. In the thermal energy range, no upscattering of neutrons through resonances will be permitted at first, but provisions will be made to take this effect into account at a later stage. Cell-averaged capture cross sections obtained in the resonance treatment will be used as part of the input to the spectrum calculation. For the spectrum calculation, an arbitrary energy grid will be allowed. The number of fine groups in the grid will be increased to 250 (100 fast and 150 thermal) and an energy-dependent buckling (by broad group) will be permitted in solving the B_1 spectrum equations. A straightforward solution will be obtained in the energy range where there is no upscattering, and an iterative method will be used in the energy range where upscattering exists. The resultant fine-group flux for the entire fast and thermal energy range will be used to average microscopic cross sections over a given broad-group structure. At the same time, the broad-group cross sections will also be punched according to the standard diffusion or transport formats, and thus simplify the amount of work which is currently necessary in the COMBO section of GGC. The fact that fast and thermal energy ranges will be part of a single energy grid will remove many of the difficulties which exist in the present version of GGC. For example, a mismatch at the energy boundary between fast and thermal ranges (due to discontinuities in the flux and current) will no longer occur.

Also, the problem of computing downscattering sources in the fast section for use in the thermal section (and vice versa) will be eliminated entirely. At the same time the programs will become easier to use because the separate inputs and data tapes for the various sections of GGC will not be required.

With the addition of GAROL (Ref. 9) to GGC (Refs. 10, 11, and 12) as an option at this time, a second resonance treatment is available to the user. The usual GAM treatment, as embodied in the subroutine GANIT (Ref. 12) and GAROL, both solve the P-0 equation in the resonance region utilizing basic

resonance data. The data for GANIT is stored on the GGC FAST data tape, while a special data tape must be prepared on GAROL. The GANIT routine treats each resonance separately, setting up a fine energy mesh (of up to 500 points) around the center of the resonance. GAROL, on the other hand, treats all resonances simultaneously by covering the entire resolved resonance region with a single fine grid (up to 7800 energy points). Thus, the effect of resonance overlap is taken into account.

The geometry in either GANIT or GAROL can be homogeneous, slab, cylindrical, or spherical. If the system is heterogeneous, the P-0 equation (with isotropic downscattering only) is solved for a unit cell. This cell consists of two regions, a central or fuel region which usually contains the resonant absorber, and an outer region which usually contains only moderating materials. The flux is assumed to be flat inside each region; the geometric effect enters the calculation only through a neutron escape probability from one region into the other.

In GANIT, two moderators may be admixed with the absorber in the central region. No specification of materials is given for the outer region. It is always assumed that the outer region is large (in terms of mean free paths) and that there are no absorptions in this region; thus, the flux solution of the P-0 equation in this region is always $1/E$. Optionally, various approximations can be introduced in the solution of the P-0 equation in the central region, e.g., the narrow resonance, infinite mass, or explicit integral formulations. In GAROL, the P-0 equation is actually solved in two regions. Up to 10 resonance absorbers or moderators can be placed in either one of the two regions. The full integral equation is then solved without further approximations.

In the most straightforward applications of both kinds of resonance treatments it is assumed that materials in each region are homogeneously distributed and that fuel rod interaction may be taken into account by using Dancoff factors or tables of generalized escape probabilities.

Based on the resonance flux, effective capture integrals are calculated from

$$I_{\text{eff},g} = \int_{E_{g+1}}^{E_g} \sigma_c(E) \phi(E) dE \quad , \quad (3)$$

where σ_c is the microscopic capture cross section of the absorber, ϕ is the resonance flux, and E_g and E_{g+1} are energies defining the limits of the g -th energy group. The flux $\phi(E)$ is normalized to $1/E$ above each resonance in GANIT but only above the highest resonance in GAROL. Thus, recovery of the flux between resonances is not assumed in GAROL. To compare effective capture integrals calculated with the two kinds of resonance treatments, typical calculations on an HTGR-type lattice were run. A Dancoff factor of 0.47 was assumed, applicable to an array of 0.5-in.-diam fuel rods in a hexagonal array with a pitch of about 1.0 in. Table 6.6 shows the composition of the unit cell, and Table 6.7 the results for I_{eff} .

Table 6.6
COMPOSITION OF TYPICAL HOMOGENIZED HTGR
LATTICE UNIT CELL

Material	Nuclear Densities	
	Central Region	Outer Region
C	6.72×10^{-2}	6.14×10^{-2}
Th ²³²	1.85×10^{-3}	---
U ²³⁵	4.97×10^{-5}	---

Table 6.7
EFFECTIVE CAPTURE INTEGRALS IN TYPICAL
HOMOGENIZED HTGR LATTICE

Case No.	Resonance Treatment	Neutron Source	Buckling	I_{eff} (barns)
1	GANIT	U ²³⁵ fission spectrum	0.0001	26.28
2	GANIT	Unit source in broad group 63	0.0001	26.28
3	GAROL	U ²³⁵ fission spectrum	0.0001	26.10
4	GAROL	U ²³⁵ fission spectrum	0.0	26.10

The effective capture integral shown in Table 6.7 is calculated from

$$I_{\text{eff}} = \sum_{g=1}^{99} I_{\text{eff},g} \quad , \quad (4)$$

where the 99 resonance groups correspond to the 99 fine groups for which information is stored on the GGC FAST data tape. The different resonance treatments lead to very small changes in I_{eff} , the GAROL result being about 0.7% smaller than the GANIT result. This difference can be attributed to the resonance overlap effect in GAROL. While the difference in the total I_{eff} is small, the difference in any particular fine group may become quite large. For example, I_{eff} for fine groups 83 and 84, which contain the large Th^{232} doublet, is 7.2% smaller in GAROL than in GANIT.

It should be noted that the fine-group cross sections developed by the resonance subroutines for subsequent use in the calculation of spectra and broad-group cross sections are determined differently in GAROL and GANIT. In GAROL,

$$\sigma_g = \frac{I_g}{\phi_g} \quad , \quad (5)$$

where

$$\phi_g = \int_{E_{g+1}}^{E_g} \phi(E) dE \quad . \quad (6)$$

In GANIT, $\phi(E)$ is available only around a single resonance, that is, in the energy interval $E_0 - \Delta$ to $E_0 + \Delta$, where E_0 is the resonance energy, and Δ is an energy width determined by the cutoff energy, E_c , of the particular resonance. In contrast with GAROL, $\phi(E)$ is not available as a continuous function in the g -th group, because each resonance in that group is treated separately. The capture integral for the i -th hyperfine group is calculated from

$$I_i = \int_{E_i}^{E_{i+1}} \sigma_c(E) \phi(E) dE \quad , \quad (7)$$

and the g -th group capture integral is calculated from

$$I_g = \sum_i I_i \quad , \quad (8)$$

where i is summed over all hyperfine groups inside the g -th group. Since $\phi(E)$ is not known everywhere in the g -th group, it is impossible to evaluate ϕ_g . Assuming, instead, that $\phi(E) = 1/E$, ϕ_g is defined as

$$\phi_g = \int_{E_g}^{E_g+1} \frac{dE}{E} = \Delta U_g, \quad (9)$$

where ΔU_g is the lethargy width of the g -th group. Thus, the capture cross section is obtained from

$$\sigma_g = \frac{I_g}{\Delta U_g}. \quad (10)$$

As a result, σ_g (GANIT) tends to be smaller than σ_g (GAROL) since ΔU_g , that is, ϕ_g (GANIT) is larger than ϕ_g (GAROL). The significance of this is discussed more fully below.

The comparisons discussed above assume a homogeneous mixture of materials in each region. However, the typical HTGR fuel element has grain structure. An HTGR fuel element is composed of an array of cylindrical fuel rods, and each rod is composed of grains of uranium and thorium. The capability of handling grain structure has been built into GAROL, and there are two methods for simulating grain structure in GANIT. These three grain approaches are described below.

The grain treatment in GAROL is applicable to situations in which the ratio of the average flux in the grain to the average flux in the region immediately surrounding it (i.e., the remainder of the central region or fuel cylinder) can be approximated by the escape probability from a single grain. The grains can then be homogenized within the fuel cylinder by multiplying the energy-dependent cross section by the energy-dependent flux ratio and a regular resonance calculation performed.

If the scattering cross section is zero within the grain, then the escape probability (P_O) is a function only of the mean chord length in the particle (ℓ_O) and the absorption cross section, i.e.,

$$P_O = P_O(\Sigma_a^{(o)}, \ell_O) \quad (\text{Ref. 13}) \quad (11)$$

When scattering is possible within the grain (Ref. 14), however,

$$P_O = \frac{P_O(\Sigma_t^{(o)}, \ell_O)}{1 - \frac{\Sigma_s^{(o)}}{\Sigma_t^{(o)}} (1 - P_O(\Sigma_t^{(o)}, \ell_O))} \quad (12)$$

This grain homogenization approximation was shown by Hurwitz and Zweifel (Ref. 15) to be accurate for cases where the grain volume was a small fraction of the fuel region volume. Doub and Randall (Ref. 16) showed the approximation to be reasonably accurate for grain volume fractions in the range of 10% in a much more elaborate analysis.

For typical HTGR applications, the grain volume fraction is of the order of 5% to 10%; hence, the GAROL treatment is expected to be satisfactory. However, the range of applicability of the GAROL grain approach remains to be shown.

Two approximations are available within GANIT for calculating the effect of grains on the resolved resonance integral. To understand these approximations, reference must be made to the equations solved by GANIT in the resolved resonance region:

$$\phi_o(\sigma_{to} + \sigma_m) = (1 - P_o^*) \frac{1}{\alpha_o} \int_E^{E/1-\alpha_o} \phi_o(E') \sigma_{so}(E') \frac{dE'}{E'} + \frac{P_o^* \sigma_{to} + \sigma_m}{E} \quad (13)$$

The cross sections are units of $\text{cm}^{-1}/\text{absorber atom}$ (e.g., Th^{232}). If the flux in the grain is desired, then

σ_{to} = the total cross section of an absorber atom,

σ_m = the scattering cross section of the moderator atoms inside the grain,

P_o^* = the generalized escape probability from the grain, and

α_o = maximum fractional decrease in energy.

It has been assumed that the flux outside the grain is $1/E$, and that the narrow resonance approximation has been applied to the moderating collisions within the grain. The former assumption is basic to GANIT but the latter is made here only for convenience. The generalized grain escape probability is given by

$$P_o^* = P_o \frac{1 - C_o}{(1 - C_o) + \ell_o \sigma_{to} N_o P_o C_o} \quad (14)$$

where P_o = the escape probability from an isolated grain, and C_o = the Dancoff factor applicable to the grains. Nordheim has shown (Ref. 17) that, for an array of randomly oriented grains,

$$C_o = \frac{1}{1 + \ell_o \sigma_m' N_o} \quad (15)$$

where N_o is the absorber number density in the grain and σ_m' is moderator scattering cross section per absorber atom in the homogenized fuel cylinder.

One grain treatment possible with GANIT, in which the flux in the grain is computed, consists of replacing σ_m' in the expression for C_0 by $(\sigma_m' + \sigma_e')$, where

$$\begin{aligned}\sigma_e' &= \text{the escape cross section from the fuel cylinder per (homogenized) absorber atom} \\ &= \frac{(1 - C')}{\ell' N_O F_O} \quad ,\end{aligned}$$

C' = the (macroscopic) Dancoff factor applicable to the array of fuel cylinders, and

F_O = the volume fraction of grains in the fuel cylinder.

The term $\sigma_m' + \sigma_e'$ is the total cross section for "nongrain" events.[†] The calculational procedure is to:

1. Use the spherical geometry option in GANIT to represent the grain.
2. Supply a Dancoff factor as input computed with $\sigma_m' + \sigma_e'$ in place of σ_m' .
3. Specify the grain absorber density for the absorber density used in resonance calculation.

A second method for handling grains in GANIT involves approximating the single-grain escape probability in Eq. (14) by the rational approximation:

$$P_O = \frac{1}{1 + \ell_O N_O} \quad . \quad (16)$$

When this is done, the generalized escape probability becomes

$$P_O^* = \frac{\sigma^*}{\sigma_{to} + \sigma^*} \quad , \quad (17)$$

[†]The rationale for this formulation of C_0 becomes a little clearer if an escape cross section for the grains is defined (Ref. 17) by

$$\sigma_e^g = \frac{1 - C_0}{\ell_O N_O} \quad .$$

The utilization of the modified expression for C_0 gives

$$\sigma_e^g = \frac{(\sigma_m' + \sigma_e')}{[1 + \ell_O (\sigma_m' + \sigma_e') N_O]} \quad .$$

As $\ell_O \rightarrow 0$, i.e., in the limit of a fine dispersion,

$$\sigma_e^g \rightarrow \sigma_m' + \sigma_e' \quad ,$$

the correct homogeneous limit.

where

$$\sigma^* = \frac{\sigma_e^g(\sigma_m' + \sigma_e')}{\sigma_e^g + \sigma_m' + \sigma_e'} \quad (18)$$

In this case, $\sigma_e^g = 1/\lambda_0 N_0$. When this expression for P_0^* is inserted in the equation for the flux in the grain, and if σ_m is set equal to zero[†], the resultant expression for the resonance flux is:

$$\phi_0(\sigma_{t0} + \sigma^*) = \frac{1}{\alpha_0} \int_E^{E/1-\alpha_0} \sigma_{s0}(E') \phi_0(E') \frac{dE'}{E'} + \frac{\sigma^*}{E} \quad (19)$$

This is, however, exactly the equation which is applicable to a homogeneous region in which the scattering cross section per absorber atom is σ^* . In this case, the asymptotic option in GANIT for the admixed "moderator" must be exercised. Equations (18) and (19) are identical to those derived in a slightly different manner by Nordheim (Ref. 17) and Lewis and Connolly (Ref. 18). They expressed the generalized escape probability by:

$$P_0^* = P_0 \left[P' + (1 - P') \frac{1 - C_0}{(1 - C_0) + C_0 \lambda_0 \Sigma_t^{(0)} P_0} \right], \quad (20)$$

where P' equals the escape probability from the (macroscopic) array of fuel cylinders and contains, in general, the Dancoff factor, C' . The first factor in Eq. (20) is the escape probability from a single grain. The first term in the brackets is the escape probability from the array of fuel regions. The second term is the probability that if a neutron does not escape from the fuel region that it will, nevertheless, collide with a moderator atom. If the rational approximation is made for P_0 and P' and if Eq. (15) is used for C_0 , then Eqs. (17) and (18) result.

In summary, the second procedure for using GANIT for taking into account the effect of grains on the resonance integral is to:

1. Select the homogeneous option in GANIT.
2. Select the asymptotic approximation for the admixed moderator.
3. Supply σ^* as the cross section per absorber atom for the admixed moderator.

(Note that to the extent that Dancoff factors are required they are included in σ^* .)

[†]For HTGR grains, σ_m is due to the carbon in the carbide fuels, e.g., ThC_2 , and its value is typically about 10. Hence, ignoring the effect of this carbon leads to only a small error.

It is clear that GANIT method 1 has fewer approximations than GANIT method 2 for treating grains. Both GANIT methods are less accurate than the GAROL grain treatment for small grain volume fractions. The above three methods for including grains in resonance calculations have been numerically studied for the lattice characterized by the data in Table 6.6. In these comparisons the outer region is composed entirely of carbon, as before, but the fuel in the central region is in the form of grains of U^{235} and Th^{232} randomly distributed in a graphite matrix. The respective densities are shown in Table 6.8.

Table 6.8
COMPOSITION OF TYPICAL HTGR LATTICE UNIT CELL - GRAIN STRUCTURE

Material	Central Region (Fuel Cylinder)		Outer Region
	Grain	Matrix Region	Homogenized
C	0.0	7.384×10^{-2}	6.140×10^{-2}
Th^{232}	2.056×10^{-2}	0.0	0.0
U^{235}	5.522×10^{-4}	0.0	0.0

NOTE:

Grain diameter 400 μ
 Volume fraction of grains
 in fuel cylinder 0.09
 Fuel cylinder, radius 0.635 cm
 Dancoff factor of fuel
 lattice, C' 0.47

The results of the grain calculations are shown on Table 6.9, and the nongrain (homogenized) results are repeated to facilitate comparisons. It is clear that all three grain treatments go to about the right limit, $\pm 0.3\%$, for small grains. Both GAROL and GANIT method 1 predict a 4% to 5% reduction in the resonance integral for the resolved region as a result of Th^{232} lumping in 400- μ -diameter grains. GANIT method 2, the least accurate of the methods, predicts a 10% effect.

The effective capture integrals shown in Tables 6.7 and 6.9 were obtained in a resonance calculation prior to the spectrum calculation. The resonance calculation prepares a set of 99 capture cross sections to be used in a B1, B2, or B3 spectrum calculation in which broad-group cross sections for a few-group diffusion theory or transport theory calculations are determined. The I_{eff} at the end of the spectrum calculation is always smaller than that computed after the resonance calculation, but it is possible to recalculate it for the resolved region at the end of the spectrum calculation. The difference is caused by several factors; the spectrum calculation is performed with more materials, using a higher-order B_N equation, and takes leakage into account. Also, the particular definition of σ_c (fine group) discussed earlier

Table 6.9
EFFECTIVE RESOLVED REGION CAPTURE INTEGRALS IN TYPICAL
HTGR LATTICE - GRAIN STRUCTURE

Case No.	Resonance Treatment	Grain Diameter (μ)	Grain Dancoff Factor (C_0)	σ^*	I_{eff}
1	GANIT	Homogeneous		---	26.28
5	GANIT, Method 1	400	0.819	---	24.95
6	GANIT, Method 1	12	0.99346	---	26.34
7	GANIT, Method 2	400	---	328	23.77
8	GANIT, Method 2	2	---	400	26.10
3	GAROL	Homogeneous		---	26.10
9	GAROL	400	---	---	25.07

Table 6.10
A COMPARISON OF I_{EFF} IN THE RESOLVED REGION BEFORE AND AFTER THE SPECTRUM CALCULATION

Case No.	Resonance Treatment	Grain Size (μ)	Buckling	Source	I_{eff}	
					After Resonance Calculation	After Spectrum Calculation
1	GANIT, Homogeneous	---	10^{-4}	U^{235} fission	26.28	22.26
2	GANIT, Homogeneous	---	10^{-4}	Unity at 3.8 kev	26.28	24.28
5	GANIT, Method 1	400	10^{-4}	U^{235} fission	24.95	21.33
6	GANIT, Method 1	12	10^{-4}	U^{235} fission	26.34	22.32
7	GANIT, Method 2	400	10^{-4}	U^{235} fission	23.77	20.46
8	GANIT, Method 2	2	10^{-4}	U^{235} fission	26.10	22.15
3	GAROL, Homogeneous	---	10^{-4}	U^{235} fission	26.10	23.39
4	GAROL, Homogeneous	---	0	U^{235} fission	26.10	23.84
9	GAROL, Grains	400	10^{-4}	U^{235} fission	25.07	22.55

affects the spectrum calculation. The generally smaller values of σ_c (GANIT, fine group) will result in relatively smaller broad-group average cross sections, at least when compared with the results of a GAROL calculation.

Results for I_{eff} after the spectrum calculation are shown in Table 6.10 for the same cases shown in Table 6.9. The values of I_{eff} after the spectrum calculation depend to a certain extent on the formula used to calculate this quantity. The results shown in Table 6.10 were evaluated from

$$I_{\text{eff}} = \frac{1}{\phi_N} \sum_g \sigma_g \phi_g, \quad (21)$$

where ϕ_g and σ_g^c are the integrated flux and the resolved-region capture cross sections, respectively, in the g -th broad group, and ϕ_N is a constant which normalizes the flux to $1/E$ at a high energy. To obtain the normalization factor it is necessary to select the highest broad group wide enough for all source neutrons to appear in that group. The lower boundary of this energy group should be above the resolved resonance region (2.5 keV or higher). If the fine-group flux were $1/E$ in the high-energy range, then the first broad-group flux should have been ΔU_1 , where ΔU_1 is the lethargy width of this broad group. However, the actual spectrum-averaged broad-group flux as calculated by GGC (from a fission source) is ϕ_1 , hence, the normalization factor should be

$$\phi_N = \frac{\phi_1}{\Delta U_1}. \quad (22)$$

This normalization guarantees that $\phi_1^{\text{normalized}} = \Delta U_1$ (or a $1/E$ flux above the resonances), as required in the expression for calculating I_{eff} .

The data on Table 6.10 point up one new fact of significance. The outputs of the resonance treatments of GANIT and GAROL were very similar for both the homogeneous cases and for the grain cases (considering GANIT method 1). However, after the spectrum calculations, the GAROL resonance integral is about 5% higher than the GANIT resonance integral. This is due to the difference in the definition, noted earlier, of the fine-group average cross sections in the two resonance treatments. The results of a multigroup diffusion theory calculation would be sensitive to this difference in GANIT and GAROL.

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Task VII
EXPERIMENTAL PHYSICS

LATTICE ASSEMBLY NO. 2

Experiments on Lattice Assembly No. 1 were completed, and the results were given in the previous quarterly report (GA-8530). Lattice No. 1 contained no thorium, only carbon and U^{235} , although the temperature-dependent reactivity of a central element containing Th^{232} was measured. The analysis of these experiments, also presented in the previous report, showed good agreement between calculation and experiment considering difficulties experienced with lattice impurities.

After the experiments on Lattice No. 1, Lattice Assembly No. 2 was loaded and brought to criticality. This lattice has a C/U ratio of 2500 and a C/Th ratio of 200, which is very typical of an HTGR lattice. Considerable efforts were made, successfully, to reduce the impurity level, particularly the hydrogen in the core.

The first experiments in Lattice No. 2 concerned control poison worths. The reactivity worths of special materials in the center of the core were measured and successfully analyzed. The radial flux distribution was measured by activating a large thin sheet of copper. The experimental technique which proved excellent, will be used in more detailed and complicated flux distribution measurements in the future.

The major experimental and analytical effort was directed toward measuring the reactivity effect of heating the central lattice element. This element was loaded with several C/Th ratios in a range spanning most HTGR concentrations of interest.

The results, both experimental and analytical, have been very good. The measured and calculated reactivity changes between 300° and 600°K agree to within about 2% for all C/Th ratios. The experimental and analytical program involved with Lattice No. 2 is continuing.

The configuration of Lattice No. 2 (see Fig. 7.1) is nearly the same as that of Lattice No. 1, which is described in a previous quarterly report (GA-8356). There are four regions: the central or lattice region containing lattice-type fuel elements with a carbon to U^{235} ratio of about 2500 and with a carbon to thorium ratio of about 200; the adjacent heterogeneous region containing one fuel element with a C/U ratio of about 859 for every two graphite columns giving a smeared C/U ratio of 2500; the reflector region; and the outermost region of aluminum honeycomb material. The effective radii of the lattice, heterogeneous driver, and reflector regions are 28.84, 69.82, and 80.76 cm, respectively. The material densities contained in these different regions are summarized in Table 7.1.

Fig. 7.1--HTGR Lattice Assembly No. 2

Table 7.1
MATERIAL DENSITIES OF LATTICE ASSEMBLY NO. 2

Core Region	Isotopic Mass Loading, $\bar{M}$ (g/cm ³) ^a						
	Carbon	Al ^b	Th	U ²³⁵	U ²³⁸	Oxygen	Water
Lattice	1.455	---	1.38-1	1.0894-2	0.803-3	---	5.40-3
Heterogeneous	1.460	0.2344	---	1.0569-2	0.771-3	0.179-2	0.80-3
Reflector	1.493	0.180	---	---	---	---	0.075-3
Voided Al Honeycomb	---	0.1980	---	---	---	---	---

^a $\bar{M}$ is the isotopic mass loading per element divided by the volume of the honeycomb unit cell where the area of honeycomb cell is 15.452 cm².

^bHoneycomb and fuel tube.

As in Lattice No. 1, the lattice logs are 35.5 in. long and 4.55 in. across the flats. The fuel and void holes are on a 0.750-in. pitch and have a 0.450-in. diameter. Two-thirds of the holes in each lattice log were filled with a mixture of PyC-coated uranium dicarbide and thorium dicarbide particles and coke diluent. The fuel particles were screened to obtain a range of diameters between 295 and 417 μ . The thorium particles were screened to obtain a diameter range between 495 and 598 μ , and the coke diluent was screened to fall between 125 and 295 μ . A number of samples of the fuel particles, thorium particles, and coke diluent taken during the loading of the lattice logs were chemically analyzed. The fuel particles contained 43.2 wt-% uranium (93.15% enriched), the remainder being carbon. The thorium particles contained 80.7 wt-% thorium with the remainder carbon. The coke, which had previously been baked out in an inert atmosphere for several hours at 2000°F, contained 0.15 wt-% hydrogen. A spectrographic analysis was performed on the coke to determine the impurity level. Small amounts of some impurities, including boron and sulfur, were detected, but the results were not definitive. Rare earths were not detected. A net impurity level equivalent to about 50 ppm of natural boron seems appropriate for this material, a point discussed more fully later on.

Using loading methods described in the previous quarterly report (GA-8530), the fuel particles, thorium particles, and coke particles were simultaneously metered into the logs, maintaining a uniform axial distribution from one end of the log to the other. Compaction was achieved by vibration. A test log was built from which samples of the loaded mixture could be removed at 2-in. intervals along the 35.5-in. length of the fuel hole. The variation in the weight of fuel or thorium particles per 2-in. sample length was less than $\pm 2\%$. The variation in the total weight of fuel or total weight of thorium particles from log to log was less than $\pm 3\%$.

The differential control rod worths were measured by the period technique. The total integrated worths were \$0.207, \$0.288, \$0.288, and \$0.29.

The total worth of a single safety rod was obtained by the subcritical-source multiplication technique using a previously calibrated regulating rod to generate the necessary inverse source multiplication curve. The results for the eight rods ranged from \$0.85 to \$0.89.

The potential worth of a nuclear fuse was determined by the inverse-source multiplication technique. A fired fuse was inserted in place of a good fuse giving a reactivity decrease of \$0.67; the two fuses therefore have a potential worth of \$1.34.

Experimental Results

Central Reactivity Worth Measurements. Central reactivity worth measurements were made at the center of the lattice using boron, U^{235} , thorium, and graphite special elements. The results of these measurements are discussed later in this task in "Analytical Results."

Copper Activations. To determine the integrated copper activation for various zones of the core assembly, a 0.001-in.-thick layer of copper foil was located at the midplane of the core where the two halves of the assembly come together. The foil was so located that about one sixth of the core and reflector area was covered. After the copper foil was activated, it was sectioned into radial zones having the same boundaries as those used in the calculations. The pieces were then dissolved in acid, and the resulting solution was gamma counted. There were three radial zones in the lattice core region; five radial zones in the C/U-2500 heterogeneous region; and the outer reflector zone.

Temperature Coefficient Measurements. The oscillator rod fuel elements are similar to the rest of the lattice fuel elements, except that they are 4.425 in. across the flats and the 0.450-in.-diameter fuel holes are on a 0.730-in. pitch.

The fuel particles were screened to obtain a range of diameters between 295 and 350 μ with a nominal substrate diameter of 150 μ . The thorium particles were screened to obtain diameters between 295 and 598 μ with a nominal substrate diameter of 450 μ ; the coke diluent was screened to obtain a diameter range between 125 and 250 μ . The fuel particles in the oscillator elements contained 40.5 wt-% uranium (93.15% enriched). The thorium particles contained 79.8 wt-% thorium. The coke was the same as that used in the lattice fuel elements.

The isotopic mass loadings of the oscillator rod elements investigated to date in Lattice No. 2 are shown in Table 7.2.

The two sections of the oscillator elements used in the temperature coefficient measurements are shown in Fig. 7.1 of the previous quarterly report (GA-8530). The oscillator technique used in Lattice No. 2 was somewhat improved over that described in the previous quarterly for Lattice No. 1. The reactor was adjusted to critical with the cold end of the oscillator rod in the core. The hot end was then quickly inserted into the core using the

calibrated servo control rod to maintain delayed criticality. The changes in the servo rod position as recorded on a strip chart recorder were used to determine the reactivity change as a function of temperature difference between the hot and cold ends.

Table 7.2
OSCILLATOR ROD ISOTOPIC MASS LOADING^a

Element Designation	Carbon Log (kg)	Coke (kg)	U ²³⁵ (kg)	Th (kg)
No thorium	21.955	5.142	0.203	0.0
C/Th 300	21.955	5.050	0.208	1.802
C/Th 200	21.955	4.968	0.206	2.698
C/Th 100	21.555	4.781	0.203	5.079

^aThe logs have a total volume of 1.946×10^4 cm³.

To minimize the heat transfer from the hot element to the rest of the core, the hot element was left in the core for only 15 sec and then returned to the oven. Since this short time period does not allow the delayed neutrons associated with the fuel in the hot element to reach equilibrium, the absolute reactivity change was determined from a system of calibration curves that related reactivity at a given time following insertion to the reactivity after equilibrium is established. A typical set of these calibration curves is shown in Fig. 7.2.

Iron-Constantan thermocouples were used to monitor the temperature of the oscillator element at four positions in the hot end, at two positions in the cold end, and at one position in the insulator-coupling section. The temperature of the core was also monitored near the midplane at points 1, 2, 3, and 4 in. radially outward from the edge of the oscillator element.

Special heating elements installed in each end of the furnace were used to compensate for the heat losses at the ends and thus maintain a flat axial temperature profile in the oscillator element throughout the entire temperature range. The temperatures recorded on the oscillator element thermocouples varied by less than $\pm 2^\circ\text{F}$ from the average of the four thermocouples.

Results of the oscillator element experiments are shown in Figs. 7.3 and 7.4.

Analytical Results

Description of Broad-group Structure. Before starting the analysis of the HTGR Lattice No. 2 core assembly, a survey was made to determine the sensitivity of the calculations to the broad group structure. This was done by collapsing the group structure while preserving certain common energy

Fig. 7.2--Reactivity change at delayed equilibrium as a function of time following insertion

Fig. 7.3--Total reactivity change relative to the no-thorium condition associated with heating the central oscillator element

Fig. 7.4--Reactivity change associated with heating the central oscillator element

boundaries and noting the change in calculated parameters, such as the effective core multiplication; the central reactivity worth of some special materials, such as boron, uranium, and thorium; the integrated radial flux distribution; and the temperature coefficient of the central oscillator element with different thorium loadings.

Three broad-group cross-section sets were considered: two 10-group sets having four broad groups below 2.38 eV, three broad groups in the thorium resonance region, and three broad groups above 961.1 eV to account for fast effects; and a 20-group set which expanded one of the 10-group sets by splitting each of the ten broad groups into two groups. One of the 10-group sets used essentially the same group structure that is used in the calculation of the large HTGR core with one additional group in the higher energy region to account for the increased leakage from the small cores used in the critical facility. The other 10-group set was so established that the fraction of thermal absorptions was approximately the same for each of the four thermal groups, the thorium absorptions were shared equally between the three broad groups in the thorium resonance region, and the fast leakage was split nearly equally among the three fast groups.

From the results of this survey, it was concluded that an adequate analysis of the lattice experiments requires from 10 to 14 broad groups. A 10-group set is sufficient for calculating the effective core multiplication factor, the relative reactor rate for central samples of boron, uranium, and thorium, and the integrated radial flux distribution for the different core and reflector zones. A 14-group set is required in order to calculate the effective delayed-neutron fraction, β_{eff} , and the reactivity change associated with heating the central fuel element in the lattice assembly. These additional thermal groups are required to account for the change in thermal reaction rate in the central element as that element is heated through 300°K.

The nuclear analysis of the experiments in HTGR Lattice No. 2 to date has been carried out using the 14-group set shown in Table 7.3 exclusively. Future experiments requiring a multidimensional analysis, such as loading discontinuity experiments, will use the 10-group set shown in Table 7.3.

Nuclear Description of HTGR Lattice No. 2. The analytical model used for calculations in Lattice Assembly No. 2 is essentially the same as that used in the first lattice assembly and is described in detail in the previous quarterly report (GA-8530). A brief summary is presented here.

Atom densities for the materials located in the HTGR lattice elements were obtained using the mass inventory data described earlier along with estimates of the impurity levels. The hydrogen has been almost completely removed from the coke leaving a nominal residual amount of 0.15 wt-%. This amounts to about 200 g of hydrogen for the whole lattice assembly. Although neither an emission spectrographic analysis nor an activation analysis showed any appreciable amounts of boron or rare earth poisons, a reactivity worth check made in the HTGR Lattice No. 2 assembly showed the coke to be worth slightly less than an equivalent mass of nuclear grade graphite. An analysis of this result assuming that coke contains a hydrogen content of 0.15 wt-% implies an equivalent parasitic poison of 50 ppm boron. This amount of poison is generally within the limits of detection by the two methods of analysis mentioned above. The uranium and thorium loadings of the lattice are believed to be accurate to within $\pm 1.5\%$.

Table 7.3
BROAD GROUP ENERGY BOUNDARIES
(in ev)

	14 Group Set	10 Group Set
1	$14.92 \times 10^6 - 1.353 \times 10^6$	$14.92 \times 10^6 - 1.353 \times 10^6$
2	$1.353 \times 10^6 - 4.978 \times 10^5$	$1.353 \times 10^6 - 1.832 \times 10^5$
3	$4.978 \times 10^5 - 1.832 \times 10^5$	$1.832 \times 10^5 - 961.1 \times 10^5$
4	$1.832 \times 10^5 - 961.1 \times 10^5$	$961.1 \times 10^5 - 214.4 \times 10^5$
5	$961.1 \times 10^5 - 214.4 \times 10^5$	$214.4 \times 10^5 - 47.85 \times 10^5$
6	$214.4 \times 10^5 - 47.85 \times 10^5$	$47.85 \times 10^5 - 2.38 \times 10^5$
7	$47.85 \times 10^5 - 17.6 \times 10^5$	$2.38 \times 10^5 - 0.414 \times 10^5$
8	$17.6 \times 10^5 - 2.38 \times 10^5$	$0.414 \times 10^5 - 0.100 \times 10^5$
9	$2.38 \times 10^5 - 0.414 \times 10^5$	$0.100 \times 10^5 - 0.040 \times 10^5$
10	$0.414 \times 10^5 - 0.200 \times 10^5$	$0.040 \times 10^5 - 0.0 \times 10^5$
11	$0.200 \times 10^5 - 0.140 \times 10^5$	--- ---
12	$0.140 \times 10^5 - 0.09 \times 10^5$	--- ---
13	$0.09 \times 10^5 - 0.04 \times 10^5$	--- ---
14	$0.04 \times 10^5 - 0.0 \times 10^5$	--- ---

The atom densities for the C/U-2500 heterogeneous core region and reflector region were the same as those used in the previous analysis of HTGR Lattice No. 1 and are reported in previous quarterly reports.

Disadvantage factors resulting from the heterogeneous loading of the U^{235} in the lattice region fuel elements was calculated to be less than 1% and therefore subsequently ignored. However, disadvantage factors resulting from the lumping of the U^{235} in the individual coated fuel particles were taken into account by assuming that the ratio of the flux in the particle to the surrounding flux could be approximated by the escape probability.

Disadvantage factors for the C/U-2500 heterogeneous region were calculated using the 1DF transport code using the same unit cell model as previously used in the calculation of the 30 group disadvantage factors for Lattice Core No. 1. The calculated values were consistent with those previously obtained.

Particle self-shielding for the thorium particles has been ignored in the calculations to date. It is anticipated that some of the measurements for the thorium-loaded oscillator elements will be repeated with thorium in the form of fine powder. At that time, the question of thorium particle self-shielding effect will be reevaluated.

All of the spatial calculations were made using a one-dimensional radial GAZE model containing three explicit regions: the lattice region, the C/U-2500 heterogeneous driver region, and the reflector region. Axial bucklings for the lattice region were obtained by iteration. Axial bucklings for the other two regions were the same as those used previously for the C/U-2500 core assembly. The lattice region was assumed to contain all of the HTGR mockup fuel elements. The graphite columns used as shims between the lattice assembly and the aluminum honeycomb were homogenized into the C/U-2500 core region. This is consistent with the assumption of an homogenized uranium concentration given by C/U-2500.

All of the effective broad-group cross sections for materials in the lattice region were averaged over a spectrum computed for that region. This included all of the cross sections for the different oscillator element loadings, including those that were calculated for different moderator temperatures. The effective resonance cross sections for thorium were calculated using the Nordheim integral approximation contained in the GAM code, as described in the last quarterly report. A Dancoff correction factor of 0.408 was used. The lump density was computed for holes of 0.450 in. diameter using the mass loadings shown in Table 7.2. Effective broad-group cross sections for materials in the C/U-2500 driver region and the reflector region were averaged over a spectrum computed for the C/U-2500 core region.

The reactivity change resulting from the heating of the oscillator element was calculated from a series of GAZE calculations in which the oscillator element was represented as a central explicit cylindrical zone. The radius of the oscillator element cell was obtained by preserving the area of the hexagonal oscillator element, i.e., the hexagonal oscillator was converted into an equivalent cylinder. The appropriate temperature-dependent carbon scattering kernels and effective thorium resonance cross sections were used in the cell. The reactivity difference resulting from a temperature change from T_1 to T_2 was defined as

$$\Delta\rho = \frac{k_1 - k_2}{k_1 k_2} \frac{1}{\beta_{\text{eff}}} ,$$

where k_1 was the eigenvalue at temperature T_1 , and k_2 was the eigenvalue at temperature T_2 .

Effective Multiplication Factor. Using the analytical model previously described, several calculations were performed for comparison with experiment to determine its adequacy. The series of measurements and a comparison with calculations are given in Tables 7.4, 7.5, and 7.6. Considering the variety of materials loaded into the graphite lattice logs, i.e., fuel, thorium, and coke particles, the uncertainty of their specific inventory, and their impurity content, the calculated value of the effective multiplication factor of 1.024 is considered to be in "good" agreement with the measured value of 1.013. This agreement is believed to be within the limits of uncertainty of the material inventories.

Table 7.4

CALCULATED AND MEASURED EFFECTIVE MULTIPLICATION FACTOR

k_{eff} (measured)	1.001
k_{eff} (measured with experimental corrections for uniform model, safety and control rod locations, fuse locations, and unfilled aluminum honeycomb region)	1.013
k_{eff} (calculated, nominal inventory of materials including impurities)	1.024
k_{eff} (calculated with no hydrogen or parasitic impurities in coke)	1.016

Table 7.5

REACTIVITY WORTH OF SPECIAL ELEMENTS AT CENTRAL POSITION

Special Element Description	Meas. Reac. Worth (\$)	Calc. Reac. Worth (\$)	Ratio Meas./Calc.
Reference carbon, 3350 g	0.0	0.0	---
0.9 density carbon	-0.008	-0.008	1.00
Boron 0.55	-0.235	-0.241	0.98
Boron 1.00	-0.412	-0.419	0.98
2500 U ²³⁵	0.067	0.064	1.05
1718 U ²³⁵	0.092	0.091	1.01
859 U ²³⁵	0.161	0.163	0.99
432 U ²³³	0.420	0.444	0.95
Depleted U-500	-0.243	-0.247	0.98

Table 7.6
RADIAL DISTRIBUTION OF INTEGRATED COPPER ACTIVATION

Radial Region Description	Fractional Area	Fractional Integrated Copper Activity		Ratio Meas./Calc.
		Measured	Calculated	
HTGR Lattice				
R = 14.42 cm	0.0319	1.767	1.758	1.01
R = 21.63 cm	0.0399	1.699	1.736	0.98
R = 28.84 cm	0.0558	1.675	1.693	0.99
Total HTGR lattice region	0.1276	1.705	1.725	0.99
C/U-2500				
R = 37.04 cm	0.0828	1.572	1.609	0.98
R = 45.23 cm	0.1034	1.418	1.451	0.98
R = 53.43 cm	0.1240	1.200	1.229	0.98
R = 61.62 cm	0.1446	0.968	0.967	1.00
R = 69.82 cm	0.1652	0.711	0.698	1.02
Total C/U-2500 heterogeneous region	0.6197	1.104	1.115	0.99
Reflector region				
R = 80.76 cm	0.2527	0.376	0.352	1.07

Central Reactivity Worths. Reactivity worths for some of the special elements used in the previous experimental program were measured in a lattice fuel element that had a 1.625-in. hole bored in the center. This element was located at the central lattice position. These results are summarized in Table 7.5 as well as the calculated results for these special elements. The values given are relative to the reference carbon element, which contains pure carbon compacts.

Radial Flux Distribution. The results of the analysis of the copper activation experiments is shown on Table 7.6. Although this is not a severe test of the accuracy of flux distribution calculations, it is encouraging. The agreement with experiment is within 2%, except in the reflector region, and this is probably due to the irregular (slightly noncylindrical) outer boundary of the reflector. This experimental method will be used in more definitive experiments in the coming months.

Calculated Reactivity Worth of the Thorium. The calculated reactivity worth of the oscillator rod fuel element containing the various thorium loadings is shown in Table 7.7. The calculations were performed for fuel element temperatures ranging from 300° to 600°K. These results, as well as the comparison with the measured results, are shown in Figs. 7.3 and 7.4. There is excellent agreement between the measured and calculated values.

Table 7.7
MEASURED AND CALCULATED REACTIVITY WORTH FOR THORIUM

Oscillator Rod Loading	Thorium RI (cutoff 2.38 ev)		Worth of Th ^a		Reactivity Change ^b	
	300°K	600°K	Meas.(\$)	Calc.(\$)	Meas.(\$)	Calc.(\$)
No Th	---	---	0.00	0.00	-0.0290	-0.0275
C/Th 300	38.82	43.32	-0.449	-0.452	-0.0546	-0.0534
C/Th 200	33.31	36.24	-0.607	-0.615	-0.0625	-0.0623
C/Th 100	26.20	28.52	-0.993	-0.953	-0.0741	-0.0739

^a-Relative to no-thorium loading.

^b-Reactivity change caused by heating oscillator element.

The reactivity change obtained by heating the central fuel element can be separated into two primary effects: the thermal base effect which results from changes in the thermal energy reaction rate for materials in or near the central fuel element and the increased reaction rate for thorium due to the Doppler broadening of the thorium resonances. The thermal base effect is taken into account in the calculations to the extent that the carbon scattering kernels used in the central zone have been calculated at the appropriate higher temperatures. The increase in the effective thorium resonance integral with temperature, resulting from Doppler broadening in the thorium, is taken into account in the explicit resonance calculations of the GAM code. The measurements and calculations thus far have involved only the total reactivity change; however, several experiments are planned that will measure the thermal base effect separately. These experiments will use a nonresonance material to simulate the thermal reaction rate for thorium.

In the analysis it was assumed that the only material change between oscillator elements was in the thorium loading. Experimental corrections were made to correct for the small differences in fuel or carbon content. The Dancoff correction factor used in computing the effective resonance cross sections for the oscillator elements was the same as that for the remainder of the lattice, even though the thorium concentration in the lump varied for the different loadings.

In Figs. 7.3 and 7.4, the calculated results are shown as a solid line. The calculated absolute worth of the thorium particles agree to within 1% of that measured for all of the loadings except the heaviest, and there the agreement is about 4%. The agreement between calculation and experiment for the reactivity change resulting from the heating of the oscillator elements is within the accuracy of the experimental results.

Task VIII
PHYSICS AND FUEL MANAGEMENT

PARAMETRIC STUDIES

For purposes of optimizing the entire reactor system, several single-parameter variation studies were performed to determine their effects on core physics characteristics and fuel cycle costs. The studies have included perturbations in power density, core geometry, degree of tilt of the axial power distribution, and average core temperature. Coupled with previous surveys which considered the effects of loadings and cycle time, the present surveys form a package which can be used to define the effects of reactor plant design changes on the fuel cycle cost.

Being single-parameter variations, the surveys are individually of limited value. For example, the effects of power-density variations assumed a constant core volume, which led to variations in the power level. A separate survey evaluated the change in neutron leakage associated with changing the core dimensions. The net effect of a change in power density on the fuel cycle cost at a constant power level requires the leakage effects and the power-density effects be combined, which is done in the CRAM code. Table 8.1 summarizes some of the results obtained in the single-parameter variation studies.

Table 8.1
EFFECTS ON FUEL CYCLE COSTS AND REACTIVITY DUE TO
PERTURBATIONS IN VARIOUS DESIGN PARAMETERS

Change in reactivity (or leakage)	0.049, mill/Kw-hr per $\Delta K/K$
Change in core height	0.11, % $\Delta K/K$ per ft
Change in core diameter	0.11, % $\Delta K/K$ per ft
Change in average core temperature	1.0×10^{-5} , $\Delta K/K$ per $^{\circ}C$
Change in power density	0.03, mill/Kw-hr per w/cm^3

CODE DEVELOPMENT

In performing fuel cycle assessment studies, the major criterion is the fuel cycle cost. Thorough evaluation of a fuel cycle requires a study of its characteristics over a period of several years, including the approach to equilibrium. A computer program, PWCOST, has been written to perform the resulting time-dependent fuel cycle cost calculations.

PWCOST has two means of evaluating fuel cycle costs as options. The first option is based on a method mentioned in Ref. 1. This method consist of present-worthing all expenditures and credits at the time when the payments are made and levelizing the sum. This automatically includes the working capital contribution.

The second method also employs a present-worthed levelizing approach but differs in that the costs are based on annual consumption, using a linear variation with time, and the accrual rather than the cash flow. Working capital charges are also evaluated on a yearly basis using the average values obtained during the year. The sum of the running costs and working capital charges are then present-worthed and levelized to yield a single fuel cycle cost for the entire time period of interest.

HTGR OFF-SITE PROGRAM SURVEILLANCE

The HTLTR facility at Battelle-Northwest is loading the HTGR lattice. This loading uses U^{235} -coated particles produced by Gulf General Atomic and delivered to Hanford early in March.

The proposed schedule of experiments include measurements of the pressure and temperature coefficient of HTLTR as well as reactivity measurements directly pertaining to the HTGR program. The staff at HTLTR expects to proceed with measurements to 1000°C during the course of these experiments. This is over 300° higher than has been reached previously. The initial loading will have a C/Th ratio of 200 and a Th/ U^{235} ratio of 40.

No analysis of these experiments has been performed by Gulf General Atomic during the quarter pending startup of the experiments.

References

1. Rosenthal, M. W., R. E. Adams, L. L. Bennett, et al., A Comparative Evaluation of Advanced Converters, ORNL 3686, January 1965.

Task IX
ADVANCED COATED PARTICLE FUELS

BARRIER COATING DEVELOPMENT

Deposition of SiC from Methyldichlorosilane

Methyldichlorosilane (MDCS) is a possible alternative reactant for use in the vapor deposition of SiC. It offers the advantage of increased coating rates over methyltrichlorosilane (MTCS) because of its higher vapor pressure. Consequently a limited study has been made of the deposition and microstructure of SiC produced from methyldichlorosilane.

The rate-controlling factor in the deposition of SiC from MDCS was found to be the rate of supply of reactant. The microstructure of the resulting deposit was primarily dependent on temperature, the grain size increasing with increasing deposition temperature. These results were identical to those observed in the case of SiC deposited from MTCS. The principal difference in SiC deposited from MDCS is the presence of considerable amounts of grown-in porosity, which is reflected in a relatively low density (97% to 98% of theoretical). However, at least in the case of high-temperature deposits, the bend strengths are comparable to those of SiC deposited from MTCS. Workers at the Dragon project have reported that α -SiC is produced from MDCS, but in these experiments only β -SiC was observed.

It thus appears that MDCS is a useful reactant for producing vapor-deposited SiC, particularly when increased coating rates are desired. The principal problem is the presence of relatively large amounts of porosity in coatings produced from MDCS.

Microstructure of Coatings on Fuel Particles

All previous observations of SiC microstructures have been made on coatings deposited on graphite disks that were included in the fluidized bed. Since it is possible that the disks could levitate differently than the particles, it was of interest to compare the microstructure of coatings on particles and on disks from the same coating run. The difficulty in examining particle-coatings has been in finding a mounting material that would not be affected by the fused salt etch. The problem was overcome by incorporating the particles into fuel rods, which were then sectioned, polished, and etched. The carbonaceous matrix of the fuel rods stood up very well to the etch. Particles and disks from four coating runs were examined. In general, the microstructure of the coatings on the particles were identical to those on the disks. In one case, however, the SiC coating on the particles had a more laminar appearance than the coating on the disks. This indicates that the particles cycled over a wider range of coating conditions.

In general, it is concluded that the microstructure of SiC deposited on disks is representative of the coatings on fuel particles. Examination of unetched particles and disks in polarized light will reveal any differences in the occurrence of laminations. The time-consuming process of polishing and etching the coatings on fuel particles should be necessary only in special cases.

Mechanical Properties of SiC Coatings

Recent observations of representative SiC coatings with the scanning electron microscope have revealed features that may explain the variability of the strength of the SiC coatings. An apparent variation of the bend strength of vapor-deposited SiC with grain size has been observed. A relatively large variation in strength of SiC having nominally the same grain size has also been observed. With the improved resolution and depth of field of the scanning electron microscope, grown-in intergranular pores and cracks have been observed in some SiC specimens. It is likely that these pores act as sites for crack initiation, so that the strength of any given specimen is determined by the largest grown-in flaw present in the gage section. The frequency of the grown-in flaws was found to vary between coating runs, which probably accounts for the variability in strength of SiC from different coating runs at the same temperature. The apparent dependence of the strength of vapor-deposited SiC on grain size is probably due to a tendency for the coarser-grained specimens to have larger grown-in flaws.

Thermal Stability Studies

Two batches of SiC-coated particles, 2107-31 and 1985-77, have been tested at 1400°C in vacuum to 18,000 hr. These particles were fabricated at Gulf General Atomic in late 1962, and each consists of a UC₂ core with successive layers of laminar carbon, SiC, and laminar carbon.

The data reported in Table 9.1 of the previous quarterly report (GA-8530) are misleading in that the conclusions listed for these two batches at that time were for examination at 8765 hr, and not at 18,000 hr. However, the migration at the end of 18,000 hr has now been found to be 1 and 15 μ , the same as after 8765 hr. The one difference noted is that there appears to have been migration of uranium through the pyrocarbon layer, and a deposition, or buildup, of uranium on the inside surface of the SiC layer. This appears in a radiograph as a thin bright ring of a heavy metal, perhaps 1 to 2 μ in thickness. This condition is noted on half of the particles of batch 2107-31 and on all the particles of 1985-77. Electron microprobe and metallographic techniques will be used to confirm this observation.

A second test including four samples with an SiC layer and two with a ZrC layer has been conducted at 1400°C under 2 psig helium, and the samples have been examined after 10,000 hr. Evaluation indicates that one sample with a ZrC barrier layer exhibited gross migration of uranium through the buffer; one sample with an SiC barrier layer exhibited moderate migration (14 μ), and four remaining samples exhibited no migration (0 to 4 μ). There was an indication that the uranium in the ZrC-coated samples had migrated and deposited on the inner surface of the ZrC. This is identical to the condition

found in the first test, and will be verified by microprobe analysis. The uranium migration data were determined using a radiographic technique and are summarized in Table 9.1.

Thermal Expansion of Vapor-deposited Silicon Carbide

Because of its high elastic modulus, silicon carbide is particularly sensitive to thermal stresses of the type arising in composite coatings on nuclear fuel particles. Calculations of such stresses require an accurate knowledge of the thermal expansion coefficient of silicon carbide. The literature shows considerable scatter in the reported values for materials made by a variety of fabrication techniques. Experimental determinations were therefore made of the thermal expansion coefficient of β -SiC deposited onto graphite substrate disks from methyltrichlorosilane-hydrogen mixtures in a fluidized bed.

Four different samples deposited at temperatures between 1300° and 1800°C were measured. The deposition conditions are listed in Table 9.2. Three strips measuring about 0.2 by 0.04 by 0.004 in. were cut from each deposit and were mounted in a silica dilatometer using a special sample holder to prevent buckling (Ref. 1). The thermal expansion was measured from room temperature to 1000°C. The measurements were repeated for two of the deposits in order to check reproducibility. The expansion coefficients between room temperature and 1000°C are shown in Table 9.2. There was no systematic dependence of the thermal expansion coefficient on the deposition conditions. The average value was $4.94 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, and the standard deviation was $0.12 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. This value is in good agreement with the published results of an X-ray determination for β -SiC crystals (Ref. 2), $4.73 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, and with the mean value for polycrystalline silicon carbide prepared by conventional techniques (Ref. 3), $5.2 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$.

Irradiation Effects in Vapor-deposited Silicon Carbide

Results from Capsule P13J. The silicon carbide samples included in piggyback crucibles in capsule P13J consisted of (1) 0.040-in.-wide diamond-lapped strips with fiducial notches for dimensional change, X-ray diffraction, and mechanical property measurements and (2) 0.080-in.-wide strips for measuring thermal diffusivity. Samples of each type were included in cell 3 (exposure = 3.8×10^{21} nvt, $E > 0.18$ Mev; mean operating temperature approximately 1000°C) and in cell 5 (exposure = 2.7×10^{21} nvt, $E > 0.18$ Mev; mean operating temperature approximately 500°C).

The linear dimensional changes in the strips were $+0.36 \pm 0.03\%$ at 500°C and $+0.06 \pm 0.03\%$ at 1000°C. These values are in good agreement with the results from capsules P13F and P13H.

The lattice parameters of the irradiated strips and of unirradiated control samples were measured from X-ray diffractometer traces. The angular positions of 12 peaks were measured, and the "best value" of the lattice parameter was obtained by an extrapolation procedure that compensates for sample positioning errors (Ref. 4). The irradiation-induced lattice parameter changes of $+0.34 \pm 0.04\%$ at 500°C and $+0.10 \pm 0.04\%$ at 1000°C are identical to the macroscopic changes within the accuracy of determinations.

Table 9.1

RESULTS OF LONG-TERM THERMAL STABILITY TESTS OF SILICON
AND ZIRCONIUM CARBIDE BARRIER COATINGS AT 1400°C

Lot No. ^a	Type of Barrier Coating	Time (hr)	Migration ^b (μ)
3325-87E	ZrC	0	0
		600	1
		1200	1
		2400	1
		5000	1
		10,000	1
3325-89E	ZrC	0	8
		600	11
		1200	20
		2400	28
		5000	35
		10,000	39
3325-117E	SiC	0	2
		600	2
		1200	3
		2400	2
		5000	2
		10,000	4
3332-139E	SiC	0	2
		600	7
		1200	6
		2400	8
		5000	12
		10,000	14
3332-141E	SiC	0	0
		600	0
		1200	0
		2400	0
		5000	0
		10,000	0
3332-149E	SiC	0	1
		600	1
		1200	2
		2400	2
		5000	2
		10,000	1

^a The core on 3332-141E is thorium-uranium oxide; all others are thorium-uranium carbide.

^b Extent of movement of heavy metal from the core into the coating as revealed by microradiography.

Table 9.2
MEAN THERMAL EXPANSION COEFFICIENT OF VAPOR-DEPOSITED β -SiC
(22° to 1000°C)

Sample	Deposition Conditions			Thermal Expansion Coefficient ($10^{-6}^{\circ}\text{C}^{-1}$)		
	Temp (°C)	Total Flow Rate (ml/min)	Hydrogen. Flowing Through Silane (%)			
				Run 1	Run 2	Mean
4032-55	1300	10,000	30	4.76	5.02	4.94 $\pm$ 0.12
3662-71	1600	10,000	10	5.08	--	
3742-83	1400	10,000	20	4.93	4.81	
4032-99	1800	10,000	10	5.06	--	
Single-crystal X-ray ^a	--	--	--	--	--	4.73
Miscellaneous polycrystalline ^b	--	--	--	--	--	5.2

^aRef. 2.

^bMean value, Ref. 3.

The X-ray peak widths were measured for reflections with θ -values out to 67° . The measured widths were corrected for doublet and instrumental broadening as described in an earlier quarterly report (GA-8356). The corrected peak widths, β , were used to calculate the quantity $\beta \cos \theta / 0.89 \lambda$, where λ is the wave length of the radiation in Å. If the line broadening is caused by internal strains, a plot of $\beta \cos \theta / 0.89 \lambda$ against $\sin \theta$ should be a straight line passing through the origin with a slope equal to $4.5 \epsilon / \lambda$, where ϵ is the mean internal strain (see previous quarterly report GA-8530). Plots of this type for the irradiated silicon carbide strips are shown in Fig. 9.1. In all cases the plots are reasonably close to straight lines through the origin. It can be seen that internal strains corresponding to the measured slopes increased from 1.0×10^{-3} for the unirradiated sample to 1.7×10^{-3} after irradiation at 500°C and 1.4×10^{-3} after irradiation at 1000°C . These strains are still relatively small and are lower than those present in some unirradiated structures after deposition at temperatures below 1400°C .

After completing dimensional and X-ray measurements on the narrow strips, it was decided to load them into capsule P20 for additional irradiation at similar temperatures. This will extend the irradiation data to longer exposures. The wide strips are being held for measurement of thermal diffusivity.

Irradiation Experiments in Progress. Strip samples of silicon carbide in capsule P13K will be used to study the effects of microstructure on the irradiation-induced changes in dimensions and mechanical properties. The behavior of the "standard" silicon carbide, whose grain size is not optically resolved, will be compared with that of materials prepared under different conditions and having a larger grain size. The sample exposures and temperatures will be about 2.2×10^{21} nvt at 700°C and at 1000°C .

Silicon carbide strips were included as piggyback samples in the first Fort St. Vrain proof test fuel element irradiation. The samples consisted of unrestrained strips of a single silicon carbide structure deposited on a large bed of particles under conditions representative of those used to prepare the particle coatings for the same experiment. The anticipated exposure and temperature are about 1.3×10^{21} nvt and 1200°C .

Piggyback silicon carbide samples were prepared and loaded into capsule P19. The samples consist of restrained and unrestrained strips of pyrolytic silicon carbide from two coating runs at 1400° and at 1650°C that had grain sizes of about 1 and 4 μ . The unrestrained strips were diamond-lapped to facilitate the measurement of postirradiation mechanical properties, and fiducial lines were scribed and their spacing measured. Restrained samples of each of the two structures were prepared by coating-oriented polycrystalline graphite substrates made from either extruded tube stock (designed to give a low strain rate under irradiation) or hot-worked graphite (designed to give a higher strain rate). Restrained and unrestrained samples were loaded into cell 1 (design temperature and dose about 650°C and 6×10^{21} nvt, $E > 0.18$ Mev) and cell 4 (1000°C and 6×10^{21} nvt) of capsule P19.

Irradiation Experiments in Preparation. Lapped strips of vapor-deposited silicon carbide that had been irradiated in capsule P13J to 3.8×10^{21} nvt at 1000°C and to 2.7×10^{21} nvt at 500°C were loaded into capsule P20 for

Fig. 9.1--Plot of $\beta \cos \theta / 0.89 \lambda$ against $\sin \theta$ for silicon carbide samples irradiated in capsule P13J (β = half-height X-ray diffraction peak width, θ = Bragg angle, and λ = wavelength)

further irradiation. The samples previously irradiated at 1000°C will be reirradiated in cell 2 for a further exposure of $5 \text{ to } 6 \times 10^{21}$ nvt. The samples previously irradiated at 500°C will be reirradiated in cell 1 at about 650°C for an additional $4 \text{ to } 5 \times 10^{21}$ nvt. The samples will then be remeasured and tested in bending in order to provide data on the changes in dimensions and mechanical properties after a total exposure of $8 \text{ to } 10 \times 10^{21}$ nvt at 500° to 1000°C.

Piggyback samples of vapor-deposited silicon carbide are being prepared for inclusion in fuel zone 3 of the second Fort St. Vrain proof test element. The samples are all unrestrained strips of the same silicon carbide structure included in test element one. The structure is representative of particle coatings prepared in large batch sizes at 1400°C. The expected temperature and exposure will be 1200°C and $1 \text{ to } 1.5 \times 10^{21}$ nvt ($E > 0.18$ Mev).

Irradiation Effects in Vapor-deposited Zirconium Carbide

Zirconium carbide has been considered a possible barrier coating material because of the relatively low cross section of zirconium. Small slivers of vapor-deposited zirconium carbide were therefore included in capsule P13J in order to obtain data on the stability of the material under irradiation.

The zirconium carbide was prepared by the decomposition of a hydrogen-zirconium chloride mixture at 2000°C in a graphite tube fluidized bed furnace. The resulting material had a grain size of about 4μ . Slivers were irradiated to 2.7×10^{21} nvt ($E > 0.18$ Mev) at 500°C and 3.8×10^{21} nvt ($E > 0.18$ Mev) at 1000°C.

The material irradiated at 500°C disintegrated completely and was not recovered. The material irradiated at 1000°C underwent considerable crumbling, which prevented dimensional change measurements being made. Metallographic examination was performed on a sample of surviving material from the 1000°C cell. The results are shown in Figs. 9.2 and 9.3, together with unirradiated material for comparison. The photomicrographs show that there was a marked increase in porosity after irradiation. After etching (Fig. 9.3) it is seen that the porosity appears to be located at the grain boundaries, but there is no general grain boundary separation.

Similar crumbling has been reported to occur in hot-pressed and slip-cast-sintered zirconium carbide irradiated to over 2×10^{21} nvt ($E > 1$ Mev) at 300° to 700°C, with the damage becoming severe beyond 3×10^{21} nvt ($E > 1$ Mev) (Ref. 5). The present results indicate a marked decrease in gross damage with increasing irradiation temperature. The present results and those reported in Ref. 5 suggest a relationship between gross damage in zirconium carbide and the irradiation conditions of the type depicted in Fig. 9.4. The range of operating temperatures and exposures over which zirconium carbide may be considered an acceptable barrier coating material is therefore quite limited.

The reason for the crumbling of the zirconium carbide is not clear. The cubic structure of the carbide requires the crystallite dimensional changes to be isotropic, and it is therefore unlikely that intergranular

Unetched

500X

Unetched

500X

Fig. 9.2--Microstructure of vapor-deposited zirconium carbide before irradiation (above), and after irradiation to 3.8×10^{21} nvt ($E > 0.18$ Mev) at 1000°C (below). Unirradiated sample fractured during mounting

500X

500X

Fig. 9.3--Microstructure of vapor-deposited zirconium carbide before irradiation (above) and after irradiation to 3.8×10^{21} nvt ($E > 0.18$ Mev) at 1000°C (below). Unirradiated sample fractured during mounting. Etched with 9 vol HNO_3 + 1 vol HF + 1 vol H_2SO_4

Fig. 9.4--Tentative relationship between gross damage in zirconium carbide and irradiation conditions (based on present results and data reported in Ref. 5)

stresses are the cause of failure. The most probable cause seems to be the generation of helium by (n,α) reactions with the zirconium atoms. The helium may then collect at the grain boundaries and cause increasing porosity and structural deterioration with increasing exposure. In addition to the micrographic evidence shown in Figs. 9.2 and 9.3, the observation that the X-ray lattice expansion accounts for only 30% to 50% of the bulk expansion (Ref. 5) also suggests the generation of porosity. The decreasing damage rate with increasing irradiation temperature may be due to the increased diffusion of helium to the free surfaces.

Coating Contamination Studies

Evaluation of the initial fission-product release from coated particles is difficult because of the presence of uranium in the particle coatings. Also, long-term release characteristics may be affected by coating contamination. Very little is known, however, about the degree of contamination in various particles, its distribution, the mechanisms by which it arises, and the means by which it can be minimized or eliminated. A series of experiments is under way to determine:

1. The uranium contamination concentration profiles through the PyC, SiC, and buffer layers in various coated particles.
2. The sources and magnitudes of coating contamination, and methods of reducing contamination levels.
3. The influence of coating contamination on short- and long-term fission-product release.

In these studies known increments of coating from 400 to 500 particles are removed by grinding, and the dust removed is subjected to activation analysis for uranium and thorium content. The chief advantage of this technique is that concentration gradients through the PyC and SiC coatings can be established, and the total uranium concentration can then be accurately determined. Contamination levels in the buffer, which are high, are determined by electron microprobe analysis.

Closely similar particles from a given batch are obtained by sieving out a narrow size range and then using a sink-float separation to obtain nearly uniform total coating thicknesses. Doublets and badly nonspherical particles are removed by visual inspection. Before and after the grinding operations, coating thicknesses are determined by microradiography; particle weight losses during each run are also determined.

The particles are abraded against a circular track of abrasive paper by air jets that rotate the particles. The dust is collected on filter paper that is activated and counted in clean vials. At present, U^{235} contents of about 1×10^{-3} μg can be detected on a filter paper.

Initially, uranium concentration profiles are being determined for TRISO-I and TRISO-II particles. Factors being investigated include:

1. The effect of inner isotropic carbon coating on over-all contamination.

2. The effect of HTI versus LTI PyC coatings
3. The effect of SiC coating thickness on outer PyC contamination.
4. The effect of a 200-hr anneal at 1300°C on contamination profiles.

The contamination profiles will give the total uranium concentration in the coatings as well as in the outer few microns and should indicate the probably source of contamination, e.g., broken particles during coating.

To establish the sources of coating contamination and the influence that various types and levels of contamination have on fission-product release, inert cores will be coated in clean coater tubes with and without deliberate contamination. The factors to be investigated that affect contamination concentrations and profiles will include:

1. Effect of coating in a contaminated coater tube.
2. Effect of deliberate contamination of SiC to known levels followed by coating with clean PyC.
3. Effect of deliberate contamination of PyC to known levels only.
4. Effect of 200-hr anneal at 1300°C on deliberate-contamination profiles.

The coated inert cores will indicate the source or sources of contamination, and will be used to provide accurate fission-product release data from coatings with known contamination. In the natural follow-on to this work, various methods of reducing or eliminating coating contamination will be studied.

Initially, the grinding parameters for the rig were established in a series of 1/2-hr runs. The thickness of PyC removed was computed from radiographs and also from weight losses. Agreement between the two methods was good and showed that the rate of decrease of particle diameter was constant with time. The removal rate of LTI coatings was found to be five to eight times slower than that of HTI coatings for TRISO particles.

Trial runs on batch 3332-101E (TRISO-II particles) were activated and counted for the uranium present. It was found, however, that the abrasive paper in the grinder had high sodium contamination, preventing accurate determination of uranium content. It was possible to establish only that the total uranium contamination was less than 5×10^{-5} fraction in the outer PyC by subsequent evaluation of the uranium contained just on the filter paper.

Experiments with highly contaminated BISO particles showed that only 2% to 3% of the coating removed in any run remains on the abrasive paper. Since this is well within experimental error, it is therefore possible to use just the filter papers (which have much lower background) for evaluation. To increase the sensitivity of uranium measurement on the filter papers, specimens are now transferred and counted in clean vials. Also, a small particle grinder has been constructed having a filter paper area only one-fourth of that previously used. Likewise, it is possible to increase the

number of particles being abraded in a given run; however, with more particles, the distribution of core sizes and coating thicknesses is greater. Other methods of increasing the sensitivity of measurement are being investigated.

Two batches of BISO particles and one batch of TRISO particles, all with HTI coatings, were evaluated by removing 6- to 12- μ increments and measuring the uranium contained in the PyC on the filter paper. The values obtained were extrapolated on the basis of constant contamination levels throughout the PyC coatings to give fractional uranium contents outside the cores. The results are presented in Table 9.3 along with those for batch 3332-101E. These figures correspond well with similar figures that were obtained previously on BISO and TRISO particles and that were given in an earlier quarterly report (GA-8356).

Table 9.3
URANIUM CONTAMINATION IN PyC

Batch	Coating Type	Uranium Contamination in Outer PyC
4601E	BISO	$\sim 1 \times 10^{-3}$
2824-19E	BISO	$\sim 7 \times 10^{-4}$
3923-79E	TRISO-I HTI	$\sim 1 \times 10^{-5}$
3332-101E	TRISO-II HTI	$< 5 \times 10^{-5}$

Since it was conjectured that the contamination in the PyC of the TRISO LTI-coated particles might be below the 1×10^{-5} fraction in the TRISO-I material, the total uranium contents in the PyC coatings of two TRISO-II batches were therefore determined. The results showed a uranium contamination in the outer PyC for batch 3923-81E (TRISO-II HTI) of about 2×10^{-5} and for batch 3923-87E (TRISO-II LTI) of less than 7×10^{-7} . This latter value for batch 3923-87E represents less than the smallest amount of uranium currently detectable, and further modification of the technique is therefore required in order to determine the contamination gradient.

Samples of each of the six batches before and after annealing in helium for 200 hr at 1300°C were subjected to electron microprobe analysis. Thorium contamination of the TRISO-II particles (batch 3332-101E) was three to four times that of uranium, and both thorium and uranium were relatively constant throughout most of the buffer layer, as shown in Fig. 9.5. (It should be noted that the values plotted in this figure represent the concentrations of uranium and thorium as weight percentages of the coating material.) A small buildup of contaminants was detected inside the inner PyC layer, however, and a much larger buildup inside the SiC layer. Outside the SiC, no thorium or uranium was detectable. The results show that the inner isotropic layer also has some effect as a "barrier" layer for uranium and thorium diffusion from the core.

Fig. 9.5--Weight percentages of uranium and thorium in coatings of typical TRISO-II particle from batch 3332-101E (determined by electron microprobe)

COATED PARTICLE IRRADIATIONS

A series of capsule irradiations is being conducted to evaluate advanced types of coated particles under potential HTGR irradiation environments. At present, these tests are directed toward the evaluation of fuel particles containing diluents other than thorium that could lead to reductions in HTGR fuel cycle costs. Additional irradiation experiments in support of the HTGR program are being conducted at ORNL, and include several high-burnup tests of advanced coated particles and tests of SiC-coated particles.

Gulf General Atomic Capsules

Capsule P13K. Capsule P13K is the first irradiation test of coated particles containing void and carbon diluents instead of thorium in the fuel cores. The objectives of this experiment are:

1. To test the irradiation stability of coated particles containing diluents other than thorium.
2. To test the applicability of current analytical models of coated particle irradiation behavior to diluent particles.
3. To compare the performance of diluent particles with both BISO-HTI and BISO-LTI coatings at HTGR maximum (1300°C) and average (900°C) fuel temperatures.

Two types of diluent particles are being tested:

1. Buffer diluted: Dense, small (100- μ) UC₂ cores that utilize a thick buffer (void + carbon) as the diluent.
2. Void diluted: Porous UC₂ cores (57% of theoretical density) that utilize the void volume in the core as the diluent.

These diluent particle designs allow considerably higher uranium loadings in the coated particles (up to 70% higher) than conventional thorium-diluted fuel.

The coated particle samples were designed using the merit factor model (Ref. 6). In order to test the applicability of the model to diluent particles, samples were designed for both failure and survival. Since merit factors near 1200 are expected to fail while those near 2000 are expected to survive, samples were designed for merit factors of 1200, 1600, and 2000. In addition, most of the samples were designed to obtain maximum uranium loadings (i.e., to have the thinnest total coating thickness yielding the desired merit factor). Samples with maximum uranium loadings provide the highest burnups (in fission/cm³ coated particle) and therefore are the most severe test of diluent particles. BISO coatings were chosen for the samples, since the merit factor model appears more applicable to the two-layer BISO coating than to composite multilayer SiC barrier coatings. Detailed descriptions of all P13K samples were presented in an earlier quarterly report (GA-8200).

Capsule P13K has finished its third and final cycle of irradiation in the ETR and will be returned to Gulf General Atomic for examination. Most fuel temperatures recorded by the thermocouples were considerably below the design 1300°C (4 cells) and 900°C (1 cell), with one as much as 225°C low.

Four of the original 15 thermocouples were operative at the end of irradiation. The fuel reached an estimated burnup of 56% FIMA for the diluent particles and 22% FIMA for the conventional thorium-diluted particles. The fast-neutron dose is estimated as 3.7×10^{21} n/cm².

Cooperative Irradiation Programs

ORNL Capsule 41-28. Capsule 41-28 was an ORNL high-burnup test of three Gulf General Atomic BISO- and triplex-coated carbides; three ORNL samples were included in the test. Each coated particle sample was tested in quadruplicate in different axial flux locations, so that for each the estimated burnups range from 15% to 31% FIMA. The estimated maximum temperature was 1200°C. The capsule completed a three-cycle irradiation in the ETR in November 1966 and is still awaiting postirradiation examination.

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Task XI
GRAPHITE RESEARCH

GRAPHITE IRRADIATIONS

Graphite irradiation studies on the HTGR Base Program are directed toward obtaining high-dose and high-temperature data on the irradiation behavior of conventional anisotropic and isotropic graphites or model carbons. The data on model carbons are being used to aid in the interpretation of the behavior of artificial polycrystalline graphites. The graphite data are being used with current theories or models that attempt to explain the bulk dimensional and crystallite changes and property changes.

Graphite Irradiations in Dragon

Four graphites, H-328, H-327, 9567, and TS-688, are being irradiated in Dragon fuel pins. All graphites were produced in large diameters and represent materials with crystallite sizes in the range from 300 to 1500 Å. Other properties of these graphites range as follows: strength in tension, from 1000 to 3000 psi; crystallite orientation by BAF, from 1.00 to 1.75; and thermal expansivity, from 0.9×10^{-6} to $5.7 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$. Dimensional changes and creep constants of these materials will be studied.

In addition to the graphite samples, a few pyrolytic carbon materials were included, and these will serve as model carbon structures. These materials were characterized prior to irradiation, and a knowledge of their behavior will be valuable when correlated with graphite data, since they represent materials of very small crystallite sizes.

The irradiation period has been altered again because of changes in the operating schedule of Dragon and the samples will now be discharged about August 1968. The specimens will accumulate about $2.0 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ Mev}$) at 850° to 1200°C .

Graphite Irradiations in Dounreay

A single graphite irradiation vehicle, or rig, sponsored by the United States, is being irradiated in the Dounreay Fast Reactor (DFR) of the UKAEA. The objective of the experiment is to extend experimental data on graphites that are of interest to advanced HTGRs to doses of about $1 \times 10^{22} \text{ n/cm}^2$ at 600° to 700°C and 1000° to 1100°C .

Details of the experiment and materials have been discussed in previous quarterly reports (Refs. 1 and 2). The rig was operated for a short time in 1967, but the Dounreay reactor is now shut down for repairs. The continuation of the experiment has been rescheduled to begin sometime after June 1, 1968. When the irradiation is resumed it will be continued for 55 days at full power.

Therefore, examination of the specimens will be delayed until sometime after September 1968.

Gulf General Atomic-BNWL Joint Irradiations

A series of capsules is being irradiated by BNWL in the ETR in support of the HTGR Base Program. The reactor space is shared by Gulf General Atomic and BNWL. The design, fabrication, and monitoring of the capsules are being done by BNWL, but each laboratory is responsible for the examination and analysis of their respective samples. Results for the Gulf General Atomic-irradiated specimens are discussed in the following section.

The objectives of the experiments planned and conducted under the Gulf General Atomic-BNWL joint irradiation program, and a description of the Gulf General Atomic specimens have been discussed previously (Refs. 1 and 3). Postirradiation examinations have been made on specimens from capsules G10 and GE-H-13-13,* and the results were reported in Ref. 2. During this quarter, specimens that had been irradiated in capsule GE-H-13-14 were examined and analyzed before being returned to BNWL for inclusion in capsule GE-H-13-15, which is under construction.† Capsule GE-H-13-15 should begin irradiation about mid-May 1968 and is scheduled to complete its irradiation exposure about September 1968.

Postirradiation Examination of Specimens from ETR Capsules

Specimens irradiated in capsule GE-H-13-14 included graphites that had previously been irradiated in capsules G10 and/or GE-H-13-13, an orientation series of hot-worked graphite and massive pyrolytic carbon and model carbons** that represent a wide range of structures.

Irradiation Effects in Anisotropic and Near-isotropic Graphites. Detailed descriptions of the graphites included in these studies, their physical and mechanical properties, and the structural parameters have been published in Ref. 3. Graphites NC-8, H-283, 711-TS, and CHN were fabricated with needle-coke and bonded with pitch. NC-8 and H-283 were impregnated once with coal-tar pitch, 711-TS was triple-impregnated with coal-tar pitch, and CHN was heavily impregnated with a nongraphitizing carbon. Graphites H-315-A and H-328 are near-isotropic graphites and were prepared with Gilsonite coke. Graphite H-319 was prepared with raw petroleum coke and is nearly isotropic. The irradiation history for these specimens is given in Table 11.1.

Dimensional changes are shown in Figs. 11.1 through 11.19. Changes in thermal expansivity measured at 400°C are given in Figs. 11.20 through 11.24.

*Capsule GE-H-13-13, the first capsule in this series, was incorrectly identified in previous reports, for example, in Ref. 2, it was identified as GE-H-13-14.

†Capsule GE-H-13-14 was the next capsule to be irradiated in the ETR. It was previously identified as GE-H-13-15 or GE-H-13-16. The next capsule to be irradiated in this program will be GE-H-13-15.

**These data were reported under Contract AT(04-3)-167, Project Agreement No. 12

Fig. 11.1--Dimensional changes of NC-8 graphite after irradiation in capsules G10 and GE-H-13-14 at 960° and 1015°C

Fig. 11.2--Dimensional changes of NC-8 graphite after irradiation in capsules G10, GE-H-13-13, and GE-H-13-14 at 1175° and 1250°C

Fig. 11.3--Dimensional changes of H-283 graphite after irradiation in capsules G10, GE-H-13-13, and GE-H-13-14 at 880° to 1015°C

Fig. 11.4--Dimensional changes of H-283 graphite after irradiation in capsules G10, GE-H-13-13, and GE-H-13-14 at 1175° and 1250°C

Fig. 11.5--Dimensional changes of 711-TS graphite after irradiation in capsules G10, GE-H-13-13, and GE-H-13-14 at 880° to 1015°C

Fig. 11.6--Dimensional changes of 711-TS graphite after irradiation in capsules G10, GE-H-13-13, and GE-H-13-14 at 1175° and 1280°C

Fig. 11.7--Dimensional changes of CHN graphite after irradiation in capsules GE-H-13-13 and GE-H-13-14 at 760° and 800°C

Fig. 11.8--Dimensional changes of CHN graphite after irradiation in capsules G10, GE-H-13-13, and GE-H-13-14 at 880° to 1015°C

Fig. 11.9--Dimensional changes of CHN graphite after irradiation in capsules G10, GE-H-13-13, and GE-H-13-14 at 1175° and 1250°C

Fig. 11.10--Dimensional changes of H-315-A graphite after irradiation in capsules G10, GE-H-13-13, and GE-H-13-14 at 950° to 1015°C

Fig. 11.11--Dimensional changes of H-315-A graphite after irradiation in capsules G10, GE-H-13-13, and GE-H-13-14 at 1175° and 1250°C

Fig. 11.12--Dimensional changes of H-319 graphite after irradiation in capsules G10, GE-H-13-13, and GE-H-13-14 at 880° to 1015°C

Fig. 11.13--Dimensional changes of H-319 graphite after irradiation in capsules G10, GE-H-13-13, and GE-H-13-14 at 1175° and 1250°C

Fig. 11.14--Dimensional changes of H-328 graphite at 760° and at 1015°C in different cells of capsule GE-H-13-14

Fig. 11.15--Dimensional changes on CHN and H-315-A graphites irradiated first at 1450°C in capsule G10 and subsequently at 1225° and 1250°C in capsules GE-H-13-13 and GE-H-13-14

Fig. 11.16--Dimensional changes of 711-TS graphite irradiated first at 1015°C in capsule G10 and subsequently at 800° and 760°C in capsules GE-H-13-13 and GE-H-13-14

Fig. 11.17--Dimensional changes of CHN graphite irradiated first at 1015°C in capsule G10 and subsequently at 800° and 760°C in capsules GE-H-13-13 and GE-H-13-14

Fig. 11.18--Dimensional changes of H-315-A graphite irradiated first at 1015°C in capsule G10 and subsequently at 800° and 760°C in capsules GE-H-13-13 and GE-H-13-14

Fig. 11.19--Dimensional changes of H-319 graphite irradiated first at 1015°C in capsule G10 and subsequently at 800° and 760°C in capsules GE-H-13-13 and GE-H-13-14

Fig. 11.20--Changes in thermal expansivity of H-283 graphite after irradiation

Fig. 11.21--Changes in thermal expansivity of 711-TS graphite after irradiation

Fig. 11.22--Changes in thermal expansivity of CHN graphite after irradiation

Fig. 11.23--Changes in thermal expansivity of H-319 graphite after irradiation

Fig. 11.24--Changes in thermal expansivity of H-315-A graphite after irradiation

Table 11.1
IRRADIATION HISTORY OF SPECIMENS IN CAPSULES G10,
GE-H-13-13, and GE-H-13-14

Capsule	Neutron Dose (n/cm ²) (E > 0.18 Mev)	Temp (°C)
G10	2.4 - 3.3 x 10 ²¹	880-1470
GE-H-13-13	0.5 - 2.1 x 10 ²¹	800-1230
GE-H-13-14	0.7 - 4.0 x 10 ²¹	760-1250

Changes in the apparent density measured by immersion in a liquid after the open pores were evacuated are shown in Figs. 11.25 and 11.26.

The dimensional changes of the needle-coke graphites, as shown on Figs. 11.1 through 11.9, have turned around and are expanding in the direction parallel to the c-axis at cumulative exposures in the range of 4 to 8 x 10²¹ n/cm². Expansions of up to 8% were observed for graphite H-283, irradiated at 1250°C. In the parallel direction, or parallel to the a-axis direction, graphites NC-8 and 711-TS show only contraction, with no sign of a decrease in the rate up to 8 x 10²¹ n/cm². The rate of contraction in the a-axis direction of graphites H-283 and CHN, however, has started to decrease and, in the case of H-283 at 1250°C, the contraction has ceased and expansion has begun.

The linear dimensions of graphites H-315-A (see Figs. 11.10 and 11.11) and H-319 (see Figs. 11.12 and 11.13) have ceased contracting in both directions, and expansions began at an exposure of about 5 x 10²¹ n/cm² at 1000°C and 1250°C.

Graphites 711-TS, CHN, H-315-A, and H-319, irradiated first at 1015°C to about 3 x 10²¹ n/cm² and subsequently at 760° to 800°C to about 4.5 x 10²¹ n/cm², show a decrease in contraction rate during the irradiation period at 760° to 800°C. These specimens have turned around and are now expanding in the direction parallel to the c-axis.

The thermal expansivity, measured at 400°C, has increased for graphite H-283 irradiated at 1250°C, but has not changed significantly for the other needle-coke graphites, CHN or 711-TS, which are heavily impregnated. The near-isotropic graphites H-315-A and H-319 show a significant decrease in thermal expansivity at 1000° and 1250°C (see Figs. 11.20 through 11.24).

The changes in the apparent density increased with exposure for graphites H-315-A and CHN at 950°C and 1250°C (see Figs. 11.25 and 11.26). The increase in density was quite pronounced at low exposures for both graphites, increasing rapidly from 2.04 g/cm³ to about 2.11 g/cm³ at 3 x 10²¹ n/cm², but slowed with further exposure. The changes in the apparent density indicate the disappearance of closed porosity within the graphite.

Fig. 11.25--Changes in apparent density of CHN graphite after irradiation

Fig. 11.26--Changes in apparent density of H-315-A graphite after irradiation

The changes in the microstructure of graphites CHN and H-315-A are shown in the series of photomicrographs in Figs. 11.27 through 11.34. These graphite specimens were first irradiated at 1450°C to 3.3×10^{21} n/cm² and subsequently irradiated to 5.9×10^{21} n/cm² at 1225°C or to a total exposure of 9.2×10^{21} n/cm². The preparation of the metallographic mounts is not consistent because the work was done at about nine-month intervals over the past three years. The specimens in Figs. 11.27, 11.28, 11.29, 11.30, and 11.34 were impregnated with epoxy resin after mounting, while those in Figs. 11.31, 11.32, and 11.33 were not. Also, the polishing characteristics changed with increasing exposure; thus, standardization of surface preparation was not possible for the series.

The nongraphitic impregnant coke is clearly visible in the CHN graphite at all stages of the irradiation. There appears to be an increase in the crack structure of the needle-coke particles as the irradiation exposure is increased. These cracks are especially prominent in the photomicrographs of Figs. 11.29 and 11.30, which were made after the c-axis direction turnaround had occurred. Large cracks are visible in the Gilsonite coke particles of the unirradiated H-315-A material (see Fig. 11.31). As the irradiation progressed, these cracks disappeared progressively until they were not visible after 9.2×10^{21} n/cm² (Fig. 11.34). The individual Gilsonite particles are no longer prominent in the microstructure.

The dimensional changes of the needle-coke graphites in the range 900° to 1250°C show an expected pronounced anisotropic behavior, a turnaround in the c-axis direction, and expansion beginning at progressively lower exposures as the irradiation temperature is increased. The presence of an impregnant coke retards the expansion of needle-coke graphites in the c-axis direction. The near-isotropic graphites show considerable anisotropic behavior in their dimensional changes which increases progressively with exposure. These materials cease to contract in both directions after an exposure of about 4 to 5×10^{21} n/cm² and expand on further exposure.

Several correlations can be made between dimensional changes and changes in properties and microstructure in these materials. At exposures of up to 4 to 5×10^{21} n/cm², the closed porosity is removed during contraction. Thermal expansivity is not significantly affected during this stage. After contraction ceases and expansion begins, the closed porosity remains essentially constant. Thermal expansivity then starts to increase in the unimpregnated needle-cokes. The thermal expansivity decreases in the near-isotropic graphites after dimensional expansion begins.

These graphites have been returned to the ETR for additional exposure in capsule GE-H-13-15. The observed correlations will be reviewed when higher cumulative exposures are obtained.

Irradiation Effects on Highly Oriented Carbons and Graphites. The irradiation-induced dimensional and physical property changes in polycrystalline graphite are complex and difficult to interpret because the changes in the constituent crystallites are modified by intercrystalline interactions and the effects of porosity. Data useful for interpreting irradiation effects in polycrystalline graphites may be obtained from experiments on highly oriented, single-phase carbons and graphites free from gross porosity. In

75X

Fig. 11.27--Photomicrograph of unirradiated CHN graphite

75X

Fig. 11.28--Photomicrograph of CHN graphite after irradiation to 3.3×10^{21} n/cm² at 1450°C

75X

Fig. 11.29--Photomicrograph of CHN graphite irradiated to 5.2×10^{21} n/cm², total exposure 3.3×10^{21} n/cm² at 1450°C followed by 1.9×10^{21} n/cm² at 1225°C

75X

Fig. 11.30--Photomicrograph of CHN graphite irradiated to 9.2×10^{21} n/cm², total exposure 3.3×10^{21} n/cm² at 1450°C, followed by 5.9×10^{21} n/cm² at 1225°C

75X

Fig. 11.31--Photomicrograph of unirradiated H-315-A graphite

75X

Fig. 11.32--Photomicrograph of H-315-A graphite irradiated to 3.3×10^{21} n/cm² at 1450°C

75X

Fig. 11.33--Photomicrograph of H-315-A graphite irradiated to 5.2×10^{21} n/cm², total exposure, 3.3×10^{21} n/cm² followed by 1.9×10^{21} n/cm² at 1225°C

75X

Fig. 11.34--Photomicrograph of H-315-A graphite irradiated to 9.2×10^{21} n/cm², total exposure 3.3×10^{21} n/cm² at 1450°C followed by 5.9×10^{21} n/cm² at 1225°C

particular, accurate estimates of the dimensional changes in constituent crystallites may be obtained from such materials.

In the present work, the specimens consisted of two series of samples cut at 0°, 30°, 60°, and 90° to the symmetry axis of (1) ATJ graphite hot-worked to 50% to 60% compressive strain at about 2700°C, and (2) massive pyrolytic carbon deposited at about 2200°C. Control samples cut parallel to the substrate plane of massive pyrolytic carbon annealed at 3300°C were also included. The densities, orientation factors, and apparent crystallite sizes of these materials are listed in Table 11.2. It may be seen that the apparent crystallite sizes span the range encountered in the components of polycrystalline nuclear graphites.

Table 11.2

STRUCTURAL PARAMETERS FOR HIGHLY ORIENTED CARBONS AND GRAPHITES
IRRADIATED IN CAPSULES GE-H-13-13 AND GE-H-13-14

Material	Density (g/cm)	BAF ^a	Apparent Crystallite Size (Å)	
			L _a	L _c ^b
Massive pyrolytic carbon	2.18	8.9	250 ^c	220
Hot-worked ATJ graphite	2.04	4.1	630 ^d	570
Annealed pyrolytic carbon	2.25	13	1300 ^d	1600

^aBacon anisotropy factor.

^bEvaluated from the (002) reflection.

^cEvaluated from (11) band.

^dEvaluated from the (110) reflection.

The samples were first irradiated in cells 1 and 9 of capsule GE-H-13-13 to exposures of 0.5×10^{21} nvt ($E > 0.18$ Mev) at 800°C (cell 1) and 1.9×10^{21} nvt ($E > 0.18$ Mev) at 1225°C (cell 9). The dimensional changes and changes in the thermal expansion coefficient were reported in Ref. 2. The samples were then reirradiated in cells 1 and 9 of capsule GE-H-13-14 to an additional exposure of 0.6×10^{21} nvt at 760°C in cell 1 and 4.0×10^{21} nvt at 1260°C in cell 9. During disassembly of the capsule, all four annealed pyrocarbon samples, one hot-worked graphite sample, and one massive pyrocarbon sample from cell 1 were lost. Dimensional change and thermal expansion coefficient measurements have been completed on the remainder of the samples.

Because of the large dimensional changes in the materials irradiated in cell 9, the samples cut at 30° and 60° to the axis of the parent block were distorted out of their original wedge-shaped form. Some of the hot-worked

graphite samples and some massive pyrocarbon samples from this cell are shown in Figs. 11.35 and 11.36. The massive pyrocarbon samples developed delamination cracks during the last irradiation, and two of the ten samples fractured. It was possible, however, to make dimensional measurements on all the samples. The dimensional changes in the 30° and 60° samples were obtained by measuring the perpendicular distance between the top and bottom faces and converting this measurement to the length of the long side of the wedge, using the measured angles between the faces.

The measured dimensional changes for all the samples are shown in Figs. 11.37 through 11.41. Data obtained in the earlier irradiation (GE-H-13-13) are also included. The c-axis expansions now exceed 80% true strain for the pyrolytic carbon samples irradiated at approximately 1250°C. All the materials irradiated in cell 9 showed a significant decrease in density (7% for annealed pyrocarbon, 9% for hot-worked graphite, and 12% for massive pyrocarbon). Except in the case of the massive pyrocarbon there was no evidence for gross irradiation-induced cracking. In order to check whether the irradiated annealed pyrocarbon contained open porosity, the density of two samples was measured by the sink-float method before and after vacuum outgassing at 400°C under a pressure of 5×10^{-6} mm Hg, followed by impregnation with a bromoform-methanol mixture. The density remained unchanged after the vacuum impregnation treatment, indicating that there was no open porosity. Metallographic examination will be made in order to check for visible changes in the crack structure in all three materials.

When the irradiation-induced dimensional changes in a polycrystalline graphite sample are small, the relationship between the macroscopic dimensional change, $\Delta L_x/L_x$, and the changes in the constituent crystallites, $\Delta X_c/X_c$ and $\Delta X_a/X_a$, is represented by the following equations (Ref. 4):

$$\frac{\Delta L_x}{L_x} = A_x \frac{\Delta X_c}{X_c} + (1 - A_x) \frac{\Delta X_a}{X_a} \quad (1)$$

A_x is related to the thermal expansion coefficient of the sample, α_x , and, in the single-crystal thermal expansion coefficients, α_a and α_c ,

$$\alpha_x = A_x \alpha_c + (1 - A_x) \alpha_a \quad (2)$$

However, if α_x is taken at 400°C where $\alpha_a = 0$,

$$\alpha_{x(400)} = A_x \alpha_{c(400)} \quad (3)$$

Thus, a plot of $\Delta L_x/L_x$ versus α_x should be a straight line whose intercepts at $\alpha_x = 0$ and $\alpha_x = 29 \times 10^{-6}$ correspond to $\Delta X_a/X_a$ and $\Delta X_c/X_c$, respectively.

Fig. 11.35--Appearance of wedge-shaped samples of hot-worked graphite from orientation series after an irradiation to $5.9 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ Mev}$) at about 1250°C . Left to right: unirradiated sample, samples cut at 0° , 30° , 60° , and 90° to axis of parent block (3X)

Fig. 11.36--Appearance of wedge-shaped samples of massive pyrolytic carbon from orientation series after an irradiation to $5.9 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ Mev}$) at about 1250°C . Left to right: unirradiated sample, samples cut at 0° , 30° , 60° , and 90° to axis of parent block (3X)

Fig. 11.37--Dimensional changes of massive pyrocarbon samples irradiated in cell 1 of capsules GE-H-13-13 and GE-H-13-14, at approximately 800°C

Fig. 11.38--Dimensional changes in hot-worked graphite samples irradiated in cell 1 of capsules GE-H-13-13 and GE-H-13-14 at 800°C

Fig. 11.39--Dimensional changes in massive pyrolytic carbon samples irradiated in cell 9 of capsules GE-H-13-13 and GE-H-13-14 at 1250°C

Fig. 11.40--Dimensional changes in hot-worked graphite samples irradiated in cell 9 of capsules GE-H-13-13 and GE-H-13-14 at about 1250°C

Fig. 11.41--Dimensional changes in annealed pyrolytic carbon samples in cell 9 of capsules GE-H-13-13 and GE-H-13-14 at approximately 1250°C

Plots of this kind are shown in Figs. 11.42 and 11.43 for the massive pyrocarbon and hot-worked graphite samples irradiated in cell 1 of capsule GE-H-13-14. The thermal expansion coefficients used were those measured on the irradiated samples. It appears that the plots agree well with the straight-line relationship of Eq. (1).

When the dimensional changes are large (as in the case of the samples irradiated in cell 9 in the GE-H-13-14 irradiation experiment), the simple relationships are modified. For samples cut from an oriented block of polycrystalline graphite at an angle θ to its symmetry axis, the angle θ changes during irradiation. If the fractional dimensional changes parallel and perpendicular to the symmetry axis are $\Delta L_{\parallel}/L_{\parallel}$ and $\Delta L_{\perp}/L_{\perp}$, respectively, the fractional dimensional change along a direction initially inclined at θ_0 to the symmetry axis is given by

$$\frac{\Delta L_{\theta}}{L_{\theta}} \left(1 + \frac{1}{2} \frac{\Delta L_{\theta}}{L_{\theta}} \right) = \cos^2 \theta_0 \frac{\Delta L_{\parallel}}{L_{\parallel}} \left(1 + \frac{1}{2} \frac{\Delta L_{\parallel}}{L_{\parallel}} \right) + \sin^2 \theta_0 \frac{\Delta L_{\perp}}{L_{\perp}} \left(1 + \frac{1}{2} \frac{\Delta L_{\perp}}{L_{\perp}} \right). \quad (4)$$

Therefore, under these conditions, a plot of

$$\frac{\Delta L_{\theta}}{L_{\theta}} \left(1 + \frac{1}{2} \frac{\Delta L_{\theta}}{L_{\theta}} \right) , \quad (5)$$

against $\sin^2 \theta_0$ should be a straight line. Plots of this relationship are shown in Figs. 11.44 and 11.45 for the massive pyrocarbon and hot-worked graphite samples irradiated in cell 9 of capsules GE-H-13-13 and GE-H-13-14. The data are in good agreement with the predicted relationship given in Eq. (4).

When the irradiation-induced dimensional changes are small, the Simmons relationship between thermal expansion and dimensional change seen in Eq. (1) has been found to be valid (Ref. 5). The crystallite dimensional changes, $\Delta X_a/X_a$ and $\Delta X_c/X_c$, may therefore be obtained by extrapolating plots of dimensional change versus thermal expansion coefficient such as shown in Figs. 11.42 and 11.43. However, when the crystallite c-axis expansion exceeds about 5%, these equations are no longer accurate and the situation is better represented by equations relating the macroscopic dimensional changes to the crystallite dimensional changes by preferred orientation parameters (Ref. 6). When the crystallite changes are large and the polycrystalline bodies highly oriented, the effects of porosity and intercrystalline restraints may be neglected and the dimensional changes are given by (Ref. 7):

$$\ln \left(1 + \frac{\Delta L_x}{L_x} \right) = R_x \ln \left(1 + \frac{\Delta X_a}{X_a} \right) + (1 - R_x) \ln \left(1 + \frac{\Delta X_c}{X_c} \right) , \quad (6)$$

Fig. 11.42--Plot of dimensional change versus thermal expansion coefficient for massive pyrolytic carbon samples of various orientations, after irradiation to $1 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ Mev}$) at about 800°C

Fig. 11.43--Plot of dimensional change versus thermal expansion coefficient for hot-worked graphite samples with various orientations, after irradiation to $1 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ Mev}$) at approximately 800°C

Fig. 11.44-- $\Delta L_\theta/L_\theta (1 + 1/2 \Delta L_\theta/L_\theta)$ plotted against $\sin^2 \theta_0$ for massive pyro-carbon samples irradiated to $5.9 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ Mev}$) at approximately 1250°C . θ = angle between axis of sample and symmetry axis of parent block; L_θ = original length of sample

Fig. 11.45-- $\Delta L_\theta/L_\theta (1 + 1/2 \Delta L_\theta/L_\theta)$ plotted against $\sin^2 \theta_0$ for hot-worked graphite samples irradiated to 5.9×10^{21} n/cm² ($E > 0.18$ Mev) at approximately 1250°C. θ = angle between axis of sample and symmetry axis of parent block; L_θ = original length of sample

where R_x is related to the direction within the block and the density of (002) plane normals, $I(\phi)$, at an angle ϕ to the symmetry axis, as determined by X-ray preferred-orientation measurements. For the direction parallel to the symmetry axis, oz ,

$$R_{oz} = \frac{\int_0^{\pi/2} I(\phi) \sin^3 \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} ; \quad (7)$$

for the perpendicular direction, ox ,

$$R_{ox} = 1 - \frac{R_{oz}}{2} ; \quad (8)$$

and at any angle θ to the symmetry axis,

$$R_{\theta} = R_{oz} + \left(1 - \frac{3R_{oz}}{2}\right) \sin^2 \theta . \quad (9)$$

In order to calculate the crystallite dimensional changes by the data from the present series of experiments, the measurements from cell 1, where the changes were small, were analyzed according to the Simmons relationship, Eq. (1). The measurements from cell 9 were analyzed by the preferred-orientation relationship as shown in Eq. (6). In each case, a straight line was fitted to the data by the least-squares method and extrapolated to give the best values for $\Delta X_a/X_a$ and $\Delta X_c/X_c$. The standard deviations of the estimates were calculated from the curve-fitting statistics. The crystallite dimensional changes are plotted as a function of exposure in Figs. 11.46 and 11.47 and tabulated in Table 11.3.

The results confirm that the crystallite change rate increases with decreasing crystallite size and increasing irradiation temperature over the temperature range 800° to 1250°C. These trends are consistent with the heterogeneous nucleation of defect clusters which is believed to occur above about 500°C (Ref. 8). If the nucleating sites are associated with the crystallite boundaries, the number of point defects which escape annihilation and which are retained in clusters increases as the separation of the nucleating sites decreases. Similarly, the amount of damage retained increases with increasing irradiation temperature because of the increased mobility of the point defects. It is interesting to note that the present results show that crystallite dimensional change rates are highly crystallite-size dependent at temperatures as low as 800°C. Thus, an important improvement in the stability of graphite components operating under neutron irradiation at this temperature can be achieved by increasing the crystallite size of the material.

The thermal expansion coefficients of the hot-worked graphite and massive pyrocarbon samples in the two principal directions are shown as a function of fast-neutron exposure in Figs. 11.48 and 11.49. At 800°C, the expansion coefficient of the hot-worked graphite parallel to the hot-working axis shows a gradual increase with neutron exposure. The coefficient remains unchanged

Fig. 11.46--Crystallite dimensional changes at 800°C as a function of fast-neutron exposure

Fig. 11.47--Crystallite dimensional changes at 1250°C as a function of fast-neutron exposure

Table 11.3
CRYSTALLITE DIMENSIONAL CHANGES IN HIGHLY ORIENTED CARBONS AND GRAPHITES IRRADIATED
IN CAPSULES GE-H-13-13 AND GE-H-13-14

Irradiation Conditions			Material	Crystallite Dimensional Changes			
Dial No.	Temp (°C)	Exposure (n/cm ² , E > 0.18 Mev)		$100 \ln 1 + \frac{\Delta X_a}{X_a}$	Standard Deviation	$100 \ln 1 + \frac{\Delta X_c}{X_c}$	Standard Deviation
1	800	0.4x10 ²¹	Massive pyrocarbon	-0.18	0.04	+0.35	0.03
			Hot-worked graphite	-0.13	0.01	+0.24	0.02
			Annealed pyrocarbon	-0.02	0.02	+0.07	0.05
		1.0x10 ²¹	Massive pyrocarbon	-0.64	0.06	+2.17	0.06
			Hot-worked graphite	-0.30	0.03	+1.12	0.06
9	1250	1.9x10 ²¹	Massive pyrocarbon	-13.2	0.3	+28.7	0.3
			Hot-worked graphite	-9.5	0.4	+19.8	0.5
			Annealed pyrocarbon	-0.9	0.1	+3.5	0.2
		5.9x10 ²¹	Massive pyrocarbon	-47.4	2.2	+107.8	2.1
			Hot-worked graphite	-29.3	0.7	+67.2	0.9
			Annealed pyrocarbon	-4.5	0.3	+16.3	0.5

Fig. 11.48--Thermal expansion coefficient measured at 400°C of hot-worked graphite as a function of neutron exposure at (a) 800°C and (b) 1250°C

Fig. 11.49--Thermal expansion coefficient measured at 400°C of massive pyrocarbon as a function of neutron exposure at (a) 800°C and (b) 1250°C

perpendicular to the axis. However, at 1250°C, the expansion coefficient parallel to the axis passes through a maximum and then falls to about half its original value at about 6×10^{21} nvt ($E > 0.18$ Mev). In the perpendicular direction it increases slightly. The massive pyrocarbon behaves somewhat differently. At 800°C, the thermal expansion coefficient is unchanged by the irradiation. At 1250°C, it increases slightly perpendicular to the deposit and shows no sign of a subsequent decrease, despite the presence of visible delamination cracks after irradiation to 5.9×10^{21} nvt (see Fig. 11.36). Parallel to the deposit there is no significant change.

The increase in the thermal expansion coefficient parallel to the axis of the hot-worked graphite at 800°C and at low exposures at 1250°C is probably caused by the closure of microcracks. This effect is commonly observed in polycrystalline graphites irradiated to low exposures (Ref. 9). The "turn-down" in expansion coefficient at high exposures at 1250°C resembles that reported in several polycrystalline graphites irradiated at 170° to 200°C (Ref. 10), where the damage retention is also very large. The effect may be due to the generation of fresh porosity at high-damage levels. The lack of a turn-down in the massive pyrocarbon is probably due to a complete lack of crystallites with basal planes oriented at 90° to the deposit. Such crystallites could provide a restraining network and allow crack closure during a thermal expansion test. By contrast, hot-worked graphite has an appreciable proportion of crystallites oriented at 90° to the principal crystallite orientation. If considerable fresh porosity were generated during a high-exposure irradiation, these crystallites would be in a position where their low expansion coefficient along the basal planes would hold down the expansion coefficient of the aggregate.

CARBON IRRADIATIONS

Data from several irradiation experiments carried to high-neutron exposures show that the irradiation-induced densification that is familiar at low exposures is replaced by an expansion process at high exposures. It is suggested that the expansion is a consequence of porosity generated by inter-crystalline irradiation creep. When the expansion process becomes apparent at high exposures, the shape changes of all the carbons taken as a group depart from the relations predicted by crystallite averaging methods. The nearly isotropic carbons behave as if either the crystallite shape change rate is enhanced by the irradiation itself or that the expansion caused by the new porosity generated at high exposures is directed perpendicular to the original deposition plane. The data also show that, for turbostratic carbons with apparent crystallite height $L_c = 120$ to 200 Å, an irradiation at about 600°C to a dose of 1×10^{21} n/cm² does not influence the neutron-induced dimensional changes that occur in a subsequent irradiation at about 900°C. Plots of density changes and dimensional changes as a function of neutron exposure are presented in Figs. 11.50 through 11.55. Additional details are included in a topical report (Ref. 11).

Fig. 11.50--Summary plots showing density changes as a function of neutron exposure ($E > 0.18$ Mev) at approximately 600°C

Fig. 11.51--Summary plots showing density changes as a function of neutron exposure ($E > 0.18$ Mev) at approximately 900°C

Fig. 11.52--Plots of the length change versus neutron exposure ($E > 0.18$ Mev) for irradiation temperatures in the range 840° to 980°C

Fig. 11.53--Plots of the length change versus neutron exposure ($E > 0.18 \text{ MeV}$) for irradiation temperatures in the range 840° to 980°C

BORONATED GRAPHITE IRRADIATION STUDIES

Irradiation Experiment BG-1

The objective of this work is to determine by a systematic irradiation experiment the importance of several potential damage mechanisms in graphite containing relatively large amounts of boron (0.35 to 0.52 g B/cm³) in the form of B₄C granules. Results of the work will facilitate design of control materials for advanced HTGRs.

Irradiation experiment BG-1 is being conducted to irradiate selected materials at 600°C in an inert gas in the ETR. An exposure of 3×10^{21} n/cm² ($E > 0.18$ Mev) and 3×10^{21} n/cm² ($E < 0.4$ ev) is planned. Rectangular prismatic specimens (0.58 in. by 0.20 in. by 0.20 in. and 0.58 in. by 0.40 in. by 0.20 in.) are shielded from thermal neutrons ($E < 0.4$ ev) on three sides, top, and bottom to simulate B¹⁰ burnup gradients similar to those experienced by wall segments of large control rods. Irradiation began in April after being delayed one cycle at the ETR.

Irradiation of Spherical B₄C

The purpose of this work was to determine indirectly the upper and lower limits for swelling of B₄C particles in boronated graphite due to damage from the B¹⁰(n,α)Li⁷ reaction. Spheres of PyC-coated and uncoated B₄C were obtained from ORNL. The density of the 200-μ-diameter B₄C spheres was 95% of theoretical (2.52 g/cm³). Results of a chemical analysis of the uncoated B₄C are shown in Table 11.4. There were 27 uncoated particles, and 26 with 100-μ-thick PyC coatings (applied at ORNL). The spheres were held loosely in individual holes in a graphite holder so there was no restraint on swelling, and self-shielding from thermal neutrons was minimized.

Table 11.4
CHEMICAL ANALYSIS OF UNCOATED B₄C^a

Element	Concentration
Boron	82 wt-%
Carbon	19 wt-% (by difference)
Copper	200 ppm
Aluminum	100 ppm
Iron	10 ppm
Titanium	60 ppm
Vanadium	200 ppm
Silicon	600 ppm

^aAll elements except B and C detected by emission spectrograph techniques.

The spheres were irradiated in capsule P13J at $500^{\circ} \pm 50^{\circ}\text{C}$ to a neutron exposure of about $2.7 \times 10^{21} \text{ n/cm}^2$ fast ($E > 0.18 \text{ Mev}$) and $1.5 \times 10^{21} \text{ n/cm}^2$ thermal ($E < 0.4 \text{ ev}$). The B_4C attained a B^{10} burnup of 78% as determined from isotopic analysis.

The appearance of the PyC-coated particles was unchanged by the exposure, as shown in Fig. 11.56. All 26 coated spheres were recovered, and no cracked coatings were observed. Several uncoated spheres were inadvertently lost or identity put in doubt during the postirradiation examination so that only 21 of the original 27 were of use in determining irradiation effects. The uncoated spheres, which originally had a dimpled but glossy surface, developed a gray matte finish, as shown in Fig. 11.57. The gray deposit was probably $\text{Li}_2\text{B}_2\text{O}_4$ which was identified by X-ray diffraction in the uncoated B_4C . Neither lithium nor its compounds were detected in the irradiated B_4C which was coated with PyC. The particles could be picked up and held by static electricity on the end of a scalpel blade. Both the coated and uncoated spheres were strong enough so that they bounced without breaking when dropped about an inch into a glass vial.

Metallographic examination of both coated and uncoated particles revealed a somewhat more cracked and porous B_4C microstructure after irradiation, as shown in Figs. 11.58 and 11.59. However, accurate evaluation of irradiation effects in microstructure was difficult because of the wide variation in apparent porosity prior to irradiation. There was also the possibility that, during irradiation, the B_4C structural integrity was degraded so that apparent porosity introduced during metallographic polishing may have been significant. Some structural degradation was suggested by X-ray analysis, which indicated a decrease in B_4C crystallinity after irradiation. The anisotropy of the PyC coatings increased during irradiation as shown by polarized light examination of metallographic mounts. Typical examples of coated particle cross sections viewed between cross polarizers before and after irradiation are shown in Fig. 11.60.

Metallographic and radiographic analysis before and after irradiation permitted measurement of dimensional change. The 200- μ -diameter uncoated spheres increased in diameter about 9.5% (approximately 30 vol-%). The PyC-coated spheres (400 μ OD) underwent an average contraction in outside diameter of about 3.7%. It was difficult to distinguish the diameter of the B_4C particle within the coating by radiography. Indirect measurements of B_4C core diameters using metallographic techniques indicated the average diameter of the B_4C had remained unchanged during the irradiation. The ability of the relatively anisotropic PyC (estimated $\text{BAF} \approx 2$) to shrink down around an unyielding core during irradiation without failure is an interesting observation, but was irrelevant to the objectives of this experiment except to the extent that it restrained swelling of the B_4C .

The irradiation-induced dimensional changes in B_4C at 78% B^{10} burnup were strongly dependent on mechanical restrictions. Therefore, B_4C granules dispersed in a boronated graphite could be restrained to a degree by the matrix. For the case of maximum restraint, the B_4C would not contribute to dimensional change during irradiation except perhaps to limit contraction. At the other extreme (no restraint of B_4C swelling during irradiation) the

20X

20X

Fig. 11.56--PyC-coated B_4C spheres before irradiation (left) and after irradiation (right). There was no apparent damage to the coatings. The small particles visible on the irradiated spheres were debris from the irradiation crucible

~20X

~20X

Fig. 11.57--Uncoated B_4C spheres before irradiation (left) and after irradiation (right). The unirradiated spheres shown are a random sample out of which were picked 200- μ -diameter spheres for irradiation

200X

200X

Fig. 11.58--Bright-field photomicrographs of uncoated B_4C before (left) and after (right) irradiation. In general, the microstructure of the irradiated B_4C appeared more porous; however, isolated examples of similar microstructure before and after irradiation could be found

50X

50X

Fig. 11.59--Bright-field photomicrographs of PyC-coated B_4C before (left) and after (right) irradiation

50X

50X

Fig. 11.60--Photomicrographs between crossed polarizers of PyC-coated B₄C before irradiation (left) and after irradiation (right). The anisotropy of the PyC increased during irradiation, as indicated by the increased intensity of the Maltese cross

contribution to dimensional change at 78% B^{10} burnup could be significant. For example, a 30 vol-% swelling of B_4C in a boronated graphite containing 35 vol-% B_4C (0.63 g B/cm^3) would contribute about 10 vol-% to the composite material. This volumetric change could be accommodated by an isotropic linear dimensional change of about 3%.

The degree of restraint would be a complex factor determined by strength of the matrix, size of the irradiated body (self-shield effects), and B^{10} burnout gradient as discussed in the proposed model (Ref. 2). The contribution of B_4C to dimensional change in actual absorbers would probably be intermediate between the two possible extremes discussed here.

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