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THE EXAMINATION AND EVALUATION OF IRRADIATED
THORIUM-11 w/o URANIUM SPECIMENS

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THE EXAMINATION AND EVALUATION OF IRRADIATED THORIUM-11 w/o URANIUM SPECIMENS

John E. Gates, Gerald E. Lamale, and Ronald F. Dickerson

Twelve irradiated specimens of thorium-11 w/o uranium were examined. The specimens were fabricated by induction melting and casting in graphite and cold su aging to about 42 per cent reduction in area. The irradiations were conducted in the MTR in capsules equipped with thermocouples.

Six specimens were irradiated to burnups ranging from 0.5 to 0.6 total a/o at average central core temperatures ranging from 1070 to 1250 F. Three specimens exhibited severe swelling or decrepitation and three appeared to be in relatively good condition. The density of these specimens decreased from 4.9 to 9.9 per cent.

The remaining six specimens were irradiated to burnups ranging from 0.9 to 1.5 total a/o at average central core temperatures ranging from 970 to 1100 F. These specimens were in relatively good condition, except for three that had swollen severely at one end. Density decreases ranging from 2.4 to 3.8 per cent were determined for these specimens.

Swelling of all specimens appeared to be a linear function of burnup to the highest level studied (1.5 total a/o) and at temperatures below about 1100 F. Swelling increased significantly above 1100 F, even at burnups as low as 0.2 a/o. Fission-gas losses averaged about 0.5 per cent for sound specimens after burnups of 1.2 to 1.3 total a/o at around 1100 F. These losses were due to diffusion and recoil; cracked specimens exhibited higher losses.

Metallographic examination of the specimens indicated that neither the matrix material nor the fuel material was seriously affected by the irradiation. No evidence of corrosion by the NaK heat-transfer medium was present.

INTRODUCTION

Atomics International, a Division of North American Aviation, Inc., is developing a thorium-low uranium alloy fuel for use in the SRE. An alloy containing 7.6 w/o uranium has been tentatively selected and an irradiation program has been in progress to evaluate the radiation stability of this fuel. Thorium alloys containing 11 w/o fully enriched uranium have been irradiated in the MTR as part of this program. The higher uranium content was used to produce sufficient heat to maintain the specimens at the desired temperature during irradiation. These specimens were irradiated individually in NaK-filled stainless steel capsules equipped with thermocouples and arranged end-to-end in a capsule train. Two of these irradiated trains, NAA-15-6 and NAA-15-7, each made up of six capsules, have been disassembled at Battelle and the specimens recovered for examination.

The position of an individual capsule (and specimen) in the train was the basis for the identification system used in the examination. Beginning with the bottom capsule, specimens and capsules in Train NAA-15-6 were numbered 1 through 6. Those in Train NAA-15-7 were assigned, on the same basis, the letters A through F.

EXPERIMENTAL PROCEDURE AND RESULTS

Specimen Fabrication and Irradiation

The specimens contained in Trains NAA-15-6 and NAA-15-7 were fabricated at Atomics International by induction melting and casting in graphite. Castings of about 0.5 in. in diameter were cold swaged to a diameter of about 0.37 in., giving a total reduction in area during swaging of 42 per cent. Specimens about 1.37 in. long were then cut from the swaged rod without further heat treatment. Appropriate preirradiation measurements were made on each specimen prior to encapsulation.

A typical capsule is shown in Figure 1. Six of these capsules were welded together to form a capsule train with thermocouples extending out of the MTR tank.⁽¹⁾ The location of the thermocouple hot junction in a tube extending into the center of each specimen was selected to provide information on the center core temperature during irradiation. The specimens were held in place in the capsule by the thermocouple thimble, around which was wrapped tantalum foil to provide thermal contact with the specimen. Stainless steel cylinders were used as thermal barriers, and NaK was the heat-transfer material. Dosimeter wires were located on the outside of the capsules and were analyzed by Atomics International.

The thermocouples attached to both trains failed during irradiation. The temperature of Train NAA-15-7 was monitored for the first 20 per cent of the total irradiation time of 1581 hr. This train remained in the same MTR position during all of the irradiation. The temperature of Train NAA-15-6 was monitored for the first 10 per cent of the total irradiation time of 3388 hr. The measured temperatures in this train were low and the train was moved to a higher flux position. During the move, the thermocouples were damaged, and it was not possible to measure temperatures in the new position. Data obtained from neutron dosimetry, the estimated neutron flux in each position, and the temperatures measured in the low-flux position were used by AI to calculate average central core temperatures for each specimen in this train. The results of the temperature measurements and the neutron dosimetry for both capsule trains are included in Table 1.

Postirradiation Examination

The postirradiation examination included disassembly of the capsule train, sampling the gas contained in selected capsules for krypton-85, opening the capsules, and recovery of the specimens. Each specimen was then examined, photographed, and measured. Selected specimens were sectioned to provide samples for metallographic examination and burnup analyses.

(1) References are at the end of the text of the report.

A-31019

FIGURE 1. A CAPSULE OF THE TYPE USED IN EXPERIMENTS NAA-15-6 AND -15-7

TABLE 1. IRRADIATION HISTORY OF CAPSULE TRAINS NAA-15-6 AND -15-7^(a)

Train	Specimen ^(b)	Calculated Average Central Core Temperature, F	Measured Maximum Temperature ^(c) , F	Estimated Neutron Flux ^(d) , 10 ¹³ nv
NAA-15-7	A	1130	1495	4.6
	B	1250	1405	4.1
	C	1180	1295	4.0
	D	1200	1250	4.3
	E	1200	1220	4.1
	F	1070	1125	3.5
NAA-15-6	1	1030 ^(e)	--	4.4
	2	1110 ^(e)	--	4.5
	3	1090 ^(e)	--	4.4
	4	1100 ^(e)	--	4.8
	5	1100 ^(e)	--	4.9
	6	970 ^(e)	--	4.5

(a) These data were supplied by Atomics International.

(b) The specimens are listed in the order of their respective capsules, starting from the bottom of each train.

(c) The temperature of NAA-15-7 was monitored during the first 20 per cent of the total irradiation time of 1581 hr. The temperature of NAA-15-6 was monitored during the first 10 per cent of the total irradiation time of 3388 hr.

(d) The neutron flux was estimated by irradiating aluminum-0.5 w/o cobalt wires with each train and determining the amount of cobalt-60 formed.

(e) The thermocouples burned out as this experiment was being moved into a higher flux. The average specimen temperatures were then calculated from dosimetry.

Disassembly

The capsule trains were disassembled by hacksawing through the chamber located between each pair of capsules. Rust-colored liquid, probably water, was observed leaking from each chamber as it was penetrated by the saw blade. In addition, small black particles fell out of the thermocouple lead tube as it was disconnected from the top of Train NAA-15-7. Water probably entered these chambers when the thermocouple lead tube was cut preparatory to removal of the capsule from the reactor tank.

Sampling of Fission Gas

The gases contained in selected capsules from each train were sampled. The gas-sampling techniques are described fully in Appendix A. Briefly, gas sampling involved puncturing the capsule, allowing the contained gases to diffuse into an evacuated manifold of known volume, and then measuring the amount of krypton-85 contained in an aliquot by gamma-ray and mass spectrometry. Three capsules from Train NAA-15-7 and five capsules from Train NAA-15-6 were sampled.

The gases contained in Capsules A, C, and F from Train NAA-15-7 were sampled by sealing the puncturing apparatus against the recessed top surface of the capsule, evacuating the entire collection system, and then puncturing the capsule. It was necessary to smooth the top surface of the capsule with a milling machine in order to make a good seal. As the puncture needle was driven through the capsule, the metal distorted and apparently broke the seal, allowing air to leak into the gas-collection system. The presence of a leak in the gas-collection system was verified by mass spectrographic analyses of the gas, which indicated the presence of water, argon, nitrogen, and oxygen. Table 2 lists the analyzed values. Helium was not detected, which was added evidence of a leak since the capsules were loaded under helium.

TABLE 2. RESULTS OF MASS SPECTROGRAPHIC ANALYSIS OF GASES
RECOVERED FROM THREE CAPSULES OF TRAIN NAA-15-7

Capsule	Gas Sample	Spectrographic Analysis, volume per cent			
		H ₂ O	Nitrogen	Oxygen	Argon ^(a)
A	4	3.2	74.7	21.1	0.94
	19	3.1	74.5	21.4	0.95
C	7	1.4	76.1	21.7	0.94
	8	0.8	76.3	21.9	0.97
F	10	Organics interfered with analyses			

(a) Air contains about 0.93 volume per cent argon.

Gamma-ray-spectrometer measurements indicated the presence of krypton-85 in the gas sampled from Capsule C. This capsule was the only one from Train NAA-15-7 in which this gas was detected. Calculations indicated that about 0.2 per cent of the total krypton-85 had been lost from the specimen during irradiation. The specimen irradiated in this capsule was later observed to be swollen and decrepitated to the extent that it could not be removed from the capsule. Under such conditions, a larger quantity of gas should have been liberated. This fact, coupled with mass spectrographic evidence of a leak in the sampling system, invalidates the gamma-ray-spectrometer data, and it is believed that as much as 50 per cent of the krypton-85 was actually released from the specimen.

The difficulties encountered in sampling the gases contained in capsules from Train NAA-15-7 led to redesign of the puncturing apparatus. A metal cup was provided to hold the capsules, and the seal to the puncturing apparatus was made on the cup rather than on the capsules. This procedure was used to sample the gas from capsules in Train NAA-15-6.

Capsules 1, 2, 3, 4, and 5 from Train NAA-15-6 were punctured in the redesigned apparatus. Data obtained from mass spectrographic analyses of the gases recovered from the capsules indicate that sampling of Capsules 2, 3, and 5 was successful. These data are presented in Table 3. Apparently a leak occurred in the system while puncturing Capsules 1 and 4. Samples of the gas recovered successfully were also analyzed with a gamma-ray spectrometer to determine the krypton-85 content. The results of this analysis are given in Table 4. The gamma-ray and mass spectrometric data were used to calculate the total amount of fission gas released from each specimen. Table 5 lists the results of these calculations.

Opening the Capsules

Each of the capsules was opened with a pipe cutter while being rotated in a powered pipe-fitter's vise. The opened capsule was placed in a can of butyl alcohol. The alcohol reacted slowly with the NaK capsule coolant. After the reaction was complete, the specimens were removed from the capsule, cleaned, and identified.

The total volume of butyl alcohol used to react the NaK from Capsule A and Capsule 1 was measured. Small aliquots were then removed for determination of cesium-137 by radiochemical analysis. The results are given in Table 6.

Visual Examination and Photography

Each specimen was examined and photographed with the aid of a stereomacro-scope. Three specimens, B, E, and F, from NAA-15-7, appeared to be in relatively good condition. The exterior surfaces were smooth, Specimens E and F appearing a little better in this respect, and there were no visible cracks, pimples, blisters, or distortion. Specimen A was badly swollen and cracked at the upper end, and part of the specimen had also chipped away near the thermocouple end. Specimen C could not be removed from the capsule because of severe swelling. The upper end of this specimen was examined as it appeared in the capsule. A large void was observed in the

TABLE 3. RESULTS OF MASS SPECTROMETRIC ANALYSES OF GAS RECOVERED FROM FIVE CAPSULES OF TRAIN NAA-15-6

Capsule	Measured Volume of Gas ^(a) , cm ³	Total Volume of Gas Released From Capsule, cm ³	Components of Gas, volume per cent										Total Kr	Total Xe	CO
			H ₂	He	CH ₄	H ₂ O	O ₂	N ₂	A ³⁹	A ⁴⁰	CO ₂	M-C ₄ ^(b)			
1	0.026	--	0.36	Nil	0.96	9.0	1.7	85.2 ^(c)	Nil	0.96	1.1	0.64	Nil	Nil	Nil
2	0.36	2.0	1.6	86.0	0.14	3.0	0.33	1.80	1.45	2.77	0.08	0.09	0.40	2.46	Nil
3	0.40	2.1	0.21	87.6	0.32	1.0	6.8	0.52	1.22	0.12	0.07	0.09	0.34	1.90	Nil
4	78.5	--	Nil	Nil	0.05	3.0	18.6	77.1	Nil	0.82	Nil	Nil	Nil	Nil	0.31
5	0.47	2.5	2.6	68.8	0.05	2.0	0.29	2.86	0.99	0.52	0.09	0.28	3.00	18.7	Nil

(a) The volume of gas found in the sample. This volume must be corrected to obtain total volume found in capsule.

(b) Unidentified organic impurities were calculated as n-butane.

(c) Represents nitrogen and/or CO.

TABLE 4. RESULTS OF GAMMA-RAY SPECTROMETRIC ANALYSES OF GAS RECOVERED
FROM THREE CAPSULES OF TRAIN NAA-15-6

Capsule	Gas Sample ^(a)	Measured Disintegration Rate of Krypton-85, photons per min	Correction Factor ^(b)	Krypton-85 Atoms Released	
				Total	Average
2	1	2.3×10^3	1.73×10^{12}	4.0×10^{15}	4.1×10^{15}
	2	6.2×10^3	7.38×10^{11}	4.6×10^{15}	
	3	5.0×10^4	7.46×10^{10}	3.7×10^{15}	
3	1	1.9×10^3	4.12×10^{12}	7.8×10^{15}	6.1×10^{15}
	2	8.1×10^3	7.75×10^{11}	6.3×10^{15}	
	3	4.6×10^4	9.20×10^{10}	4.2×10^{15}	
5	1	1.1×10^5	7.11×10^{11}	7.8×10^{16}	1.1×10^{17}
	2	3.3×10^4	3.98×10^{12}	1.3×10^{17}	
	3	3.3×10^4	3.72×10^{12}	1.2×10^{17}	

(a) Samples of about 1.5 cm^3 total volume were analyzed.

(b) Included are volume and branch decay corrections.

TABLE 5. CALCULATED TOTAL FISSION GAS LOST FROM SPECIMENS IRRADIATED IN
THREE CAPSULES OF TRAIN NAA-15-6

Capsule	Specimen Burnup, total a/o	Total Fission Gas Lost, cm ³		Total Fission Gas Formed, cm ³	Fission Gas Loss, per cent	
		Gamma Ray	Mass Spectrographic		Gamma Ray	Mass Spectrographic
2	1.3	0.015	0.049	9.5	0.14	0.61
3	1.2	0.020	0.043	8.7	0.23	0.49
5	1.5	0.36	0.49	11	3.6	4.9

TABLE 6. RESULTS OF ANALYSES OF NaK FROM CAPSULE A FROM TRAIN NAA-15-7
AND CAPSULE 1 FROM TRAIN NAA-15-6 FOR CESIUM-137

Capsule	Total Volume of Analyzed Solution, cm ³	Total Cesium-137 Found, disintegrations per min	Specimen Burnup, total a/o	Calculated Total	Estimated Amount of Cesium-137 Lost From Specimen, per cent
				Cesium-137 Formed, disintegrations per min	
A	578	2.4×10^{11}	0.65	1.5×10^{13}	18
1	530	0.33×10^{11}	0.92	2.3×10^{12}	1.8

center of the specimen and the thermal shields had apparently been forced against the outer capsule wall by the specimen. This specimen was examined and photographed under kerosene to reduce the spread of radioactive contamination in the hot cell. Part of Specimen D near the end containing the thermocouple had apparently sloughed off during irradiation. The general appearance of each of the specimens is shown in Figures 2 through 7.

The specimens irradiated in NAA-15-6 appeared to be in generally better condition than those from NAA-15-7. All of the specimens showed defects after irradiation, but these were generally associated with the top end of the specimen and could possibly be the result of a low NaK level in the capsules. The condition of each of the specimens is shown in Figures 8 through 13.

Measurements of Physical Dimensions and Density

The dimensions of each specimen were measured, if at all possible, with vernier micrometers. Diameter measurements were made at several points along the length, and then were repeated after the specimen was rotated 90 deg. Length measurements were difficult because of the tantalum foil protruding from the drilled thermocouple hole in one end of each specimen. Attempts to remove the foil were not successful and the measurements were completed by aligning the micrometers on the outer edges of each specimen. The results of the dimensional measurements are included in Tables 7, 8, and 9.

An indication of the amount of bowing of intact specimens was obtained by measuring the effective height of the specimen across its diameter as it was rotated about its longitudinal axis on a flat plate. The differences between the maximum and minimum measurements are included in Tables 7 and 8.

The apparent density of each intact specimen was measured by weight difference in carbon tetrachloride at room temperature. It was necessary to cut off about 0.51 in. of the specimen at the end containing the tantalum foil and also the severely swollen end of Specimens A, D, 4, 5, and 6, prior to the measurement. The cutting was accomplished under water with an abrasive cutoff wheel. The results of the density measurements are also included in Tables 7, 8, and 9. After the density measurements were completed, it was necessary to again section the specimens for radiochemical burnup analyses and metallographic inspection.

Radiochemical Burnup Analyses

Small disks about 0.1 in. thick were cut from Specimens A, D, and F, Train NAA-15-7, and Specimens 1, 3, and 6, Train NAA-15-6. The relative location of each burnup disk is shown on the sketch of the appropriate specimen in Figures 14 and 15. Details of the specimen dissolution and subsequent analyses for cesium-137 are given in Appendix B. The results of the analyses, based on a 30-year half-life for cesium-137, are included in Table 10.

4X

HC1472 and HC 1173

a. Over-All View

Note bulged top end and tantalum foil
protruding from bottom end of specimen

16X

HC1474

b. Detailed View of Bulged Top End of Specimen

FIGURE 2. SPECIMEN A OF NAA-15-7 AFTER IRRADIATION TO A BURNUP OF 0.65 TOTAL a/o
AT AN AVERAGE CENTRAL CORE TEMPERATURE OF 1130 F

Maximum measured temperature was 1495 F.

4X

a. Over-All View

HC1478 and HC1477

6X

b. Bottom End

HC1476

16X

c. Detailed View of Surface Near Top End

HC1479

6X

d. Top End

HC1475

Note tantalum foil in drilled hole.

FIGURE 3. SPECIMEN B OF NAA-15-7 AFTER IRRADIATION TO A BURNUP OF 0.59 TOTAL a/o AT AN AVERAGE CENTRAL CORE TEMPERATURE OF 1250 F

Maximum measured temperature was 1405 F.

FIGURE 4. TOP END OF SPECIMEN C OF NAA-15-7 AFTER IRRADIATION TO A BURNUP OF 0.57 TOTAL a/o AT AN AVERAGE CENTRAL CORE TEMPERATURE OF 1180 F

Maximum measured temperature was 1215 F. The specimen was photographed while still in the capsule and under kerosene.

4X

a. Bottom End

HC1481

4X

b. Top End

HC1482

Note eroded area.

FIGURE 5. SPECIMEN D OF NAA-15-7 AFTER IRRADIATION TO A BURNUP OF 0.60 TOTAL a/o AT AN AVERAGE CENTRAL CORE TEMPERATURE OF 1200 F

Maximum measured temperature was 1250 F.

4X

HC1484 and HC1485

a. Over-All View

6X

HC1486

b. Bottom End

16X

HC1483

c. Detailed View of Surface Near Top End

6X

HC1487

d. Top End

Note tantalum foil in drilled hole.

FIGURE 6. SPECIMEN E OF NAA-15-7 AFTER IRRADIATION TO A BURNUP OF 0.59 TOTAL a/o
AT AN AVERAGE CENTRAL TEMPERATURE OF 1200 F

Maximum measured temperature was 1250 F.

4X

HC1491 and HC1490

a. Over-All View

Note stain near top end.

6X

HC1488

16X

b. Bottom End

Note tantalum foil in drilled hole.

HC1492

6X

c. Detailed View of Surface Near Top End

HC1489

d. Top End

Note stains.

FIGURE 7. SPECIMEN F OF NAA-15-7 AFTER IRRADIATION TO A BURNUP OF 0.51 TOTAL a/o
AT AN AVERAGE CENTRAL CORE TEMPERATURE OF 1070 F
Maximum measured temperature was 1125 F.

4X

HC1498 and HC1499

a. Over-All View
Note crack near top end.

6X

b. Bottom End

Note tantalum foil in drilled hole.

HC1496

16X

c. Detailed View of Surface and Crack Near Top End

HC1500

6X

HC1497

d. Top End

FIGURE 8. SPECIMEN 1 OF NAA-15-6 AFTER IRRADIATION TO A BURNUP OF 0.92 TOTAL a/o
AT AN ESTIMATED AVERAGE CENTRAL CORE TEMPERATURE OF 1030 F

4X

HC1502 and HC1503

a. Over-All View With Top End to Right

6X

HC1505

b. Bottom End

Note tantalum foil and small deposits on surface.

16X

HC1501

c. Detailed View of Surface Near Bottom End

A particle of paper is adhering to surface.

6X

HC1504

d. Top End

Particles of paper are adhering to surface.

FIGURE 9. SPECIMEN 2 OF NAA-15-6 AFTER IRRADIATION TO A BURNUP OF 1.3 TOTAL a/o
AT AN ESTIMATED AVERAGE CENTRAL CORE TEMPERATURE OF 1110 F

4X

HC1507 and HC1506

a. Over-All View

Note slight bulge at top end.

6X

b. Bottom End

Particles of paper adhering to surface.

HC1510

16X

c. Detailed View of Surface Near Top End

HC1508

6X

d. Top End

HC1509

FIGURE 10. SPECIMEN 3 OF NAA-15-6 AFTER IRRADIATION TO A BURNUP OF 1.2 TOTAL a/o
AT AN ESTIMATED AVERAGE CENTRAL CORE TEMPERATURE OF 1090 F

4X

a. Over-All View

HC1515 and HC1514

Note chipped area near top end.

6X

b. Bottom end

Note tantalum foil.

HC1512

16X

HC1513

c. Detailed View of Chipped Area Near Top End of Specimen

6X

d. Top End

Note cracked area.

HC1511

FIGURE 11. SPECIMEN 4 OF NAA-15-6 AFTER IRRADIATION TO A BURNUP OF 1.4 TOTAL a/o
AT AN ESTIMATED AVERAGE CENTRAL CORE TEMPERATURE OF 1100 F

4X

a. Over-All View

HC1520 and HC1519

Note bulged top end.

6X

b. Bottom End
Note tantalum foil.

HC1517

16X

c. Detailed View of Chipped Area Near Top End

HC1518

6X

d. Top End
Note cracks.

HC1516

FIGURE 12. SPECIMEN 5 OF NAA-15-6 AFTER IRRADIATION TO A BURNUP OF 1.5 TOTAL a/o
AT AN ESTIMATED AVERAGE CENTRAL CORE TEMPERATURE OF 1100 F

4X

a. Over-All View

HC1525 and HC1524

Note bulged and cracked top end.

6X

b. Bottom End

Note tantalum foil.

HC1522

16X

c. Detailed View of Surface Near Top End

HC1523

6X

d. Top End

Note appearance of surface.

HC1521

FIGURE 13. SPECIMEN 6 OF NAA-15-6 AFTER IRRADIATION TO A BURNUP OF 0.1, TOTAL AVERAGE
AT AN ESTIMATED AVERAGE CLT COIL TEMPERATURE OF 370 F

TABLE 7. PHYSICAL DIMENSIONS OF SPECIMENS IRRADIATED IN CAPSULE TRAIN NAA-15-7

Specimen	Preirradiation Dimensions ^(a)			Postirradiation Dimensions			Bowling, in.
	Diameter ^(b) , in.	Length, in.	Density, g per cm ³	Diameter ^(b) , in.	Length ^(b) , in.	Density, g per cm ³	
A	0.3738	1.373	12.14	0.4333	--(c)	11.28	0.0042
	0.3728			0.4079			
	0.3716			0.3821			
B	0.3735	1.374	12.08	0.3818	1.3990	11.49	--(d)
	0.3721			0.3798			
	0.3714			0.3775			
C	0.3762	1.374	12.06	--(c)	--(c)	--(c)	--(d)
	0.3736						
	0.3720						
D	0.3742	1.372	12.11	0.3785	--(c)	11.63	--(d)
	0.3733			0.3783			
	0.3722			0.3781			
E	0.3740	1.373	12.15	0.3795	1.3908	11.61	0.0022
	0.3730			0.3774			
	0.3721			0.3753			
F	0.3730	1.379	12.08	0.3829	1.3994	11.74	0.0016
	0.3728			0.3765			
	0.3726			0.3743			

(a) The preirradiation data were supplied by Atomics International.

(b) The maximum, average, and minimum measurements are given in that order.

(c) Specimen was not measured because of its condition.

(d) Not measured.

TABLE 8. PHYSICAL DIMENSIONS OF SPECIMENS IRRADIATED IN CAPSULE TRAIN NAA-15-6

Specimen	Preirradiation Dimensions ^(a)			Postirradiation Dimensions			Bowing, in.
	Diameter ^(b) , in.	Length, in.	Density, g per cm ³	Diameter ^(b) , in.	Length ^(b) , in.	Density, g per cm ³	
1	0.3725	1.374	12.02	0.3794	1.3903	11.71	0.0066
	0.3722			0.3772	1.3889		
	0.3720			0.3764	1.3871		
2	0.3725	1.376	12.16	0.3790	1.3935	11.65	0.0045
	0.3723			0.3772	1.3930		
	0.3720			0.3756	1.3923		
3	0.3728	1.374	12.06	0.3837	1.3934	11.58	0.0036
	0.3724			0.3785	1.3929		
	0.3721			0.3767	1.3919		
4	0.3727	1.372	12.17	0.3972	1.3983	11.60	0.0053
	0.3723			0.3811	1.3975		
	0.3721			0.3764	1.3969		
5	0.3729	1.377	12.16	0.4288	1.4109	11.60	--(c)
	0.3723			0.3786	1.4107		
	0.3719			0.3769	1.4105		
6	0.3732	1.376	12.08	0.4156	--(c)	11.71	--(c)
	0.3727			0.3767			
	0.3720			0.3756			

(a) The preirradiation data were reported by Atomics International.

(b) The maximum, average, and minimum dimensions are given in that order.

(c) Not measured.

TABLE 9. CHANGES IN PHYSICAL DIMENSIONS OF SPECIMENS IRRADIATED
IN BOTH CAPSULE TRAINS

Capsule Train	Specimen	Average Central Core Temperature ^(a) , F	Burnup ^(b) , total a/o	Change, per cent			Change in Density Per Total a/o Burnup, per cent
				Diameter	Length	Density	
NAA-15-7	A	1130	0.65	9.3	--	7.1	10.9
	B	1250	0.59 ^(c)	2.2	1.7	4.9	8.3
	C	1180	0.57 ^(c)	--	--	--	--
	D	1200	0.60	1.3	--	4.0	6.2
	E	1200	0.59 ^(c)	1.1	1.2	4.4	7.5
	F	1070	0.51	1.1	1.4	2.8	5.5
NAA-15-6	1	1030	0.92	1.3	1.1	2.6	2.8
	2	1110	1.3 ^(c)	1.3	1.2	4.2	3.2
	3	1090	1.2	1.6	1.4	4.0	3.3
	4	1100	1.4 ^(c)	2.4	1.9	3.9	2.8
	5	1100	1.5 ^(c)	1.6	2.4	4.6	3.4
	6	970	0.90	1.1	--	3.1	3.4

(a) Temperatures supplied by Atomics International.

(b) Burnups were determined by radiochemical analysis for cesium-137 using a half-life of 30 years except as noted.

(c) The burnup of these specimens was estimated by correlating the radiochemical burnup with the neutron flux supplied by Atomics International.

FIGURE 14. SKETCHES OF SPECIMENS FROM CAPSULE TRAIN NAA-15-7 SHOWING THE RELATIVE LOCATION OF SECTIONS USED FOR VARIOUS MEASUREMENTS

Specimen C was not removed from capsule.

FIGURE 15. SKETCHES OF SPECIMENS FROM CAPSULE TRAIN NAA-15-6 SHOWING THE RELATIVE LOCATION OF SECTIONS REMOVED FOR VARIOUS MEASUREMENTS

TABLE 10. BURNUP OF SELECTED SPECIMENS AS DETERMINED BY RADIOCHEMICAL ANALYSES FOR CESIUM-137

Train	Specimen	Burnup by Radiochemical Analyses ^(a) , total a/o	Location of Analyzed Section of Specimen
NAA-15-7	A	0.65	Base of thermocouple well
	D	0.60	Base of thermocouple well
	F	0.51	Base of thermocouple well
NAA-15-6	1	0.92	Base of thermocouple well
	1-A	1.1	Section 0.137 in. thick removed from top end of specimen
	1-B	0.96	Section 0.111 in. thick starting 0.189 in. from top end of specimen
	3	1.2	Base of thermocouple well
	6	0.90	Base of thermocouple well

(a) Based on 30-year half-life for cesium-137.

The radiochemically determined burnups were correlated with the integrated neutron flux reported by AI for Train NAA-15-7. A linear relationship was observed between the experimentally determined integrated neutron flux and burnup for three specimens. The burnup of the remaining three specimens from this experiment was then estimated from this relationship. Such a linear relationship was not observed in the case of Train NAA-15-6.

The neutron-flux data reported for Train NAA-15-7 were used in conjunction with the radiochemically determined burnups to calculate a flux-depression factor of 0.45 for three capsules. The relationship

$$\text{Total a/o burnup} = \frac{N_{235}}{N_T} \frac{\sigma_f}{\sigma_a} \left(1 - e^{-k\phi\sigma_a t} \right) 100 ,$$

was used to calculate the depression factor where:

N_{235} = number of uranium-235 atoms in specimen

N_T = total number of atoms in specimen

σ_f = cross section for fission, $582 \times 10^{-24} \text{ cm}^2$

σ_a = absorption cross section, $696 \times 10^{-24} \text{ cm}^2$

k = depression factor

ϕ = neutron flux

t = time of irradiation, 5.69×10^6 sec for NAA-15-7 and 1.22×10^7 sec for NAA-15-6.

This factor should be the same for all capsules in both experiments. The flux-depression factor and the neutron flux reported for Train NAA-15-6 were used to estimate the burnup of the specimens irradiated in this capsule train. The results of the calculations compare with the radiochemically determined burnups of only one of three specimens as listed in Table 11. For the purposes of this report, the radiochemically determined burnup of Specimens 1, 3, and 6 and the calculated burnup of Specimens 2, 4, and 5 were used.

TABLE 11. CALCULATED BURNUPS FOR SPECIMENS IRRADIATED IN NAA-15-6

Specimen	Reported Neutron Flux, 10^{13} nv	Burnup, total a/o		Calculated Neutron Flux Required to Produce Analyzed Burnup, 10^{13} nv
		Analyzed	Calculated	
1	4.4	0.92	1.3	3.0
2	4.5	--	1.3	--
3	4.4	1.2	1.3	4.4
4	4.8	--	1.4	--
5	4.9	--	1.5	--
6	4.5	0.90	1.3	3.0

Metallographic Examination

Sections from Specimens A, D, and E from NAA-15-7 and Specimens 3 and 5 from NAA-15-6 were examined metallographically. A section from the interior thermal shield from Capsule D was also examined since a peculiar deposit was observed on the surface adjacent to the specimen. The location of each of the metallographic sections is shown in the sketches in Figures 14 and 15.

Several different methods of polishing and etching unirradiated specimens of this alloy were investigated in an attempt to improve the resolution of the structure. The specimens were supplied by AI, and were reported to be from the same material used to produce the irradiation specimens. The work with the unirradiated control material indicated that the best metallographic technique involved the use of vacuum-cathodic etching. Since no vacuum-cathodic-etching equipment was available in the hot cell, chemical- and electrolytic-etching procedures were also investigated. It was difficult to delineate the structure by these techniques because of the cold-worked structure retained by the specimens. As is the case with any cold-worked material, normal metallographic techniques do not produce the sharply defined structure which is desirable and, because thorium is at best a difficult metal to prepare for metallographic examination, the worked structure provided a severe handicap. The etching technique finally adopted consisted of electrolytically etching the specimens in a lactic acid bath containing 2 per cent sulfuric acid. This etch was applied at 20-v dc. A typical structure of an unirradiated alloy is illustrated in Figure 16.

FIGURE 16. TYPICAL MICROSTRUCTURE OF UNIRRADIATED THORIUM-URANIUM ALLOY AFTER LACTIC-SULFURIC ELECTROLYTIC ETCHING

The white inclusions are uranium and the dark gray inclusions are thorium oxides or, possibly, carbides.

The irregular light-colored inclusions evident in the microstructure shown in Figure 16 are uranium while the smaller dark-colored inclusions can be identified as thorium oxide. It is interesting to note that, although there is a tendency for the larger particles of uranium to be in grain boundaries, there is also a reasonable dispersion of smaller particles throughout the grains. A close study of the structure will show the highly strained cold-worked structure which makes grain-boundary etching by chemical or electrolytic means without subsequent "pull-out" of the uranium particles very difficult.

The sections from each irradiated specimen were mounted in Bakelite and then ground through 600-grit silicon carbide paper using kerosene as a lubricant. Polishing was performed on Syntron vibratory polishers using 1- μ alumina, Linde A, and Linde B abrasives on Microcloth with kerosene as a lubricant. The polished surfaces were then electrochemically etched in a solution of 2 volume per cent H_2SO_4 in lactic acid at 20-v dc.

This etchant was very difficult to apply correctly to the irradiated material. If the specimens were etched heavily enough to show grain structure, the uranium fuel particles and the nonmetallic inclusions became heavily pitted and interpretation of any radiation-induced damage was impossible. It was therefore decided to ignore the grain structure and etch to show the condition of the fuel particles and the nonmetallic inclusions.

During the final polishing operation a cloth tore loose from the vibratory polisher. This necessitated regrinding and repolishing the surface of each specimen. During the second grinding operation, Specimens A and 5 were inadvertently ground through. Observation of these specimens during the first polishing operations indicated that the microstructures were generally similar to those of the remaining specimens.

In the metallographic study of the irradiated specimens the most striking difference noted between the irradiated material and the unirradiated material (Figure 16) was the content of nonmetallic inclusions. Figures 17 and 18 illustrate areas containing agglomerated inclusions in Specimen E. Areas of this type were noted at frequent intervals in both the 15-6 and 15-7 series of specimens. These nonmetallics were not picked up during fabrication but were either in the melting stock or were the result of crucible reactions during melting. It is interesting to note that in Figure 18 some of the gray inclusions are ringed with another material which might be uranium. In each case, the uranium is the light-colored phase dispersed throughout the structure. There has been little apparent effect of irradiation on either the uranium or the matrix in these particular areas of the specimen. Again it is interesting to note the difference in size of the uranium particles in the specimen illustrated in Figure 16 (unirradiated material) and the irradiated material shown in Figures 17 and 18. The fine dispersion of uranium in Specimen E indicates a much more rapid cool from the molten state than is indicated by the unirradiated specimen structure.

Figure 19 illustrates an area in Specimen E which was free from agglomerated oxides. Again it can be seen that a burnup of about 0.59 per cent of the total atoms has little visible effect on the condition of the fuel particles or the matrix. Figure 20 illustrates a typical area in Specimen 3 which was subjected to a burnup of 1.2 per cent of the total atoms. No damage to the fuel particles as a direct result of the irradiation is apparent. A careful study of the photomicrograph will show that some of the fuel particles have become pitted or have been removed. It is believed that the effect of the etchant is more pronounced on the irradiated fuel and actually removes some of the particles. It is interesting to note the nonmetallic inclusions trapped in the uranium fuel particles located at about 11 o'clock in the photograph. This is further evidence of the degree of contamination present in the alloy.

Figure 21 illustrates a photomicrograph of a typical area on Specimen E that was overetched. It will be noted that the uranium particles have been partially removed and that those remaining have been stained. This structure could easily be misinterpreted if one were not aware of the fact that the uranium particles were in place prior to the etching operation. It is postulated that fission products released from the outside of the particles provided a zone which was rather rapidly attacked by the etchant. This allowed the uranium particles to be loosened and in some cases fall from the matrix. It is believed that in no case should these voids be associated with fission gas or swelling of the fuel alloy.

A small ring of apparently different structure was observed on the inside surface of the thermal shield from Capsule D. The ring appeared to be a deposit on the surface of the shield that was adjacent to a severely damaged area near the bottom of Specimen D. Although metallographic examination of the area in question on the fuel specimen showed no obvious explanation of the damage, a metallographic examination of the area in question on the thermal shield showed a structure indicating corrosion by some medium. Figure 22 illustrates the roughened inner surface (top of photograph) and the progression of grain-boundary corrosion into the metal of the thermal shield. This thickening of grain boundaries would give the impression of a deposit of a different material when examined macroscopically. The cause of this corrosion is unknown, but it seems to be related in some way to the damaged area of Specimen D.

FIGURE 17. LARGE NONMETALLIC INCLUSIONS OF OXIDE OR CARBIDE

The uranium appears as the light-colored particles.

FIGURE 18. NONMETALLIC INCLUSIONS SURROUNDED BY UNIDENTIFIED PHASE

FIGURE 19. AN AREA OF SPECIMEN E FREE FROM NONMETALLIC INCLUSIONS

The light-colored phase is uranium.

FIGURE 20. AN AREA FROM SPECIMEN 3, SHOWING NONMETALLICS TRAPPED IN PARTICLES OF URANIUM

Careful examination will show some of the fuel particles have been etched out.

FIGURE 21. APPEARANCE OF URANIUM PARTICLES WHICH HAVE BEEN ETCHED OUT

This illustrates the possibility of misinterpreting an etched structure.

FIGURE 22. EXAMPLE OF SURFACE AND INTERGRANULAR CORROSION OCCURRING ON INNER SURFACE OF THERMAL SHIELD FOR CAPSULE D

DISCUSSION OF RESULTS

It is apparent from the data that the relatively small difference in average irradiation temperature between the NAA-15-7 and NAA-15-6 specimens greatly increased the swelling rate. This is shown graphically in Figures 23 and 24 where the decrease in density is plotted as a function of irradiation temperature and burnup. Several factors may affect these data to some extent:

- (1) During the time in which the specimen temperatures were monitored in NAA-15-7, maximum temperatures as much as 200 to 300 F higher than the calculated average were noted (Table 1). There is no reason to believe that the observed temperature fluctuations did not continue during the remainder of the irradiation after the thermocouples became inoperative. This observation may be tempered somewhat by the fact that detailed knowledge of the irradiation history of this capsule train was not available.
- (2) Some of the specimens exhibited severely swollen ends, as if they had been subjected to temperature extremes in these areas. Although the swollen ends were removed prior to the density measurements, it is possible that the phenomenon producing the swollen ends could have indirectly affected the swelling of the remainder of the specimen. Since the swelling of the ends is believed due to a low NaK level in the capsule which resulted in reduced removal of heat, effects resulting from this condition could not be attributed to irradiation. The effect of this possibility on the measured density changes is believed to have been minor, since the density changes of specimens without swollen ends compare favorably with density changes observed in specimens with the swollen ends removed.
- (3) The temperature of specimens in NAA-15-6 was never measured in the second position of higher neutron flux to which the train was moved. It is not possible to evaluate this effect since detailed information regarding the temperature calculation is not available.

The curve shown in Figure 23 gives an indication that the swelling rate increases rapidly at temperatures above 1100 F. There is considerable scatter in some of the data and a dotted line was used to indicate what is believed to be the best fit. Two curves are shown in Figure 24, one for the data obtained from NAA-15-7 and one for those obtained from NAA-15-6. Apparently, at temperatures below about 1100 F, the change in density of this fuel material is linear with increasing burnup, at least up to about 1.4 total a/o. At temperatures over about 1100 F, the density change increases rapidly with burnup, as indicated by the curve drawn through the NAA-15-7 data. The increased swelling rate at temperatures over about 1100 F apparently begins at about 0.2 to 0.4 total a/o burnup.

The top ends of several specimens were observed to have swollen considerably during irradiation. This swelling was probably due to the material being subjected to high temperatures in this region. A plausible explanation for the occurrence of high temperatures at only the top end of the specimens is a low NaK level in the capsule. If

FIGURE 23. DENSITY CHANGE OF THORIUM-11 w/o URANIUM SPECIMENS AS A FUNCTION OF IRRADIATION TEMPERATURE

FIGURE 24. DENSITY CHANGE OF THORIUM-11 w/o URANIUM SPECIMENS AS A FUNCTION OF BURNUP

the capsule were insufficiently loaded with NaK, the upper end of the specimen might protrude slightly above the surface of the NaK. Since heat would then not be removed rapidly from this area, temperatures would increase, producing the type of swelling that was observed. Metallographic examination of these swollen regions did not reveal other explanations for the phenomenon.

The specimen irradiated in Capsule C was observed to have swollen until it had completely filled the capsule. The thermal shields around the specimen could not be easily identified and there apparently was only a small amount of NaK left in the capsule. For some unexplained reason, this specimen apparently operated at a temperature sufficiently high to produce gross swelling.

The amount of fission gas released from the specimens during irradiation was measured by two methods. Of the two, the mass-spectrometer measurements are believed to be more reliable than the gamma-ray-spectrometer measurements, principally because larger fractions of the total gas were analyzed, thus reducing aliquoting errors, and the quantities of several isotopes were measured rather than only one. The data indicate that about 0.5 per cent of the total fission gas was released from specimens that did not fail during irradiation to a burnup of 1.2 to 1.3 total a/o and at temperatures in the vicinity of 1100 F. Failure of the fuel material results in larger quantities of the gas being released. In the case of Specimen 5, which bulged and cracked at one end, about 4.5 per cent of the fission gas was released. The same type of relationship was observed in measurements of cesium-137 loss to the NaK capsule coolant from two specimens.

In the case of severely cracked Specimen A, a total of 18 per cent of the cesium-137 formed during irradiation escaped. Only 1.8 per cent of the cesium-137 escaped from Specimen 1, which was in relatively good condition except for one small crack. It does not appear that the cesium-137 loss is large enough to materially affect the results of radiochemical burnup analyses in the case of uncracked specimens. However, in the case of damaged specimens an analysis of a cracked section would provide erroneous results. Only sections from undamaged areas of these specimens were analyzed.

Three sections of Specimen 1 were analyzed for cesium-137 to determine the burnup. One section was removed from near the middle of the specimen, while the other two sections were removed from one end. The results indicated that the burnup was about 22 per cent higher in the end section than in the center. It is not believed that the higher burnup occurring in the ends resulted in the severe swelling of the ends of several specimens. If this had been the case, both ends of the specimen should have swollen.

An unusual type of failure was observed in Specimen D. This specimen exhibited a large area near the lower end that had apparently sloughed off during irradiation. The remainder of the specimen appeared to be in good condition. A ring was also observed on the surface of the inner stainless steel thermal shield adjacent to the damaged area of the specimen. Both the specimen and thermal shield were examined metallographically to try to determine causes of the damage. The examination of the fuel specimen did not indicate anything unusual near the damaged surface, but the examination of the thermal shield showed that surface and grain-boundary corrosion had occurred. The results of this examination did not indicate any causes of the specimen failure or reasons for the corrosion of the thermal shield.

The metallographic examination of the various specimens showed no apparent effects of irradiation on either the fuel particles or the matrix. It is postulated that release of fission products from the fuel-particle surfaces may have created a zone around the particles which was quickly attacked by the etchant. This was evidenced by the difficulty encountered in retaining the fuel particles after an etchant was applied.

The irradiated specimens examined contained a much higher contaminant level than did the unirradiated alloy which was studied. The inclusions had the appearance of either massive carbides or oxides (metallographic identification of these two compounds is difficult since both can occur in rather massive form). If the fuel material were melted in a graphite crucible, it is probable that the largest percentage of the inclusions were carbide. If the melts were at no time exposed to carbon, the inclusions are oxide carried through from the original melting stock or picked up from an oxide crucible.

CONCLUSIONS

The following conclusions are based upon the available information concerning specimen-fabrication and -irradiation history.

- (1) Swelling of the thorium-11 w/o uranium specimens appeared to be a linear function of burnup, up to the highest burnup (1.5 total a/o) studied and at temperatures below about 1100 F.
- (2) Swelling of the specimens appears to increase rapidly above a temperature of about 1100 F, even at low burnups. This effect appears to become significant at burnups above 0.2 to 0.4 total a/o.
- (3) Measurements indicate that about 0.5 per cent of the fission gas was lost from specimens that were in good condition at burnups of 1.2 to 1.3 total a/o and temperatures near 1100 F. This loss is due to diffusion and recoil. Higher losses will occur when cracks develop in the material.
- (4) The specimens did not exhibit any signs of corrosion by the NaK.
- (5) Metallographic examination of the specimens indicated that neither the matrix material nor the fuel material was seriously affected by irradiation to the levels experienced by the specimens which were examined.

REFERENCES

- (1) Starr, C., and Dickinson, R. W., Sodium Graphite Reactors, Addison-Wesley Publishing Company, Reading, Massachusetts (1958), pp 109-13.
- (2) Katcoff, S., "Data Sheet No. 24 - Fission-Product Yields From U, Th, and Pu", Nucleonics, 16 (4), 78 (April, 1958).
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- (4) Crouthamel, C. E., and Johnson, C. E., "Spectrophotometric Determination of Uranium by Thiocyanate Method in Acetone Medium", Anal. Chem., 24, 1780 (1952).
- (5) Glendenin, L. E., and Nelson, C. M., Paper 283, "Perchlorate Method for Determination of Cesium Activity in Fission", National Nuclear Energy Series, Vol 9, Book 3, McGraw-Hill Book Company, Inc., New York (1957).

JEG:GEL:RFD/bjw

APPENDIX A

FISSION-GAS MEASUREMENTS

APPENDIX A

FISSION-GAS MEASUREMENTS

The gas contained in selected capsules was sampled by puncturing the top end of the capsule and allowing the gases to diffuse out into a collection system of known volume. About 90 per cent of the gas released from the capsule was removed from the in-cell collection system in two glass bulbs of about 100-cm³ capacity. One of the two bulbs of gas was held in reserve while the other was used for analyses.

The selected bulb was connected to a second system of known volume which included a Toepler pump, manifold, and sample vials. The Toepler pump was used to transfer about 99.9 per cent of the gas from the collection bulb to the evacuated manifold system. Three aliquots about 1.5 cm³ in volume were removed from the manifold for gamma-ray-spectrometer analysis and two about 100 cm³ in volume for mass spectrographic analysis. The size of the sample tubes used in the gamma-ray spectrometer was limited by the sensitive volume of the NaI(Th) well-counter scintillation crystal. Since different fractions of the total gas recovered from the capsule were contained in each aliquot, it was necessary to multiply the measured quantities by a volume factor.

Mass-Spectrometer Measurements

The results of the mass spectrometric analysis of the gas recovered from capsules in Trains NAA-15-7 and NAA-15-6 were included in the text in Tables 2 and 3, respectively. The data indicated that air had leaked into all the samples recovered from NAA-15-7 and from Capsules 1 and 4 from NAA-15-6. The calculations involved in estimating the total fission gas contained in Capsules 2, 3, and 5 of NAA-15-6 are outlined below.

Fission Yields

The yields of the fission gases as given in the literature⁽²⁾ were used in the calculations and are listed in Table A-1. The radioisotope xenon-133 was not considered because of its relatively short half-life of 5.27 days.

(2) References are at the end of the text of the report.

TABLE A-1. YIELDS OF THE FISSION GASES^(a)

Isotope	Yield, per cent	Calculated Conversion Factor
Kr ⁸³	0.544	--
Kr ⁸⁴	1.00	--
Kr ⁸⁵	0.293	87.7
Kr ⁸⁶	2.02	12.7
Xe ¹³¹	2.93	--
Xe ¹³²	4.38	5.87
Xe ¹³⁴	8.06	3.19
Xe ¹³⁶	6.46	3.98
Total gas yield	25.7	

(a) From Reference (2).

The fission yields were used to calculate conversion factors for determining total fission gas from analysis for a selected isotope.

Correction for Air Contamination

Each gas sample was found to contain small amounts of certain components which were believed to result from either air leaks into the collection system or residual gases left during evacuation of the system. These are listed in Table A-2.

TABLE A-2. SUSPECTED CONTAMINANT GASES

Component	Amount in Indicated Sample, volume per cent		
	Capsule 2	Capsule 3	Capsule 5
CH ₄	0.14	0.32	0.05
H ₂ O	3.00	1.00	2.00
O ₂	0.33	0.52	0.29
N ₂	1.80	6.80	2.86
CO ₂	0.08	0.07	0.09
N-CH ₄	0.09	0.09	0.28
Total	5.44	8.80	5.57

Calculation of Total Gas Contained in the Capsule

The measured volume of gas contained in each sample vial was corrected for the suspected air contaminants. The total gas contained in the capsule was then calculated using the sampling factors. The results are listed in Table A-3.

TABLE A-3. TOTAL GAS CONTAINED IN CAPSULES 2, 3, AND 5 AS MEASURED BY MASS SPECTROGRAPH

Capsule	Measured Gas Volume, cm ³	Total Gas Volume, cm ³	Suspected Contaminants, volume per cent	Total Gas Contained in Capsule, cm ³
2	0.36	2.1	5.44	2.0
3	0.40	2.3	8.80	2.1
5	0.47	2.7	5.57	2.5

Isotopic Ratios

The isotopic ratio of the various gas isotopes was estimated from the mass-spectrometer measurements. The ratios are given in Table A-4 along with ratios calculated from fission-yield data. Since the ratio of each isotope should be the same in each capsule, the isotopic ratios indicate the precision of the measurements. Note that the greatest difference between the measured and calculated ratio for any isotope occurred with xenon-136.

TABLE A-4. ISOTOPIC RATIO OF VARIOUS GASES FROM CAPSULES 2, 3, AND 5 AS DETERMINED BY MASS SPECTROGRAPH

Capsule	Isotopic Ratio							
	Kr ⁸³	Kr ⁸⁴	Kr ⁸⁵	Kr ⁸⁶	Xe ¹³¹	Xe ¹³²	Xe ¹³⁴	Xe ¹³⁶
2	12.9	34.7	5.0	47.3	13.4	16.0	30.9	39.7
3	18.9	27.9	10.4	42.9	11.0	16.9	30.5	41.6
5	14.3	27.4	7.5	50.8	10.9	16.8	30.2	42.0
Calculated value ^(a)	14.1	25.9	7.6	52.4	13.3	20.2	37.0	29.5

(a) Calculated from fission-yield data.

Calculation of the Total Fission Gas Released Using Mass-Spectrometer Data

The data given in Tables 3 and A-4 were used to calculate the total volume of selected isotopes and then the total volume of fission gas contained in each capsule. The results are given in Table A-5.

TABLE A-5. TOTAL AMOUNT OF FISSION GAS CONTAINED IN CAPSULES 2, 3, AND 5 AS DETERMINED FROM MASS-SPECTROMETER MEASUREMENTS

Capsule	Isotope	Total Volume of Isotope, cm ³	Conversion Factor	Total Volume of Fission Gas, cm ³
2	Xe ¹³²	0.0082	5.87	0.048
	Xe ¹³⁴	0.016	3.19	0.050
	Xe ¹³⁶	0.020	3.98	0.080
	Kr ⁸⁶	0.0039	12.7	0.050
3	Xe ¹³²	0.0074	5.87	0.043
	Xe ¹³⁴	0.013	3.19	0.043
	Xe ¹³⁶	0.018	3.98	0.073
	Kr ⁸⁶	0.0033	12.7	0.042
5	Xe ¹³²	0.082	5.87	0.48
	Xe ¹³⁴	0.148	3.19	0.47
	Xe ¹³⁶	0.21	3.98	0.82
	Kr ⁸⁶	0.040	12.7	0.50

The total fission-gas volumes calculated from the data obtained for each isotope are in good agreement except in the case of xenon-136. In each case, the fission-gas volumes calculated from the measured volume of xenon-136 are higher. Apparently, another isotope of the same mass was present in the sample since the measured isotopic ratio for xenon-136 was much higher than the ratio calculated from fission-yield data.

Gamma-Ray-Spectrometer Measurements

The amount of 10.3-year krypton-85 contained in each of the small vials was determined by measuring the number of photons emitted with 0.54-Mev energy, which is the energy of the photon emitted during the decay of krypton-85. The measurements were made with a gamma-ray spectrometer using a NaI(Th) crystal of the well type. This equipment was calibrated and the data were corrected for counting efficiency and geometry. The branch decay scheme⁽³⁾ of krypton-85 was taken into consideration in calculating the total amount of krypton-85 in the analyzed samples. The total amount of krypton-85 released from the capsule was then calculated using the volume factors. The results are included in Tables 4 and A-6.

TABLE A-6. TOTAL AMOUNT OF FISSION GAS CONTAINED IN CAPSULES 2, 3, AND 5 AS CALCULATED FROM GAMMA-RAY-SPECTROMETER MEASUREMENTS

Capsule	Total Krypton-85 Atoms Contained in Capsule	Conversion Factor	Total Volume Fission Gas, cm ³
2	4.1×10^{15}	87.7	0.013
3	6.1×10^{15}	87.7	0.020
5	1.1×10^{17}	87.7	0.36

Calculation of Total Fission Gas Formed

The total fission gas formed in each specimen was calculated. The results are given in Table A-7.

TABLE A-7. TOTAL AMOUNT OF FISSION GAS FORMED IN SPECIMENS IRRADIATED IN CAPSULES 2, 3, AND 5

Capsule	Specimen, Weight, g	Burnup, total a/o	Total Fissions	Fission-Gas Yield, per cent	Total Fission Gas Formed, cm ³
2	29.33	1.3	9.88×10^{20}	25.7	9.5
3	29.31	1.2	9.12×10^{20}	25.7	8.7
5	29.29	1.5	11.3×10^{20}	25.7	11

Comparison of the Mass and Gamma-Ray-Spectrometric Data

The total release of fission gas from the specimens was calculated from both mass and gamma-ray-spectrometer data. The results are compared in Table A-8. The data derived from the two techniques agree reasonably well for only Capsule 5. The specimen in this capsule was cracked and the fission-gas loss was high, as would be expected. Since more gas was available for analysis, more accurate analyses were obtained.

TABLE A-8. CALCULATED LOSS OF FISSION GAS FROM SPECIMENS IRRADIATED IN CAPSULES 2, 3, AND 5

Capsule	Amount of Fission Gas in Capsule, cm ³		Volume of Fission Gas Formed, cm ³	Fission-Gas Loss, per cent	
	Gamma-Ray Spectrometer	Mass Spectrometer		Gamma-Ray Spectrometer	Mass Spectrometer
2	0.013	0.049	9.5	0.14	0.52
3	0.020	0.043	8.7	0.23	0.49
5	0.36	0.49	11.	3.3	4.5

It was difficult to select the better method of analysis. Sufficient quantities of gas were available in each instance to give good counting statistics with the gamma-ray spectrometer. However, by necessity the analyzed volume of gas was only a small fraction of the total, thus magnifying small errors in volume measurements. In the case of mass spectrometry, the analyzed fraction of gas was a reasonable portion of the total. However, the small amounts of gas actually present in the samples required that the measurements be performed at the highest possible gain setting. This produced electronic noise in the instrument which interfered with the measurements. The

only basis for selection of one method over the other appears to be the relative quantity of available data. The mass-spectrometer analyses provided information on the volumes of several isotopes and reasonably good correlation was achieved in the calculation of total fission-gas release using these data. In addition, the calculation based on the mass-spectrometer data produces higher gas-release values than the gamma-ray-spectrometer data. It is therefore suggested that the mass-spectrometer data be accepted as the most accurate.

APPENDIX B

URANIUM-BURNUP ANALYSES

APPENDIX B

URANIUM-BURNUP ANALYSES

The radiochemical determination of uranium burnup was based upon two post-irradiation analyses, one for the fission-product cesium-137 and the other for non-fissioned uranium.

The fuel specimens were cut in such a manner as to provide small wafers about 1/8 in. thick from the area at the base of the thermocouple hole in selected specimens. These wafers were dissolved in a solution of 30 ml of concentrated HCl, 30 ml of concentrated HNO₃, 0.2 ml of HF, and 39.8 ml of H₂O to produce a homogeneous liquid sample containing uranium, fission products, and thorium. Approximately 50 mg of cesium carrier was added to the solution.

A volume aliquot of this solution was taken for uranium analysis. The uranium was extracted from an aluminum nitrate salted solution into diethyl ether by three contacts with fresh solvent. The distribution ratio for a single contact is about 20 in favor of the organic phase. Following extraction, the organic phases were combined and evaporated over 1 ml of water in a steam bath. The aqueous residue was then rinsed into a volumetric flask and reagents added for spectrophotometric determination of uranium as the yellow thiocyanate complex in an acetone-water medium⁽⁴⁾.

The analysis for cesium-137 was performed on an aliquot of the original specimen solution which had been diluted with 1M nitric acid to a point where a suitable amount of cesium-137 activity could be obtained. Duplicate aliquots were pipetted into 2 ml of solution containing 20.0 mg of nonradioactive cesium, as chloride, to act as carrier. The cesium was then separated by the perchlorate method as described by Glendenin⁽⁵⁾. The final cesium perchlorate precipitate was filtered through a weighed glass-fiber filter circle, dried, weighed, and counted by an end-window flow-proportional counter. Similarly mounted cesium-137 standards were counted at the same time for counter calibration. (If cesium-134 is present, a correction is made by counting the sample in a gamma-ray spectrometer. The count rate of the sample above two energy-level base lines is compared with the count rate of cesium-137 and cesium-137 standards under similar conditions. The cesium-134 contribution is subtracted algebraically. This method of correction is accurate to ± 2 per cent.)

The counting data for cesium-137 were corrected by counter efficiency to disintegration rate; by dilution to disintegration rate in the original solution; by fission yield of 5.9 per cent and half-life of 30.0 years to fissions of uranium in the original solution. The number of uranium fissions was divided by the sum of the number of fissions and the number of uranium atoms present following irradiation to give the fractional uranium burnup. This value was multiplied by 100 to give the uranium burnup. This value can be converted to burnup based on a 33-year half-life of cesium-137 by multiplying by 1.10.

(4) References are at the end of the text of the report.

The cesium-137 standard was prepared from radiochemically pure cesium-137 obtained from ORNL and standardized by 4 pi beta counting. The uranium standard was prepared from chemically pure uranyl nitrate, precipitated, and ignited to U_3O_8 . The accuracy of the burnup analysis is ± 13 per cent in units of standard deviation, the major portion of the uncertainty being due to the cesium-137 half-life, which is considered accurate to ± 10 per cent.