Uranium Loss from Biso-Coated Weak-Acid-Resin HTGR Fuel

R. L. Pearson
T. B. Lindemer

OAK RIDGE NATIONAL LABORATORY

OPERATED BY UNION CARBIDE CORPORATION FOR THE ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy \$4.00; Microfiche \$3.00

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Energy Research and Development Administration/United States Nuclear Regulatory Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ORNL/TM-5552
Dist. Category UC-77

Contract No. W-7405-eng-26
CHEMICAL TECHNOLOGY DIVISION
HTGR BASE TECHNOLOGY PROGRAM
Fuel Chemistry Studies (189a 01329)

URANIUM LOSS FROM BISO-COATED WEAK-ACID-RESIN HTGR FUEL

R. L. Pearson
T. B. Lindemer

Date Published: February 1977

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
1. INTRODUCTION	1
2. EXPERIMENTAL PROCEDURE	1
3. RESULTS	3
3.1 Weak-Acid-Resin UC_2	3
3.2 Fully Dense UC_2	8
3.3 Weak-Acid-Resin UO_2	13
3.4 Weak-Acid-Resin UO_2-UC_2	13
4. ANALYSIS OF DATA	16
5. DISCUSSION	22
6. CONCLUSIONS	24
7. ACKNOWLEDGMENTS.....	25
8. REFERENCES.....	26

URANIUM LOSS FROM BISO-COATED WEAK-ACID-RESIN HTGR FUEL

R. L. Pearson and T. B. Lindemer

ABSTRACT

Recycle fuel for the High-Temperature Gas-Cooled Reactor (HTGR) contains a weak-acid-resin (WAR) kernel, which consists of a mixture of UC_2 , UO_2 , and free carbon. At $1900^\circ C$, BISO-coated WAR UC_2 or UC_2 - UO_2 kernels lose a significant portion of their uranium in several hundred hours. The UC_2 decomposes and uranium diffuses through the pyrolytic coating. The rate of escape of the uranium is dependent on the temperature and the surface area of the UC_2 , but not on a temperature gradient. The apparent activation energy for uranium loss, ΔH , is ~ 90 kcal/mole. Calculations indicate that uranium loss from the kernel would be insignificant under conditions to be expected in an HTGR.

1. INTRODUCTION

During 1974, a decision was made to change the reference recycle fuel for the High-Temperature Gas-Cooled Reactor (HTGR). A weak-acid-resin (WAR) fissile kernel containing a mixture of UC_2 and UO_2 was selected because of its superior irradiation performance.¹ This report discusses some properties of WAR particles, especially their potential to lose uranium when UC_2 -containing particles are exposed to high temperatures for long periods of time.

2. EXPERIMENTAL PROCEDURE

All of the kernels used in this study were prepared from weak-acid resins. The characteristics of the particles are given in Table 1. About 50 particles from each batch were mounted in a carbon disc and heat-treated in a graphite-resistance furnace where a known temperature and temperature gradient were maintained. The details of the procedure used to prepare particles for heat treatment have been published previously.² Particle

Table 1. Characterization of WAR coated particles prepared for use in studies of uranium loss

Coated particle	OR-2215	A-599	OR-2120-H	OR-2238-H	OR-2121-H
Batch number	0	69.4 ± 2.1	92	~ 100	92
Percent conversion	15.55	17.32	23.66	23.52	20.03
Uranium content, wt %					
	Mean ^a	Mean ^a	Mean ^a	Mean ^a	Mean ^a
Kernel					
Diameter, μm	371.3 (15.4)	354.2 (15.9)	315.3 (29.1)	340.9 (19.9)	315.3 (29.1)
Density, g/cm ³	3.66	3.03 ⁴	5.28	3.17	5.28
Buffer layer					
Thickness, μm	69.3 (9.8)	58.8 (9.4)	74.9 (11.3)	81.9 (3.9)	74.6 (11.3)
Inner carbon coating					
Thickness, μm					36.1 (3.8)
SiC layer					
Thickness, μm					28.4 (2.7)
Outer carbon coating					
Thickness, μm	42.0 (3.0)	35.4 (3.5)	88.6 (6.6)	62.3 (3.6)	49.2 (3.3)

^aNumbers in parentheses are standard deviations.

position and changes in kernel diameter were determined from radiographs of the mounted discs taken before and after heating. In this report, kernel diameter is defined as the diameter of the uranium-containing portion of the WAR kernel; the original diameter of the entire WAR kernel did not change with heat treatment. Uranium contents within the particles were obtained by microprobe analysis of a metallographic specimen; the uranium content is defined here relative to the uranium content in as-coated kernels from the same batch.

3. RESULTS

3.1 Weak-Acid-Resin UC_2

Two discs containing BISO-coated WAR kernels which had been essentially fully converted to UC_2 ,³ batch numbers OR-2120-H and OR-2288-H, were heat-treated at a maximum temperature of 1940°C in a 278°C/cm gradient. Radiographs of the discs were taken as prepared and after 143, 365, and 551 hr in the furnace. The kernel diameters decreased, the rate depending on the temperature of the individual particles. Shrinkage of the kernels could be detected in particles heat-treated at temperatures as low as 1700°C. One of the particles heated at 1900°C had no kernel remaining after 551 hr, as can be seen in Fig. 1.

Two particles, Nos. 22 and 23 of batch OR-2288-H, which had been held at 1800°C for 551 hr, were photographed after metallographically polishing one of the discs. The results revealed that the structure of the resin kernel was intact in each case and that little or no densification had occurred; however, there was a distinct, observable boundary line within the resin kernel. The diameter of the section enclosed by the boundary was the same as that of the uranium-bearing portion of the kernel, as observed in the radiograph. Particles 22 and 23 were also submitted for microprobe analysis. Backscattered electron and UM_{α} x-ray intensity images were prepared. Photographs depicting the results of four types of analyses on the two particles are shown in Figs. 2 and 3 respectively. Microprobe data for both particles, as well as for ten as-coated archive particles chosen at random from batch OR-2288-H, are plotted in Fig. 4. Step scans were

Fig. 1. Radiographs of a BISO-coated WAR UC₂ particle heat-treated at 1900°C for various times.

Fig. 2. Uranium distribution in BISO-coated WAR UC_2 fuel particle 22, which had been heat-treated at 1800°C for 551 hr. The arrow points to the retreating UC_2 interface.

Fig. 3. Uranium distribution in BISO-coated WAR UC_2 fuel particle 23, which had been heat-treated at $1800^{\circ}C$ for 551 hr. The arrow points to the retreating UC_2 interface.

ORNL DWG. 75-8782

Fig. 4. Uranium content in BISO-coated WAR UC_2 kernels heat-treated at 1800°C for 551 hr vs distance from original edge of kernel.

taken every 5 μm along 100 μm of the outer radius of the kernels in particles 22 and 23. Each kernel had little uranium present in the outer portion, and the uranium loss often appeared to be occurring in a 15- μm -wide region. Two scans of particle 23 were made, one parallel and one normal to the temperature gradient; the uranium behavior in Fig. 4 corresponds to that shown in Fig. 3. Calculations based on diameter measurements showed that almost 50% of the uranium in particle 22, which was originally 365 μm in diameter, had escaped from the kernel. About 80% of the uranium had escaped from particle 23. No significant amount of uranium was detected in either the buffer or the LTI layer.

Measurements of the kernel diameters in Fig. 1 were plotted as a function of time, as seen in Fig. 5. A linear relationship between kernel diameter and time was observed for BISO-coated UC_2 WAR particles. This linear dependence was reasonably typical.

Some of the kernels selected at random from BISO-coated WAR batch OR-2120-H were TRISO coated and identified as batch OR-2121-H. These particles were then loaded into a disc and heat-treated for periods as long as 665 hr. A sequence of radiographs of a pair of particles heated at 1862°C in a 278°C/cm temperature gradient is included in Fig. 6. As seen, the uranium has diffused into all parts of the particle inside the SiC layer but has not penetrated the SiC. The kernel diameter of this particle vs time is shown in Fig. 5; it apparently decreased slightly. Several dozen particles of batch OR-2121-H placed loosely in a hollow carbon rod were heated at 2100°C for 233 hr. Figure 7 shows photographs of one of the particles after it had been mounted and polished to midplane. The relative concentration of the uranium within the particle is plotted in Fig. 8. Volumetric mass-balance calculations indicate that the uranium lost by the kernel is approximately equal to that found in the buffer and LTI layers, again indicating that the TRISO particles retained all the original uranium content.

3.2 Fully Dense UC_2

BISO-coated, fully dense UC_2 kernels were heated in the same discs that contained the WAR UC_2 particles. Shrinkage of the fully dense UC_2 kernels was never observed.

Fig. 5. Kernel diameters vs time for various WAR particles heat-treated at the specified temperatures.

Y-137565

0 hr

309 hr

582 hr

665 hr

PARTICLE - TRISO WAR - UC_2
TEMPERATURE - $1862^{\circ}C$
TEMPERATURE GRADIENT - $278^{\circ}C/cm$

Fig. 6. Radiographs of a TRISO-coated WAR UC_2 particle heat-treated at $1862^{\circ}C$ for various periods.

Y-139672

150 μm

OPTICAL

100 μm

BACKSCATTERED ELECTRONS

U Ma X-RAYS

HEAT TREATED FOR 233 HR. AT 2100°C

Fig. 7. Uranium redistribution in a TRISO-coated WAR UC_2 particle heat-treated at 2100°C for 233 hr.

ORNL DWG 76-1481R1

Fig. 8. Relative uranium concentration in a TRISO-coated WAR UC_2 particle heat-treated at 2100°C for 233 hr vs distance from the SiC layer.

3.3 Weak-Acid-Resin UO_2

The diameters of BISO-coated WAR UO_2 kernels held at 1931°C for 435 hr in a $278^\circ\text{C}/\text{cm}$ temperature gradient were unchanged, as shown in Fig. 5. There was no redistribution of uranium within the particle.

3.4 Weak-Acid-Resin $\text{UO}_2\text{-UC}_2$

A disc containing BISO-coated WAR kernels of the composition 31% UO_2 --69% UC_2 (batch A-599) was heated for as long as 730 hr at a maximum temperature of 1927°C in a $278^\circ\text{C}/\text{cm}$ gradient. The initial rate of decrease of kernel diameter at 1927°C was the same as that for a 100% UC_2 kernel up to ~ 200 hr, when the rate of kernel shrinkage began to decrease. The diameter of a kernel heated at 1927°C decreased up to 582 hr but then remained essentially constant with further heating. Radiographs of this particle are shown in Fig. 9. The final uranium-containing volume was $\sim 30\%$ of the original kernel volume. This strongly suggests that the UC_2 was lost, leaving only the original UO_2 content. It also suggests that the WAR conversion of UO_2 to UC_2 during kernel manufacture proceeds from the outside to the inside of the kernel.

All of the uranium associated with UC_2 within a loose sample of these 31% UO_2 --69% UC_2 particles was lost when they were held at a uniform, constant temperature of 2100°C for 325 hr. Therefore, the mechanism for uranium loss is not dependent on a temperature gradient.

An examination of the radiographs for some of the particles in the disc revealed interesting characteristics of the uranium loss (see Fig. 10). Sufficient uranium collected in the buffer layer on the hotter side during the initial heat-treating times to be detected in the radiographs; however, this buffer-layer uranium content was gradually lost with time, as illustrated. The outside of the kernel develops a lower content of uranium than the central portion, and an interface between the two regions can therefore be detected in the radiographs. This in-kernel effect can be seen in Fig. 9 at 73 hr; here, because of a higher temperature, the uranium loss is in a more advanced stage. The central uranium-containing portion also develops a tendency to become located off-center relative to the original

Y-137564

0 hr

73 hr

158 hr

582 hr

PARTICLE - BISO WAR UO_2 (31%) - UC_2 (69%)
TEMPERATURE - 1927°C
TEMPERATURE GRADIENT - 278°C/cm

Fig. 9. Radiographs of a BISO-coated WAR (31% UO_2 - 69% UC_2) particle heat-treated at 1927°C for various times. The cold side of the particle is at the top. The final volume of the uranium-containing kernel represents $\sim 30\%$ of the original kernel volume, thus indicating that only UO_2 is left in the particle.

0 hr

53 hr

75 hr

127 hr

PARTICLE - BISO WAR UO_2 (31%) - UC_2 (69%)
TEMPERATURE - 1863°C
TEMPERATURE GRADIENT - 278°C/cm

Fig. 10. Radiographs of a BISO-coated WAR (31% UO_2 --69% UC_2) particle heated at 1863°C in a 279°C/cm gradient; the hot side is at the bottom. These radiographs demonstrate some of the characteristics of uranium loss (see text).

kernel surface, as seen in Figs. 9 and 10. This portion is always oriented toward the cold side of the particle, probably as the result of local equilibrium for

The CO pressure (P_{CO}) is constant everywhere and would approximate that for the mean temperature. Consequently, P_{CO} at the hotter side of the particle would be below that for the existence of UO_2 ; thus more UC_2 would be formed. The reverse process would occur at the cold side.

4. ANALYSIS OF DATA

Quantitative representation of the time-dependent data for the uranium loss is dependent on the proper selection of a mathematical model for the loss rate. The loss rate might be controlled either by steady-state diffusion of uranium through the LTI layer or by the rate of uranium evaporation at the surface of the UC_2 crystallites in the WAR kernels. Solid-state diffusion within the UC_2 crystallites is not a viable possibility for rate control because no such diffusion is necessary for the loss process; UC_2 always exists at the receding UC_2 -C interface.

A model for rate control by uranium evaporation in the WAR UC_2 kernels will be developed first. A general statement of the model is:

$$(\text{U lost}) = (\text{rate constant})(\text{surface area})(\text{time}) \quad (2)$$

or

$$\rho_{\text{U}} \frac{4\pi}{3} (r_o^3 - r_f^3) = k_s \left\{ \left(\frac{S}{\bar{V}} \right) \bar{V} \right\} t , \quad (3)$$

in which ρ_{U} is the density of uranium in the WAR kernel, r_o and r_f are the initial and final kernel diameters, k_s is the rate constant in (g of uranium) $\text{cm}^{-2} \text{sec}^{-1}$, S/V is the measured surface area per unit volume of WAR kernel in cm^2/cm^3 , and t is time in sec. The term $\bar{V}$ is the mean-value-theorem average volume, in cm^3 , from which the uranium has vaporized over the entire experimental time. The volume of kernel from which the uranium is vaporizing during any time increment, Δt_1 , is depicted in Fig. 11; here

ORNL DWG. 1082

Fig. 11. Representation of a WAR UC_2 kernel from which the uranium is released from the incremental volume ΔV_i .

C is the depth of the layer from which uranium is vaporizing. During any Δt_i , one obtains

$$\Delta V_i = \frac{4\pi}{3} \left[r_i^3 - (r_i - C)^3 \right]. \quad (4)$$

Therefore, over all time, the mean-value theorem leads to:

$$\bar{V} = \frac{4\pi}{3} \frac{1}{(r_o - r_f)} \int_{r_f}^{r_o} [r^3 - (r - C)^3] dr \quad (5)$$

$$= \frac{4\pi}{3} \frac{1}{(r_o - r_f)} \left\{ C(r_o^3 - r_f^3) - \frac{3C^2}{2} (r_o^2 - r_f^2) + C^3 (r_o - r_f) \right\}. \quad (6)$$

Equation (6) can be substituted in Eq. (3) and k_s solved for in terms of experimentally measured parameters. A simplified equation is achieved as long as C is much smaller than r_f ; in this case, one obtains:

$$\rho_U \left(r_o^3 - r_f^3 \right) \approx k_s \frac{S}{V} t \frac{(r_o^3 - r_f^3)}{(r_o - r_f)} C \quad (7)$$

or

$$r_o - r_f = \frac{k_s}{\rho_U} \frac{S}{V} C t. \quad (8)$$

Thus, $(r_o - r_f)$ is proportional to t ; since the experimental r_f is generally observed to be linearly dependent on t , this is consistent with the premise that the rate-controlling mechanism is evaporation of uranium from the UC_2 -containing WAR kernel.

In the case of rate control by evaporation of uranium from the surface of a fully dense UC_2 kernel, the rate equation would be:

$$\rho_U^* \frac{4\pi}{3} (r_o^3 - r_f^3) = k_s \bar{S} t, \quad (9)$$

in which ρ_U^* is the uranium density in the fully dense kernel and the average surface area of the shrinking kernel is:

$$\bar{S} = 4\pi \frac{1}{r_o - r_t} \int_{r_f}^{r_o} r^2 dr. \quad (10)$$

Combination of the last two equations gives

$$r_o - r_f = \frac{k_S}{\rho_U} t . \quad (11)$$

For rate control by steady-state diffusion of uranium through the LTI layer, the uranium flux would be constant. Therefore, the volume of UC_2 lost from the WAR kernel would be linearly dependent on time. In other words,

$$\frac{4\pi}{3} \rho_U (r_o^3 - r_f^3) = k_D t , \quad (12)$$

in which k_D is the rate constant in (g of uranium) $cm^{-2} sec^{-1}$. [Equation (12) would also be applicable to rate control by a mechanism operating at an interface such as the LTI-buffer or LTI-matrix interfaces.] Calculation of k_D at different heating times for the same particle sometimes resulted in constant k_D values for all times. These data, therefore, did not lead to constant k_S values from Eq. (8) at all times. However, as mentioned earlier, Eq. (8) was more often followed and will be used to correlate all the data collected in this study.

The data analysis was accomplished with a simple procedure. The r -vs- t data for each particle were fitted to the linear equation $r = r_o - bt$ by least-squares techniques; both r_o and b were solved for. Thus, $r_f = r_o - bt_f$ and Eq. (8) were used to give:

$$k_S = \frac{\rho_U b}{C\left(\frac{S}{V}\right)} . \quad (13)$$

These values are given in Fig. 12 vs $10^4/T$ for the WAR data. The apparent activation energy for the data in Fig. 12 was found to be 97.9 kcal/mole (409 kJ/mole) by least-squares techniques. For the WAR 31% UO_2 --69% UC_2 data, the slope b was determined as above from the initial r_f -vs- t values. The k_S values, which are plotted in Fig. 13, can be seen to be nearly equivalent to the values in Fig. 12.

Because the data of Figs. 12 and 13 overlap and the ΔH values are nearly the same, and because the volume of kernel remaining in the 31% UO_2 --69% UC_2 kernel was 30%, we concluded that both types of particles show identical characteristics of UC_2 loss. In other words, the uranium originated only with the UC_2 fraction of the fuel. An average value of $\Delta H = 90$ kcal/mole (377 kJ/mole) was used in further calculations, and the average

Fig. 12. Temperature characteristics of uranium vaporization from BISO-coated WAR UC_2 . The least-squares fit of these data is shown and can be represented by $k_s = 0.0441 \exp(-97,300/RT)$.

Fig. 13. Temperature characteristics of uranium vaporization from BISO-coated WAR 31% UO_2 --69% UC_2 . The least-squares fit of these data is shown and can be represented by $k_S = 0.00124 \exp(-82,400/RT)$.

behavior of the data in Figs. 12 and 13 can be represented by the equation

$$k_S = 0.0075 \exp(-90,000/RT). \quad (14)$$

5. DISCUSSION

We can offer a plausible explanation for the loss of UC_2 , but not UO_2 , from the kernels. The UC_2 , UO_2 , and carbon are in thermodynamic equilibrium and establish given gas pressures P_U and P_{CO} within the particle. As uranium is lost from the particle, the system attempts to maintain the equilibrium P_U via the reaction $UC_2 \rightarrow U_{(g)} + 2C$. Once the UC_2 has completely disappeared, however, the equilibrium $UO_2 + 2C \rightleftharpoons U_{(g)} + 2CO$ becomes established. For a short while, uranium is lost from the particle while CO is retained and P_{CO} is increased within the particle. However, since the equilibrium constant $k_{eq} = P_{CO}^2 / P_U$ must be satisfied, P_U is lowered drastically in the particle, thus reducing the uranium gradient across the particle coatings to the point where no significant uranium flux is possible. Note that intact irradiated oxide HTGR particles have been shown to retain CO, krypton, and xenon, with CO pressures orders of magnitude higher than those for the UO_2 - UC_2 -C-CO equilibrium in the present particles.⁴⁻⁷

Observations of uranium loss from WAR UC_2 -containing particles, but not from fully dense UC_2 particles, may be explained via Eqs. (8) and (11). The ratio of Eq. (8) to Eq. (11) gives, for identical k_S and t ,

$$\begin{aligned} \frac{(r_o - r_f)_{WAR}}{(r_o - r_f)_{dense}} &= \frac{\rho_U'}{\rho_U} \frac{S}{V} C \\ &\approx \frac{11}{2.9} \times \left(120 \times 10^{11} \frac{cm^2}{cm^3} \right) (15 \times 10^{-11} cm) \\ &\approx 4800. \end{aligned} \quad (15)$$

Here S/V was obtained from a measured $37 \text{ m}^2/\text{g}$ for WAR UC_2 particles by multiplying the latter number by the density of the WAR particles. Therefore, in the time required for a WAR UC_2 kernel to disappear ($r_o - r_f \approx$

150 μm), the radius of a fully dense kernel would decrease only 150/4800 or 0.032 μm , an unobservable amount.

A recent report issued by the General Atomic Company⁸ summarizes the results of tests which are part of an extensive program directed toward the development of fuel for the first commercial HTGRs. These results have led to the selection of TRISO-coated UC_2 as the reference fresh fissile particles and TRISO-coated WAR UC_2 as the reference recycle fissile particles. Calculations were performed with the data published in this report to demonstrate the possible effect of uranium loss during the ~ 4 -year fuel life. These calculations were performed with Eqs. (8) and (14) at $t = 4$ years. From Eq. (8) the value of the product $(S/V)C t/\rho_U$ is $\sim (120 \times 10^4)(15 \times 10^{-4})(1.26 \times 10^8)/2.9$ or $7.9 \times 10^{10} \text{ cm}^3 \text{ sec (g U)}^{-1}$. Thus $(r_o - r_f)/(7.9 \times 10^{10}) = k_g = 0.0075 \exp(-90,000/RT)$. This equation can be used along with the relation between radius and volume to calculate the uranium losses shown in Table 2 for a BISO-coated WAR UC_2 particle having $r_o = 0.0165 \text{ cm}$. A distribution of peak and time-average centerline temperatures of fuel in a planned commercial HTGR reactor was recently published in a report by Harmon and Scott.⁸ The data in the right-hand column of Table 2 were derived from Fig. 8 of that report. Clearly, the extent of uranium loss calculated here is inconsequential to the performance of the total TRISO-coated WAR UC_2 fuel in a core at HTGR design temperatures. However, the results in Table 2 would seem to advise against exposure of WAR UC_2 fuel to higher temperatures in any future HTGR design; the uranium would probably permeate the entire particle within the SiC layer in a manner similar to that shown in Figs. 6-8 and subsequently lead to particle failure.

Table 2. Calculated uranium loss in 4 years from 330- μ m-diam, BISO-coated UC_2 -containing WAR particles

T ($^{\circ}$ C)	Percent uranium lost ^a	Volume percent of fuel whose time-average temperature is $\geq T^b$
1590	99.9	0
1500	60.0	0
1400	16.0	0
1350	7.2	0
1300	3.0	≤ 0.5
1250	1.2	≤ 1
1200	0.43	≤ 10
1100	0.046	≤ 50
1000	0.0034	≤ 70

^aUranium is lost only from the UC_2 portion of the kernel, not from the UO_2 portion.

^bSee Fig. 8 in ref. 8.

6. CONCLUSIONS

1. The present work has demonstrated a loss of uranium from the UC_2 in either UC_2 or UC_2 - UO_2 WAR kernels contained in BISO-coated HTGR fuel particles. This loss is not dependent on a temperature gradient and occurs at easily measurable rates at $T \geq 1650^{\circ}$ C with an activation energy of ~ 90 kcal/mole (377 kJ/mole).
2. TRISO particles containing UC_2 or UC_2 - UO_2 WAR kernels apparently retain the uranium; although uranium is lost from the kernels, a significant gain is observed in the uranium content of the buffer and LTI layers within the SiC layer.
3. The uranium loss from WAR kernels appears to be a consequence of the extensive surface area, $\sim 120 \times 10^4$ cm²/cm³. It apparently occurs across a ~ 15 - μ m-wide interface that recedes toward the center of

the WAR kernel. On the other hand, the surface area of fully dense UC_2 kernels is only that of the geometrical surface area and is insufficient to permit observable uranium loss.

4. Uranium loss was not observed either from WAR UO_2 kernels in BISO particles or from the UO_2 portion of WAR UC_2 - UO_2 kernels in BISO particles. A probable explanation for the loss of uranium from UC_2 , but not from UO_2 , has been developed from the thermodynamics of the UO_2 - UC_2 -C-CO- $U_{(g)}$ system.
5. Uranium loss from UC_2 -containing WAR kernels is calculated to be inconsequential under conditions expected to be encountered in an HTGR. All of the uranium would apparently be retained within the SiC coatings of the HTGR TRISO particles. It might accumulate to a small extent within the inner LTI layers of the highest-temperature particles in the HTGR core, but these particles constitute only a small fraction of the total fissile particles in the core.
6. The observed loss of uranium from BISO particles and the redistribution of uranium within TRISO particles would appear to preclude the use of UC_2 -containing WAR particles at temperatures higher than those of the present HTGR design.

7. ACKNOWLEDGMENTS

The authors wish to thank R. L. Beatty, G. W. Weber, W. J. Lackey, Jr., W. D. Mason, E. T. Rose, R. S. Crouse, and O. B. Cavin for their assistance with preparation and examination of fuel particles. Appreciation is also expressed to Martha Stewart, Betty Drake, and Christine Flanary for the editing and typing of this manuscript.

8. REFERENCES

1. F. J. Homan, T. B. Lindemer, E. L. Long, Jr., T. N. Tiegs, and R. L. Beatty, "Stoichiometric Effects on Performance of HTGR Fuels from the U-C-O System," submitted to Nucl. Technol.
2. T. B. Lindemer and R. L. Pearson, Kernel Migration for HTGR Fuels from the Th-U-C-O-N System, ORNL/TM-5207 (April 1976); also accepted for publication in J. Am. Ceram. Soc.
3. G. W. Weber, R. L. Beatty, and V. J. Tenmery, "Processing and Composition Control of Weak-Acid Resin-Derived Fuel Microspheres," submitted to Nucl. Technol.
4. HTGR Fuels and Core Development Program, Quarterly Progress Report for Period Ending Aug. 31, 1975, GA-A13592 (1975), pp. 98-113.
5. G. W. Horsley, G. J. Weldrick, J. A. Turnbull, and R. Shipp, "Influence of Irradiation Temperature, Burnup, and Fuel Composition on Gas Pressure (Xe, Kr, CO, CO₂) in Coated Particle Fuels," J. Am. Ceram. Soc. 59, 1-4 (1976).
6. T. B. Lindemer, "Measurement and Interpretation of CO and Kr + Xe in Irradiated ThO₂-Containing Particles," submitted to J. Am. Ceram. Soc.
7. L. W. Graham, "The Development and Performance of HTGR Core Materials," presented at the Gas-Cooled Reactor Information Meeting, Oak Ridge, Tenn., April 27-30, 1970; CONF-700401 (April 1970), pp. 494-517.
8. D. P. Harmon and C. B. Scott, Development and Irradiation Performance of LHTGR Fuel, GA-A13173 (October 1975).

ORNL/TM-5552
Dist. Category UC-77

INTERNAL DISTRIBUTION

1. E. J. Allen	42. K. J. Notz
2. R. A. Bradley	43. A. R. Olsen
3. A. J. Caputo	44. G. W. Parker
4. J. A. Carpenter	45. H. Postma
5. T. E. Cole	46-54. R. L. Pearson
6. C. F. Coleman	55. W. H. Pechin
7. J. H. Coobs	56. R. H. Rainey
8. W. P. Eatherly	57. J. M. Robbins
9. D. E. Ferguson	58. J. H. Shaffer
10. P. A. Haas	59. J. W. Snider
11. F. E. Harrington	60. Martha Stewart
12. C. C. Haws	61. V. J. Tennery
13. F. J. Homan	62. T. N. Tiegs
14. J. D. Jenkins	63. D. B. Trauger
15. D. R. Johnson	64. V. C. A. Vaughen
16-23. P. R. Kasten	65. G. W. Weber
24. W. J. Lackey	66. J. R. Weir
25-32. T. B. Lindemer	67. R. P. Wichner
33. E. L. Long, Jr.	68. R. G. Wymer
34. R. A. Lorenz	69-70. Central Research Library
35. A. L. Lotts	71. Document Reference Section
36. J. C. Mailen	72. Laboratory Records, ORNL-RC
37. A. P. Malinauskas	73-82. Laboratory Records
38. W. J. McDowell	83. W. K. Davis (consultant)
39. C. S. Morgan	84. E. L. Gaden, Jr. (consultant)
40. M. T. Morgan	85. C. H. Ice (consultant)
41. F. H. Neill	86. R. B. Richards (consultant)

EXTERNAL DISTRIBUTION

87. Research and Technical Support Division, ERDA-ORO, P. O. Box E, Oak Ridge, Tn. 37830
88. Director, Reactor Division, ERDA-ORO, P. O. Box E, Oak Ridge, Tn. 37830
- 89-90. Director, Division of Nuclear Fuel Cycle and Production, ERDA, Washington, D.C. 20545
- 91-92. Director, Division of Reactor Research and Development, ERDA, Washington, D.C. 20545
- 93-268. Given distribution as shown in TID-4500 under category UC-77 - Gas-Cooled Reactor Technology