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SUBJECT: Determination of ^{232}U Daughter Products Released from HTGR Fuel During Refabrication, Part 2

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ABSTRACT

During the heat treatment step of High Temperature Gas-Cooled Reactor (HTGR) fuel beads, the ^{233}U -loaded fuel beads are exposed to temperatures as high as 1700°C . Since ^{233}U fuel beads unavoidably contain a small percentage of ^{232}U , decay products of ^{232}U might be released during the heat treatment step. To avoid shielding requirements, experiments were conducted using ^{232}Th -loaded fuel beads rather than ^{232}U -loaded fuel beads. Decay products of ^{232}U and ^{232}Th are the same after ^{223}Th .

Experimental data were obtained by monitoring the 583 and 2614 keV gamma emissions of ^{208}Tl . Computer simulations of the decay process and experimental data were used to infer what relative amount of the daughter products was removed.

The carbonization step ($300 - 500^\circ\text{C}$) has an effect on the loss of daughter products in the conversion step. Using uncarbonized fuel beads, approximately 50% of ^{220}Rn was removed at 300°C and approximately 20% of ^{220}Rn was removed at 200°C . At most, 5% of ^{220}Rn was removed from uncarbonized beads at 25°C . Marginal ^{220}Rn loss was detected at 100°C using pre-carbonized beads. At 1400°C , 92% ^{212}Pb , 70-90% ^{212}Bi , and 0% ^{224}Ra losses were observed. At 1600°C , 100% ^{212}Pb , 80-100% ^{212}Bi , and 3-7% ^{224}Ra losses were observed. At 1750°C , 100% ^{212}Pb , 80-100% ^{212}Bi , and 62% ^{224}Ra losses were observed. At 1800°C , 100% ^{212}Pb , 80-100% ^{212}Bi , and 86% ^{224}Ra losses were observed.

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1. SUMMARY

The design of an HTGR fuel refabrication facility requires attention since radioactive particles might be discharged to the off-gas. Such losses might occur when the fuel beads loaded with recycled ^{233}U and trace ^{232}U contaminant are heat treated at low temperatures ($\sim 600^\circ\text{C}$) to carbonize the bead and at high temperatures ($\sim 1700^\circ\text{C}$) to convert uranium oxide to uranium carbide. The heat treatment process may cause the release of ^{232}U daughter products into the off-gas.

Since ^{232}U and ^{232}Th have the same daughter products after ^{226}Ra , fuel beads loaded with ^{232}Th were heated in a fluidized furnace. Uncarbonized and precarbonized beads were used. Each heat treatment run was assumed to be conducted at constant temperature. Precarbonized beads were heated at $150^\circ\text{C}/\text{min}$ and uncarbonized beads were heated at $10^\circ\text{C}/\text{min}$. The fuel beads were kept at final temperature for about four hours except for two uncarbonized low temperature runs (200 and 300°C) which were held for six hours. The activity of the samples was then counted in a Ge-Li detector that monitored the 583 and 2614 keV emissions of ^{208}Tl . The experimental results were then compared with MATEXP computer simulations to infer which daughter products had been lost.

About a 5% ^{220}Rn loss was observed at room temperature from uncarbonized beads. A loss of 90% of ^{220}Rn was observed using uncarbonized beads at 500°C . Forty percent of ^{220}Rn was lost at 500°C using precarbonized beads. Less than 10% ^{220}Rn was lost at 100°C using precarbonized beads.

Four high temperature runs were conducted at 1400 , 1600 , 1750 , and 1800°C . One hundred percent of ^{220}Rn was assumed lost at the high temperatures. ^{212}Bi losses were between 80-100%. ^{212}Pb losses were 92% at 1400°C and 100% at higher temperatures. One, 3-7, 62, and 86% of ^{224}Ra were lost at 1400 , 1600 , 1750 , and 1800°C , respectively.

2. INTRODUCTION

2.1 Background

The Metals and Ceramics Division of ORNL is presently designing a pilot plant for refabrication of fuel from an HTGR. A description of the refabrication process can be found elsewhere (1). During the refabrication process the beads are heated to 600°C at $2^\circ\text{C}/\text{min}$ to decompose and remove constituent hydrocarbons and to drive off volatile material. This step is called carbonization. The beads are further heated to 1700°C at approximately $90^\circ\text{C}/\text{min}$ to partially convert the UO_2 to UC_2 . This step is called conversion. During carbonization and conversion steps, ^{232}U daughter products might be released. The determination of daughter products released will be used in the equipment specifications of the treatment facilities of the off-gases produced by the pilot plant as well as the full-scale plant.

The extracted ^{233}U from spent fuel elements will contain about 500 ppr ^{232}U that disintegrates to ^{212}Bi and ^{208}Tl which emit highly penetrating gamma rays. The handling of spent fuel elements requires extensive shielding. Due to the extremely long half life of ^{232}Th (1.39×10^{10} yr) compared to the half life of ^{232}U (74 yr), higher concentrations of ^{228}Th are expected from ^{232}U decay than from ^{232}Th decay. Daughter products of ^{232}U and ^{232}Th are identical after ^{228}Th as shown in Fig. 1. To eliminate heavy shielding, the experiments were performed using ^{232}Th -loaded beads instead of ^{232}U -loaded beads.

All ^{228}Th daughter products have much shorter half lives than ^{228}Th , so a secular equilibrium is created between ^{228}Th and ^{208}Tl after approximately 36 days (10 half lives of ^{224}Ra). A disturbance of the secular equilibrium concentrations of ^{228}Th daughter products will be detected by changes in ^{208}Tl gamma activity. ^{228}Th daughter products have different half-lives ranging from 3.64 days (^{224}Ra) to 0.158 sec (^{210}Po). Therefore the effect on ^{208}Tl gamma activity from a loss of one daughter product with a short half-life may be masked by the loss of another daughter product with a longer half-life. When ^{220}Rn , ^{212}Bi , and ^{212}Pb are lost, the return to secular equilibrium as measured by ^{208}Tl activity will follow closely the ^{212}Pb concentration changes. Secular equilibrium will have been established between ^{220}Rn and ^{208}Tl after 5 min and between ^{212}Pb and ^{212}Bi after 5 hr. ^{212}Pb having the longest half-life of the three daughter products will control the return to secular equilibrium between ^{208}Tl and ^{228}Th . If in addition ^{224}Ra is lost, ^{224}Ra will control the return to secular equilibrium between ^{208}Tl and ^{228}Th because ^{224}Ra has the longest half-life (3.64 days) of ^{228}Th daughter products. When ^{212}Pb and ^{224}Ra are lost, 100% ^{220}Rn is assumed removed and ^{212}Bi losses cannot be accurately determined. ^{210}Po losses are indeterminate and no attempt has been made to quantify these losses.

2.2 Objective and Method of Attack

To determine the percentage of ^{232}U daughter products lost during heat treatment of precarbonized and uncarbonized HTGR fuel beads at low temperatures (25 - 500°C) and at high temperatures (1400 - 1800°C), the following method of attack was proposed:

1. Replicate previous MIT experimental procedure (1) at 500°C using uncarbonized beads to ensure reproducibility.
2. Determine the effect of the carbonization step (100-500°C) on the structural matrix of the beads and the release of daughter products.
3. Determine the relative amounts of daughter products which are released at 25°, 200°, and 300°C from uncarbonized beads. This is important since uncarbonized beads loaded with ^{233}U are handled at room temperature and the beads are dried at 100°C.

4. Determine the relative amounts of daughter products which are released at high temperatures (1400 - 1800 C). This is important since the beads are exposed to temperatures as high as 1700 C during the conversion step.

5. Modify the MATEXP (2) computer program to simulate relative ^{208}Tl activity as a function of time. The computer simulations and the experimental data would be compared to infer which daughter products are lost.

2.3 Decay Equations for ^{228}Th Decay Chain

The decay chain of ^{232}U is shown in Fig. 1 to be identical to the decay chain of ^{232}Th after the common daughter product, ^{228}Th . A mathematical simulation of the decay chain which includes the ^{232}Th daughter products from ^{228}Th through ^{208}Tl has been developed. Since the half-life of ^{228}Th is 1.9 yr and the period of experimentation is only one week, changes in the ^{228}Th concentration due to decay are neglected; thus a ^{228}Th secular equilibrium is established for all species from ^{228}Th through ^{208}Tl .

Differential mass balances written for each species describe the overall decay process:

$$d[^{228}\text{Th}]/dt = 0.00 \quad (1)$$

$$d[^{224}\text{Ra}]/dt = \lambda_{\text{Th}}[^{228}\text{Th}] - \lambda_{\text{Ra}}[^{224}\text{Ra}] + Z_{\text{Ra}} \quad (2)$$

$$d[^{220}\text{Rn}]/dt = \lambda_{\text{Ra}}[^{224}\text{Ra}] - \lambda_{\text{Rn}}[^{220}\text{Rn}] + Z_{\text{Rn}} \quad (3)$$

$$d[^{212}\text{Pb}]/dt = \lambda_{\text{Rn}}[^{220}\text{Rn}] - \lambda_{\text{Pb}}[^{212}\text{Pb}] + Z_{\text{Pb}} \quad (4)$$

$$d[^{212}\text{Bi}]/dt = \lambda_{\text{Pb}}[^{212}\text{Pb}] - \lambda_{\text{Bi}}[^{212}\text{Bi}] + Z_{\text{Bi}} \quad (5)$$

$$d[^{208}\text{Tl}]/dt = (0.36)\lambda_{\text{Bi}}[^{212}\text{Bi}] - \lambda_{\text{Tl}}[^{208}\text{Tl}] + Z_{\text{Tl}} \quad (6)$$

A forcing function, Z , is included to simulate the release of various percentages of the species due to heat treatment through perturbation of the set of equations. For example, an 80% loss of a species is assumed to mean that the concentration of that species is 20% of what it would have been had none of that species been released; therefore, the rate of release is not a constant if species in the decay chain prior to the species being considered are also being released. Thus the form of the forcing function is:

$$Z_B = -f_A \lambda_A [A] \quad (7)$$

where f_A is the forcing function parameter (equal to the percentage of species A lost) (see Appendix 9.1 for a more detailed discussion) and A and B are successive species in the decay chain. In the previous study (1), a constant rate of daughter product release was assumed. As in the previous study, ^{216}Po is neglected as a member of the decay chain since its half-life is only 0.158 sec.

At ^{228}Th secular equilibrium, Eqs. (2) through (7) reduce to:

$$\begin{aligned} K &= \lambda_{\text{Th}} [^{228}\text{Th}] = \lambda_{\text{Ra}} [^{224}\text{Ra}] = \lambda_{\text{Rn}} [^{220}\text{Rn}] = \lambda_{\text{Pb}} [^{212}\text{Pb}] \\ &= \lambda_{\text{Bi}} [^{212}\text{Bi}] = (0.36)^{-1} \lambda_{\text{Tl}} [^{208}\text{Tl}] \end{aligned} \quad (8)$$

Since all simulations are performed on relative percent concentrations of ^{228}Th secular equilibrium values as a basis, K is assumed to be one for computational convenience. After initial conditions and percent loss of each daughter product are selected, the six simultaneous linear differential equations are solved to determine the concentration profile as a function of time for each species. A description of the solution technique is presented in Appendix 9.1.

3. APPARATUS AND PROCEDURE

3.1 Furnace Operation

The possible fracturing of uncarbonized resin beads during heat treatment is of primary concern. A previous study (1) found that thermal stresses caused uncarbonized beads to fracture whenever the furnace heatup rate was greater than 10 °C/min; a maximum heatup rate of 10 °C/min was specified. In the case of precarbonized beads, the fracturing problem does not exist. Therefore, a much higher heatup rate was used to minimize the amount of time to reach the desired temperature.

The amount of material charged to the furnace also depends on whether uncarbonized or precarbonized beads were used. Sample weight was 7.50 ± 0.01 gm for experiments with precarbonized beads. Uncarbonized beads experience both a weight and a volume decrease during heat treatment. Therefore, a larger amount of the uncarbonized resin (12 gm) was used so that the post-treatment sample weight would be approximately the same as the post-treatment sample weight for precarbonized beads.

After a sample has been weighed, it is placed in a glass flask containing argon. In those experiments using precarbonized beads, a second sample of the same weight is prepared, placed in an argon-filled aluminum container, labeled, and set aside as an untreated standard.

Figure 2 shows a schematic of the graphite resistance furnace. An empty, tared, aluminum container is secured to the bottom of the furnace. The sample beads are poured from the top of the furnace into the core, and the argon flow rate is adjusted to maintain fluidization. At this point, and for the remainder of the heat treatment, the beads are fluidized in the constricted portion of the furnace core, referred to in Fig. 2 as the fluidization chamber.

The temperature of the fluidized bed is monitored directly by a chromel-alumel thermocouple for temperatures below 800°C. For high temperature experiments, an optical pyrometer is used to monitor the temperature of the outer surface of the graphite tube. Bed temperature is raised to the desired level by adjusting power delivered to the furnace heating element. This temperature is kept constant for the period of heat treatment (usually four hours). When power is switched off, a helium cooling stream is passed over the heating element. Argon continues to flow through the core until bed temperature reaches 30°C, at which point the argon flow is stopped, fluidization is no longer maintained, and the resin beads fall through the bottom of the furnace core into the sample container. The sample is removed from the furnace, capped, and weighed. The sample is placed in a clean plastic bag, and taken to the gamma detector system for monitoring.

3.2 Air Purge Apparatus and Procedure

An apparatus was assembled to contact a sample of uncarbonized beads with air at room temperature over a period of several days. The apparatus consisted of a 4-in.-sintered-glass filtration funnel mounted on a ring stand and connected by plastic tubing to a small vacuum pump drawing one-third cubic foot of air per minute. Four grams of resin beads placed in the funnel formed a single layer across the surface.

To achieve the greatest possible change in relative ^{208}Tl activity, the air purge operation was continued for three days. The change in ^{208}Tl activity for a small loss of ^{220}Rn is maximized by allowing ^{208}Tl to come to a new secular equilibrium with ^{220}Rn . The presence in the decay chain of ^{212}Pb with its half life of 10.6 hr prevents ^{208}Tl from reaching secular equilibrium with ^{220}Rn until at least 74 hr or seven half-lives of ^{212}Pb , after the occurrence of any change in the amount of ^{220}Rn . At the end of three days the purging operation was halted. The sample was re-weighed, placed in an aluminum container, and taken to the gamma detection apparatus for monitoring.

3.3 Gamma Detection Apparatus and Procedure

Samples were monitored for gamma activity using a germanium-lithium detector. The detection apparatus was interfaced with a PDP-11 computer that was programmed to analyze the gamma spectrum obtained by the detector. The histogram analysis procedure has been described by Jackson et al. (1). Instantaneous activity can be measured by making the counting period very short. However, counting error decreases as the counting period increases. A counting period of 12 min was chosen since the error per count at 99% confidence was more than 10% for shorter intervals. In the counting procedure six peaks of the gamma ray histogram are monitored and analyzed. The six corresponding gamma energies and their sources are listed in Table 1.

Table 1. Sources of Gamma Emissions from Thoria-Loaded Resin Beads

<u>Gamma Ray Energy (keV)</u>	<u>Nuclide Source</u>
239	^{212}Pb
511	^{208}Tl
583	^{208}Tl
727	^{212}Bi
860	^{208}Tl
2614	^{208}Tl

Four thallium peaks are monitored. At 99% confidence, however, only the 583 and 2614 keV peaks have counting errors of less than 10%. The 510 and 860 keV peaks had counting errors of 10.4% and 16.8%, respectively, for the same confidence limit. Only the 583 and 2614 keV peaks were used in the calculation of relative ^{208}Tl activity.

Although an analysis of the 239 keV peak could determine directly the relative activity of ^{212}Pb , the resolution of the computer analysis routine was inadequate to exclude a peak corresponding to ^{224}Ra activity at 241 keV. Therefore, the relative ^{212}Pb activity computed for each spectrum is of doubtful accuracy. Similarly, an analysis of the 727 keV could determine directly the relative activity of ^{212}Bi . However, the counting error at 99% confidence was about 20%. Therefore no conclusions were drawn from the activity measurements for this peak. In future studies only the 583 and 2614 keV peaks should be monitored.

After a resin sample had been heated in the furnace, the beads were cooled, placed in a container, and transported to the detection apparatus. At least one-half hour elapsed between the time when power to the furnace

was switched off and the time when the first spectrum was recorded. Activity was monitored overnight for each experimental run. However, the automatic monitoring procedure was terminated prematurely for two experiments due to computer hardware failures.

Since the ^{208}Tl activity as a percentage of its secular equilibrium value was desired, the samples were monitored periodically until no further change in activity was observed. In experimental runs at or below 1600°C the return to equilibrium was governed by ^{212}Pb , with a half-life of 10.6 hr. A period of seven half-lives, or 74 hr, was required for the sample to return to secular equilibrium with ^{228}Th . For experiments at 1750 and 1800°C , however, sample activity continued to rise after three days, so these samples were monitored for a period of 8 days. These two samples should be monitored after 30 days to see if activity levels off.

3.4 Normalization Procedure

In those experiments involving the use of precarbonized beads, activity was normalized to the average activity of five untreated, standard samples (see Sect. 9.2). The normalized activities of the 583 and 2614 keV peaks were averaged for each count. Section 9.3 includes a sample normalization calculation.

In those cases where uncarbonized beads were used, activity was normalized to the sample activity three days after heat treatment. The assumption that ^{212}Pb controls the return to secular equilibrium proved correct when activity stopped increasing after three days. Errors associated with sample weighing and with self-shielding effects were avoided by using the treated sample as its own normalizing standard.

4. RESULTS

The experimental runs conducted are listed in Table 2. The experimental results and the computer simulations are presented in graphical form. The abscissa is time in hours and the ordinate is the percentage of secular equilibrium activity of ^{208}Tl (see Appendix 9.1). Time zero corresponds to the time at which the beads reached the heat treatment temperature. Experiments with precarbonized beads and the 500°C experiment with uncarbonized beads were normalized against the predetermined standard (see Appendix 9.2). Experiments with uncarbonized beads were normalized against their respective activities three days after the heat treatment. The graphs were prepared by plotting percentage of ^{208}Tl activities as a function of time. A computer simulation was then visually fitted to the experimental data.

Table 2. Experimental Conditions

Run No.	Heat Treatment Temperature (°C)	Duration at Heat Treatment Temperature (hr)	Heating Rate (°C/min)	Type of Beads
1	25 (air purge)	-	-	uncarbonized
2	100	4	90	precarbonized
3	500	4	10	uncarbonized
4	500	4	90	precarbonized
5	200	6	10	uncarbonized
6	300	5	10	uncarbonized
7	1400	4	150	precarbonized
8	1600	4	150	precarbonized
9	1750	4	150	precarbonized
10	1800	4	150	precarbonized

In Fig. 3 the data of the 500°C runs with precarbonized and uncarbonized beads are plotted; two computer simulation curves which encompass the data of the uncarbonized run are also shown. In Fig. 4 the data of the 100°C run with uncarbonized beads are plotted; no computer simulation curve has been fitted. In Figs. 5 and 6 the data of the 300 and 200°C runs with uncarbonized beads are plotted.

The data of the 1400, 1600, 1750, and 1800°C runs with precarbonized beads are presented in Figs. 7, 8, 9, and 10, respectively. In Fig. 11, the data of the high temperature runs (1400, 1600, 1750, and 1800°C) are plotted for a 75-hr duration.

5. DISCUSSION OF RESULTS

Once the forcing function parameter is assumed, a comparison is made between the simulation and experimental data to infer the relative amount of daughter products which have been lost. Therefore the inferred percentage loss of daughter products is very dependent upon the form of the forcing function. Since no attempt was made to study rates or mechanisms of daughter product removal, the modeling method was deemed appropriate. Different forms for the forcing functions will result in different values for the percentage removal of daughter products.

Losses of ^{212}Bi are presented as ranges because large ^{212}Bi losses are masked by ^{212}Pb losses. When 100% ^{212}Pb occurs, ^{212}Bi losses will be indeterminate because of the short ^{212}Bi half-life (60 min) compared to the heat treatment time (4 hr). Since ^{216}Po has a very short half-life (0.158 sec) compared to other ^{228}Th daughter products, ^{216}Po losses are ignored. The computer simulations of the high temperature runs assumed 100% ^{220}Rn losses.

^{208}Tl activity is presented as gamma emission per unit weight of bead after the heat treatment. A maximum of 7% weight loss occurred in the high temperature runs. Therefore total losses must also include this loss. Since experiments using precarbonized beads and without ^{224}Ra losses returned to the secular equilibrium existing prior to the heat treatment, all the daughter products must have been lost in proportion to the amount of bead lost. Experiments using uncarbonized beads were normalized against their activity measured after three days.

The uncarbonized beads which were exposed to room temperature air for three days showed about a 5% ^{220}Rn loss. An assumption was made that only ^{220}Rn was lost; therefore, a new secular equilibrium between ^{208}Tl and ^{228}Th is achieved after three days (7 half lives of ^{212}Pb). ^{220}Rn loss is equal to the decrease in ^{208}Tl activity. This experiment should be replicated since the sample activity was not measured overnight. An error of $\pm 6\%$ with 95% confidence limit exists in the data due to the counting procedure.

Experiments at 500°C with uncarbonized and precarbonized beads were compared (Fig. 4). The 500°C run with uncarbonized beads showed a 90% loss of ^{220}Rn while the 500°C run with precarbonized showed about a 40% loss of ^{220}Rn . Since the experimental technique was the same, the difference can be explained by the effect of the carbonization step: the carbonization step might cause bulk flow out of the beads. The 500°C precarbonized sample was not counted overnight; therefore, a replication of the experiment should be made to allow comparison with computer simulations with various amounts of ^{220}Rn losses.

Jackson et al. (1) reported a 500°C run using uncarbonized beads. Using their simulation technique, they report a 100% ^{220}Rn loss. When their experimental data are fitted with our simulation technique, their data lie below the 100% ^{220}Rn loss simulation curve.

Daughter product loss at 100°C was examined with precarbonized beads (Fig. 5) and at 300°C (Fig. 6) and 200°C (Fig. 7) with precarbonized beads. Forty five and 20% of ^{220}Rn was lost at 300 and 200°C , respectively. The data of the 300°C run has been fitted by two simulation curves to indicate the sensitivity of ^{208}Tl activity with different ^{220}Rn loss. At most, 10% ^{220}Rn was lost at 100°C . A further experiment should be made at 100°C using uncarbonized beads to determine ^{220}Rn loss since fuel beads loaded with uranyl nitrate are dried at 100°C .

Since 90% of ^{220}Rn is removed at 500°C from uncarbonized beads, it was assumed that 100% of ^{220}Rn was removed at higher temperatures. Therefore, the computer simulations assumed 100% ^{220}Rn loss. ^{212}Bi losses are presented as a range since the activity count was not done immediately after

the heat treatment. As a result, ^{212}Bi was approaching a secular equilibrium with ^{212}Pb . ^{212}Bi losses could be more precisely determined if the activity count could be made a few minutes after the heat treatment. The results of the high temperature experiments are presented in Table 3.

Table 3. Percentage Losses of ^{228}Th Daughter Products

Temperature (°C)	^{224}Ra (%)	^{212}Bi (%)	^{212}Pb (%)
1400	0	80-100	92
1600	3-7	80-100	100
1750	62	80-100	100
1800	86	80-100	100

^{212}Pb loss is complete by 1600°C. ^{224}Ra loss increases with increasing temperature. A series of experiments in which the time of heat treatment is varied should be performed at the high temperatures where ^{224}Ra is lost to check the assumption of a uniform rate of daughter product withdrawal. If daughter product withdrawal occurs as a pulse, then the results would indicate the same effect on ^{208}Tl activity regardless of heat treatment time.

Since the studies were conducted using ^{232}Th -loaded beads instead of ^{232}U loaded beads, the empirical results are not necessarily valid for uranium-loaded beads.

6. CONCLUSIONS

Based on experimental data fitted by computer simulations, the following conclusions have been made:

1. Ninety percent ^{220}Rn was released at 500°C from uncarbonized beads while 40% ^{220}Rn was released at 500°C from precarbonized beads. The carbonization step is responsible for the difference.
2. A maximum of 5% of ^{220}Rn was released from the uncarbonized beads which were exposed to a continuous stream of air.
3. A maximum of 5% of ^{220}Rn was released from precarbonized beads at 100°C.
4. ^{220}Rn losses were 45 and 20% at 300 and 200°C, respectively, with uncarbonized beads.

5. The results of the high temperature runs are tabulated in Table 4. It was assumed in computer simulations that 100% ^{220}Rn was lost. ^{212}Bi losses are indeterminant when high ^{212}Pb losses occur; therefore, ranges of ^{212}Bi losses are given instead of more precise estimates.

Table 4. Percentage Losses of Daughter Products

Temperature (°C)	^{224}Ra (%)	^{220}Rn (%)	^{212}Pb (%)	^{212}Bi (%)
1400	0	100	92	80-100
1600	~5	100	-	80-100
1750	62	100	100	80-100
1900	86	100	100	80-100

7. RECOMMENDATIONS

1. Replicate the room temperature experiment and count the ^{208}Tl activity overnight to determine more precisely ^{220}Rn loss.
2. A series of experiments in which the time of heat treatment is varied should be performed at the higher temperatures to test the assumption that a constant fraction of the daughter products present is released during heat treatment.
3. Future experiments should be made with urania-loaded beads to investigate the difference between urania- and thoria-loaded beads.
4. The existing data should be fitted by computer simulations with different forcing functions to study the variation of inferred loss.
5. The HTGR fuel refabrication off-gas treatment system should be designed for 100% loss of all daughter products.

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9. APPENDIX

9.1 The Matrix Exponential Method for Solving Simultaneous Differential Equations

A set of non-homogeneous equations which describe a decay chain may be represented by the array:

$$\begin{aligned}
 dX_1/dt &= a_{11}X_1 + a_{12}X_2 + \dots a_{1n}X_n + Z_1 \\
 dX_2/dt &= a_{21}X_1 + a_{22}X_2 + \dots a_{2n}X_n + Z_2 \\
 &\vdots \\
 dX_n/dt &= a_{n1}X_1 + a_{n2}X_2 + \dots a_{nn}X_n + Z_n
 \end{aligned} \tag{9}$$

Or more completely by a matrix differential equation:

$$d\bar{X}/dt = \bar{A}\bar{X} + \bar{Z} \tag{10}$$

where:

$$\bar{X} = \begin{bmatrix} X_1 \\ X_2 \\ \vdots \\ X_n \end{bmatrix}; \quad \bar{A} = \begin{bmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{bmatrix}$$

and

$$\bar{Z} = \begin{bmatrix} Z_1 \\ Z_2 \\ \vdots \\ Z_n \end{bmatrix}$$

The general incremental solution to Eq. (10) over a time interval τ is:

$$\bar{x}_{t+\tau} = e^{\bar{A}\tau} \bar{x}_t + e^{\bar{A}(t+\tau)} \int_t^{t+\tau} e^{-\bar{A}\tau} \bar{Z}_\tau d\tau \quad (11)$$

For a zero $\bar{Z}$ vector, Eq. (11) reduces to:

$$\bar{x}_{t+\tau} = e^{-\bar{A}\tau} \bar{x}_t \quad (12)$$

The matrix exponential in Eq. (12) is approximated by a series solution:

$$e^{\bar{A}\tau} = \bar{I} + \bar{A}\tau + \frac{(\bar{A}\tau)^2}{2!} + \frac{(\bar{A}\tau)^3}{3!} + \dots \frac{(\bar{A}\tau)^k}{k!} \quad (13)$$

A more detailed description of the history and background of the matrix exponential solution method is included in the MATEXP manual (2).

As was mentioned in Sect. 2.4.2, the rate of daughter product release is not constant and thus the forcing function, Z_i , is not constant. Since the forcing function varies with concentration, it was incorporated into the A matrix:

$$d[^{224}\text{Ra}]/dt = \lambda_{\text{Th}}[^{228}\text{Th}] - \lambda_{\text{Ra}}[^{224}\text{Ra}] \quad (14)$$

$$d[^{220}\text{Rn}]/dt = (1 - f_{\text{Ra}})\lambda_{\text{Ra}}[^{224}\text{Ra}] - \lambda_{\text{Rn}}[^{220}\text{Rn}] \quad (15)$$

$$d[^{212}\text{Pb}]/dt = (1 - f_{\text{Rn}})\lambda_{\text{Rn}}[^{220}\text{Rn}] - \lambda_{\text{Pb}}[^{212}\text{Pb}] \quad (16)$$

$$d[^{212}\text{Bi}]/dt = (1 - f_{\text{Pb}})\lambda_{\text{Pb}}[^{212}\text{Pb}] - \lambda_{\text{Bi}}[^{212}\text{Bi}] \quad (17)$$

$$d[^{208}\text{Tl}]/dt = (1 - f_{\text{Bi}})(0.36)\lambda_{\text{Bi}}[^{212}\text{Bi}] - \lambda_{\text{Tl}}[^{208}\text{Tl}] \quad (18)$$

where:

$$f_i = \text{fractional loss of species } i$$

The fraction $(1 - f_{Rn})$ in Eq. (16) is incorporated to simulate the effect of a fractional release of ^{220}Rn on the concentration profiles of ^{212}Pb through ^{208}Tl . However, there is no term in Eq. (15) to simulate the effect of ^{220}Rn release on ^{220}Rn concentration. Since a fractional release, f_i , was defined to mean that the concentration of specie i is $(1 - f)$ times the concentration if i was not released, the effect of the release of i on the concentration profile of i can be determined by:

$$[i]^* = (1 - f_i)[i] \quad (19)$$

where:

$[i]^*$ = concentration of i with release of i

$[i]$ = concentration of i with no release of i

The computational algorithm for the daughter concentrations is shown in Fig. 12. The computations performed by the computer are divided into two time periods, the time during the heat treatment and the time after the heat treatment, since daughters were assumed to be released only during heat treatment. During the heat treatment, the A matrix is determined as $(1 - f)\lambda$ and after the heating period it is set to λ and the concentrations allowed to return to their ^{228}Th secular equilibrium values.

All daughter product releases were simulated as step changes at time zero since the heatup was less than 5% of the heat treatment period.

9.2 Standards

Secular equilibrium of carbonized beads was established by counting five untreated pre-carbonized 7.5-gm samples for 50 min over a period of one week. The activity of the various energy levels was averaged over the five samples and the results are given in Table 4. Since the averaged activities had a $\pm 1.5\%$ relative precision, the averaged activities are a good estimate of the true activities. Therefore their use is justified in the normalization procedure.

Table 4. Standard Activities

Source	Energy Level (keV)	Averaged Activity (counts/sec/wt)	Standard Deviation	Relative Precision (%)
^{212}Pb	238	4.61	0.063	1.38
^{208}Tl	511	0.481	0.0069	1.44
^{208}Tl	583	1.52	0.020	1.29
^{212}Bi	727	0.244	0.0036	1.32
^{208}Tl	860	0.159	0.0046	2.88
^{208}Tl	2614	0.428	0.0065	1.52

9.3 Sample Normalization Calculation

The value of gamma peak activity is divided by peak activity of the normalizing standard sample and the quotient is multiplied by 100, thus giving peak activity as a percent. Percent activities of the 583 and 2614 keV gamma peaks are then averaged. For example,

$$\% \text{ activity (583 keV)} = (100) \left(\frac{\text{sample activity @ 583 keV}}{\text{standard activity @ 583 keV}} \right)$$

For the tenth spectrum of the 1400°C experiment,

$$\% \text{ activity} = (100)(0.5) \left(\frac{1.170}{1.525} + \frac{0.312}{0.428} \right) = 74.8\%$$

9.4 Nomenclature

- $\bar{A}$ matrix of coefficients
- a matrix coefficient
- f fractional release
- I identity matrix

K secular equilibrium constant, $\mu\text{m}/\text{cm}^3\text{-hr}$
 t time
 $\bar{X}$ matrix of variable
 X differential equation solution variable
 $\bar{Z}$ forcing function matrix
 Z forcing function
 λ decay constant, hr^{-1}
 τ time interval, hr

Subscripts

e final
 h heating period

Symbols

$[]$ concentration

9.5 Location of Original Data

The original data are contained in ORNL Databook A-7216-G, pp. 18-100, and Databook A-6982-G, pp. 1-80, on file at the MIT School of Chemical Engineering Practice, Bldg. 3001, ORNL.

9.6 Literature References

1. Jackson, P.B., H.H. Ficke, S.A. Reber, and C.I. Teich, "Determination of ^{232}U Daughter Product Release Rates from HTGR Fuel During Refabrication," ORNL-MIT-206 (1974).
2. Ball, S.J., and R.K. Adams, "MATEXP, A General Purpose Digital Computer Program for Solving Ordinary Differential Equations by Matrix Experimental Method," ORNL-TM-1933 (August 30, 1967).