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ISOTOPIC POWER FUELS MONTHLY STATUS REPORT FOR JUNE 1973

Eugene Lamb

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ISOTOPIC POWER FUELS MONTHLY
STATUS REPORT FOR JUNE 1973

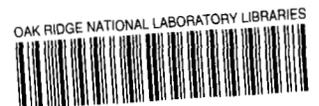
Eugene Lamb

Isotopes Division

AUGUST 1973

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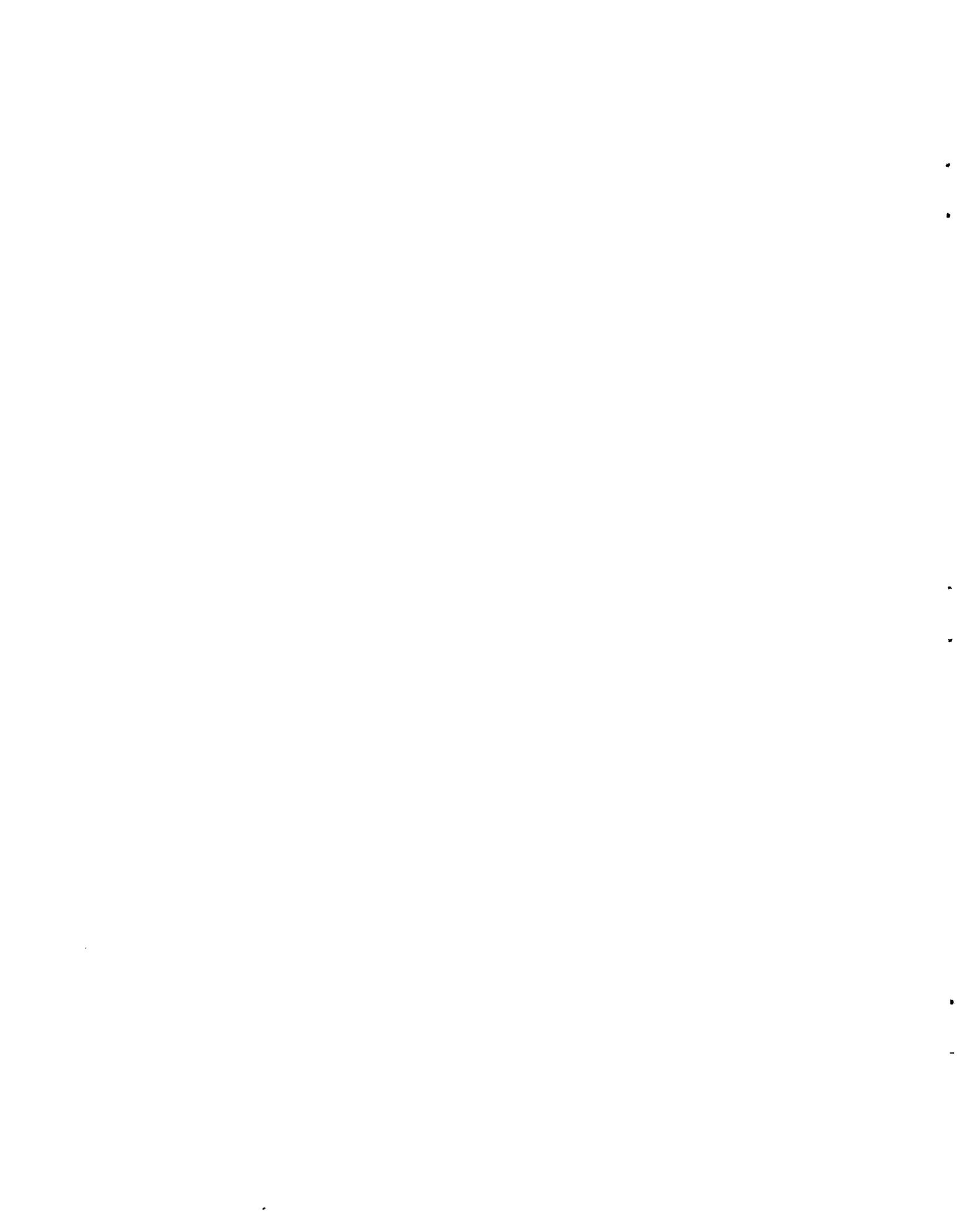


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ISOTOPIC POWER FUELS MONTHLY
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Eugene Lamb

CURIUM-244 FUEL DEVELOPMENT

(Division of Space Nuclear Systems Program 04 30 05 03)

$^{244}\text{Cm}_2\text{O}_3$ Compatibility Program

Compatibility Couple Tests

(T. A. Butler and J. R. DiStefano)

The status of the 900, 1100, and 1400°C compatibility test matrix is summarized in Table 1.

Table 1. Status of Compatibility Tests

Set ^a	Start of Test	Thermal Cycles	Cumulative Hours	Projected End of Test
1	5-3-73	None	1344	11-28-73
2	5-3-73	None	1344	11-28-73
3	4-16-73	3	1697	8-4-73
4	4-16-73	3	1697	8-4-73
5	4-17-73	2	1574	8-9-73
6	4-17-73	2	1574	8-9-73
7	5-3-73	2	1231	12-3-73
8	5-3-73	2	1231	12-3-73
9	5-3-73	2	1224	12-3-73
10	5-3-73	2	1224	12-3-73

^aSet identifications:

- 900°C; 5000 hr; helium atmosphere; Ir, C, Pt, Hf-1% Pt-0.5% Pd, Hastelloy C-276, Haynes 25, Haynes 188, ThO₂, Pt-20% Rh, and Pt-26% Rh-8% W.
- 900°C; 5000 hr; graphite, helium atmosphere; Ir, Pt, Hf-1% Pt-0.5% Pd, Hastelloy C-276, Haynes 25, Haynes 188, ThO₂, Pt-20% Rh, and Pt-26% Rh-8% W.
- 1100°C; 2500 hr; graphite, helium atmosphere; Ir, Pt, Pt₃Ir, and Pt-26% Rh-8% W-0.5% Ti.
- 1100°C; 2500 hr; dynamic vacuum; Ir, Pt, Pt₃Ir, C, and Pt-26% Rh-8% W-0.5% Ti.
- 1100°C; 2500 hr; helium atmosphere; Ir, Pt, Pt₃Ir, C, and Pt-26% Rh-8% W-0.5% Ti.
- 1100°C; 2500 hr; graphite, dynamic vacuum; Ir, Pt, Pt₃Ir, and Pt-26% Rh-8% W-0.5% Ti.
- 1400°C; 5000 hr; graphite, helium atmosphere; Ir, C, Mo, Mo-46% Re, Ta, T-111, W, and W-26% Re.
- 1400°C; 5000 hr; dynamic vacuum; Ir, Mo, Mo-46% Re, Ta, T-111, W, and W-26% Re.
- 1400°C; 5000 hr; helium atmosphere; Ir, Mo, Mo-46% Re, Ta, T-111, W, and W-26% Re.
- 1400°C; 5000 hr; graphite, dynamic vacuum; Ir, C, Mo, Mo-46% Re, Ta, T-111, W, and W-26% Re.

Curium Prototype Compatibility Test Facility (*K. W. Haff*)

Fabrication of shielding tanks for the facility is approximately 50% complete. Installation of the concrete block shielding on the upper part of the enclosure is approximately 20% complete. Shielding work is expected to be completed by the end of July. Shipment of the surplus equipment which is to be used in these tests was delayed until mid-August. We expect to receive the equipment in late August.

 Cm_2O_3 Compatibility With Ceramic Materials (*P. Angelini*)

The present plan of experiments is presented in Table 2.

Table 2. $^{244}\text{Cm}_2\text{O}_3$ Compatibility Experiments

Experiment	Material	Temperature (°C)	Time (hr)
A	ThO_2	1500	24
B	ThO_2	1300	100
C	ThO_2	1500	t_3
D	ThO_2	1300	t_4
E	ZrO_2	1500	24
F	ZrO_2	1300	100
G	ZrO_2	1500	t_3
H	ZrO_2	1300	t_4
I	Al_2O_3	1500	24

Experiments A and B (see Table 2) have been performed, and the couples have been transferred to HRLEL for examination. Experiments E and F are being readied. The design for fabricating the capsules and inserts for Experiment I has been given to the shops for fabrication. One of the as-fabricated $^{244}\text{Cm}_2\text{O}_3$ pellets has been sent to HRLEL for optical microscopy study.

The compatibility couples will be examined using an electron-beam microprobe. This examination will yield data such as concentration of ^{244}Cm versus distance in the oxide to be tested. From that data the diffusion coefficient of curium in those oxides can be calculated. Some optical microscopy will also be performed to define areas in the compatibility couple to be examined using the electron-beam microprobe.

Experiments C, D, G, and H will be performed after the preliminary analyses of Experiments A and B. Thus, different exposure times, t_3 and t_4 , at temperature may be chosen for the remaining couples in order to derive more information from the experiment.

Free Energy Calculations for the Reaction of Beryllium with Cm_2O_3 (E. E. Ketchen)

The thermodynamics of the reaction of Cm_2O_3 with beryllium to form CmO or curium metal have been investigated to evaluate the possibility of the reaction of Cm_2O_3 with beryllium metal.

The free energy was calculated for Eq. 1 using Eq. 2 which was developed by P. K. Smith and D. E. Peterson.¹ The authors have presented indirect evidence that Cm_2O_3 will vaporize to CmO and oxygen as the main products. The formation of CmO as the major vaporization product needs to be verified by mass spectrometer measurements.



$$\Delta G = -RT \ln k = -2.303 RT \{ \log 0.335 + 3[7.32 - (29,050/T)] \} \quad (2)$$

where

k = equilibrium constant for equation,
T = temperature in °K, and
R = 1.9872 cal/deg·mole.

The free energy values for Eq. 1 combined with data from the JANAF tables² and a compilation of data by Alvin Glassner³ were used to calculate the free energy of Eq. 3. The results are shown in Table 3. No reaction would be expected in the 600–1800°C temperature range.

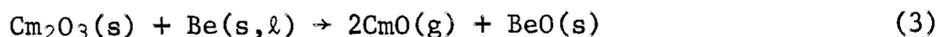


Table 3. Gibbs Free Energy as a Function of Temperature for Eq. 3

ΔG (kcal/GFW)	Temperature (°C)
143.98	600
131.98	800
120.04	1000
108.17	1200
96.03	1400
84.10	1600
72.10	1800

¹P. K. Smith and D. E. Peterson, "High Temperature Evaporation and Thermodynamic Properties of Cm_2O_3 ," *J. Chem. Phys.* 52(10), 4963–72 (1970).

²R. Stull and H. Prophet (eds.), *JANAF Thermochemical Tables*, 2nd Ed., NSRDS-NBS-37, Office of Standard Reference Data, National Bureau of Standards (1971).

³Alvin Glassner, *The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K*, ANL-5750, Argonne National Laboratory (1957).

The free energy was calculated for Eq. 4 using the free energy of formation of Pu_2O_3 (ref. 4) as a stand-in for Cm_2O_3 and the free energy of formation of BeO from a compilation of data by Alvin Glassner.³ The free energy values are shown over a range of 600 to 1800°C in Table 4.

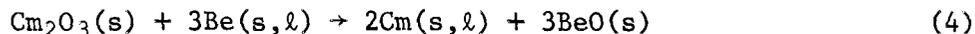


Table 4. Gibbs Free Energy as a Function of Temperature for Eq. 4

$-\Delta G$ (kcal/GFW)	Temperature (°C)
14.89	600
13.65	800
12.21	1000
10.55	1200
8.74	1400
6.29	1600
3.72	1800

The Gibbs free energy values for Eq. 4 are negative over the range of temperatures considered, hence the reaction should occur. However, it is believed that a protective coating of BeO or $\text{BeO}\cdot\text{Cm}_2\text{O}_3$ will be formed over the metal which will inhibit the reaction.

Reaction of Cm_2O_3 With ZrO_2 and Al_2O_3 (E. E. Ketchen)

In the application of $^{244}\text{Cm}_2\text{O}_3$ as a heat source, it may be desirable to have the curium compact in contact with ceramic materials such as ZrO_2 or Al_2O_3 . Will the ZrO_2 or Al_2O_3 interact with Cm_2O_3 in the 600-1000°C temperature range?

Reaction With ZrO_2 — The thermodynamic data needed to calculate the free energies of reaction between ZrO_2 and Cm_2O_3 are not available for either curium sesquioxide or the rare-earth sesquioxides. It appears that the rare-earth sesquioxides react with ZrO_2 to form $\text{RE}_2\text{Zr}_2\text{O}_7$ as one of the major compounds. The heat of reaction at 25°C for Eq. 5 is shown in Table 5.⁵ Unfortunately the heat capacities of these compounds have not been measured, hence it is not possible to calculate the heat of reaction in Eq. 5 at 600-1000°C.



where RE represents one of the rare-earth elements.

³F. L. Oetting, "The Chemical Thermodynamic Properties of Plutonium Compounds," *Chem. Rev.* 67, 261-97 (June 1967).

⁵V. R. Korneev, V. B. Glushkova, and E. K. Keller, "Heats of Formation of Rare Earth Zirconates," *Inorg. Mater.* (Russian) 7(5), 781-2 (1971).

Table 5. Enthalpy of Formation of $\text{RE}_2\text{Zr}_2\text{O}_7$
From RE_2O_3 and ZrO_2 at 25°C

Compounds	$-\Delta H_f$ (kcal/GFW)
$\text{La}_2\text{Zr}_2\text{O}_7$	30.1
$\text{Pr}_2\text{Zr}_2\text{O}_7$	28.7
$\text{Nd}_2\text{Zr}_2\text{O}_7$	26.5
$\text{Sm}_2\text{Zr}_2\text{O}_7$	25.5
$\text{Eu}_2\text{Zr}_2\text{O}_7$	19.1
$\text{Gd}_2\text{Zr}_2\text{O}_7$	18.1
$\text{Y}_2\text{Zr}_2\text{O}_7$	11.4

V. A. Krzhizhanovskaya and V. B. Glushkova⁶ have performed experiments to study the reaction of Nd_2O_3 with ZrO_2 at various temperatures. They have studied the kinetics of the reaction as low as 1200°C . The reaction rate constants decrease as the temperature is lowered from 1500 to 1200°C . The activation energy of formation is 112 kcal/GFW for the reaction of Nd_2O_3 with 2ZrO_2 to form $\text{Nd}_2\text{Zr}_2\text{O}_7$. Since the activation energy of solid solutions of ZrO_2 and Nd_2O_3 is 80 kcal/GFW, the solid solution will be formed as an intermediate product before the neodymium zirconate is formed.

The Cm_2O_3 would be expected to form a curium zirconate ($\text{Cm}_2\text{Zr}_2\text{O}_7$) similar to the rare earths. There would probably be little reaction between Cm_2O_3 and ZrO_2 at 600 to 1000°C , but the rate of reaction at the Cm_2O_3 - ZrO_2 interface would be expected to increase with temperature.

Reaction With Al_2O_3 — The thermodynamic data needed to calculate the free energy of formation of CmAlO_3 have not been measured. However, the reactions to produce CmAlO_3 (ref. 7), CeAlO_3 (ref. 8), and NdAlO_3 (ref. 9) have been investigated.

The CmAlO_3 was prepared by the reaction of Cm_2O_3 and Al_2O_3 powder at 1380°C in a 4% H-96% He atmosphere. Both CeAlO_3 and NdAlO_3 were prepared at temperatures above 1600°C . These aluminates are stable in the region below

⁶V. A. Krzhizhanovskaya and V. B. Glushkova, "Formation of Solid Solutions and Compounds in the System Nd_2O_3 - ZrO_2 ," *Inorg. Mater.* (Russian) 8(1), 109-13 (1972).

⁷W. C. Mosley, "Self-Radiation Damage in Curium-244 Oxide and Aluminate," *J. Am. Ceram. Soc.* 54(10), 475-9 (1971).

⁸A. I. Leonov, A. V. Andreeva, V. E. Shavaiko-Shvaikovskii and E. K. Keler, "High-Temperature Chemistry of Cerium in the Systems Cerium Oxides - Al_2O_3 , Cr_2O_3 , Ga_2O_3 ," *Inorg. Mater.* (Russian) 2, 445-50 (1960).

⁹N. A. Toropov and T. P. Kiseleva, "The Al_2O_3 - Nd_2O_3 Binary System and Some Data on the Al_2O_3 - Nd_2O_3 - SiO_2 System," *Russ. J. Inorg. Chem.* 6(10), 1193-6 (1961).

1000°C, when under an inert atmosphere. In the absence of free energy data, the reaction of Cm_2O_3 and Al_2O_3 below 1000°C cannot be predicted, but it is conceivable that a slow reaction may occur. Compatibility experiments are needed to determine the extent of Cm_2O_3 reaction with Al_2O_3 .

$^{244}\text{Cm}_2\text{O}_3$ Property Characterization

Helium Release (*P. Angelini*)

The aluminum water-cooled tank for the three furnaces has been replaced with one of stainless steel. The furnaces and tank have been installed in the glove box.

Preliminary vacuum and temperature checks have been completed on the vacuum headers and furnaces. A final vacuum check is in progress. The furnaces have been taken to the maximum experimental temperature of 800°C. The operating temperature at which the three experiments will be conducted are 800°C, 650°C, and 500°C.

The pellets needed for this experiment have been fabricated and are in storage. The experimental procedure for the helium release experiment will be basically the same as that of the previous steady-state helium release experiments performed with $^{244}\text{Cm}_2\text{O}_3$ (ref. 10) and $^{238}\text{PuO}_2$ (ref. 11). The pellets will be heated in vacuum to the required temperature. The helium released from each pellet will be stored in their respective tubes. At prescribed intervals, the helium from the storage tubes will be measured. When the helium release rate from a pellet equals the helium generation rate, that part of the experiment will be terminated and the sample assembly will be heated to 1900°C in a different furnace to determine the helium inventory in that sample.

Block diagram drawings of the equipment used in this experiment together with a description of the procedure for operation of the equipment and of the glove box are being prepared.

Vapor Pressure (*P. Angelini and J. C. Posey*)

The vacuum furnace has been installed and leak checked. A leak was located in the liquid nitrogen cold trap, and a new trap was ordered.

The glove box windows have been installed, and the checking of the glove box for air leaks has been completed. The oxygen concentration in the glove box with a normal purge flow of 0.5 ft³/min argon is less than 50 ppm during operations.

¹⁰P. Angelini, *Helium Release from $^{244}\text{Cm}_2\text{O}_3$* , ORNL-4785, Oak Ridge National Laboratory (in publication).

¹¹P. Angelini *et al.*, *Helium Release in $^{238}\text{PuO}_2$ Microspheres*, ORNL-4507, Oak Ridge National Laboratory (March 1970).

The drawings and description of this experiment required by the safety regulations are being prepared.

A new beam chopper assembly for the mass spectrometer furnace is being fabricated. The previous system failed during tests due to defects in the ball bearings and belt drive system. The new unit has the rotor coupled directly to the motor shaft.

Vapor Pressures of Curium, Plutonium, and Americium Oxides (*P. Angelini*)

The vapor pressures of plutonium, curium, and americium oxides previously reported in the literature are presented in Table 6.

A graph of the vapor pressure data listed in Table 6 is presented in Fig. 1. The identification numbers in Table 6 coincide with the identification numbers in Fig. 1.

In all of the above mentioned data the vapor specie was not determined experimentally but was inferred by calculation and vaporization trends in various other oxides. The experiments were all of the Knudsen cell type, and the vapor pressures were calculated using the Knudsen equation. The vapor specie has to be known so that a true vapor pressure can be calculated.

Table 6. Vapor Pressure of Plutonium, Curium, and Americium Oxides

Number	Solid Phase	Vapor Phase ^a	log P _e (atm)		Temperature Range (°C)	Method (effusion cell)	Reference
			= A + (B/T)				
1	PuO _{1.6} -Pu ₂ O ₃	PuO	8.13	-27,910	1790-2075	Tantalum	12
2	PuO _{~1.6} -Pu ₂ O ₃	PuO	8.09	-27,800	1645-2105	Tantalum	13
3	Cm ₂ O ₃	Cm ₂ O ₃	7.32	-29,050		Tungsten	14
4	Am ₂ O ₃	AmO	8.19	-25,650	1645-2105	Tantalum	13
5	PuO _{~1.87}	PuO ₂	7.82	-29,700	1990-2380	Tungsten	15
6	PuO _{~1.92}	PuO ₂	7.50	-29,260	1640-2070	Tungsten	13
7	AmO ₂	AmO ₂	7.28	-28,260	1640-2070	Tungsten	13

^aCalculated for log P_e equation.

¹²T. E. Phipps, C. W. Lears, and O. C. Simpson, *J. Chem. Phys.* **18**, 724 (1950).

¹³R. J. Ackermann, R. L. Faircloth, and M. H. Rand, *J. Phys. Chem.* **70**(11), 3698-3706 (1966).

¹⁴P. K. Smith and D. E. Peterson, *J. Chem. Phys.* **52**(10), 4963-72 (1970).

¹⁵R. N. R. Mulford and L. E. Lamar, *Plutonium*, Cleaver-Hume Press, London, 1960, p. 19611,411.

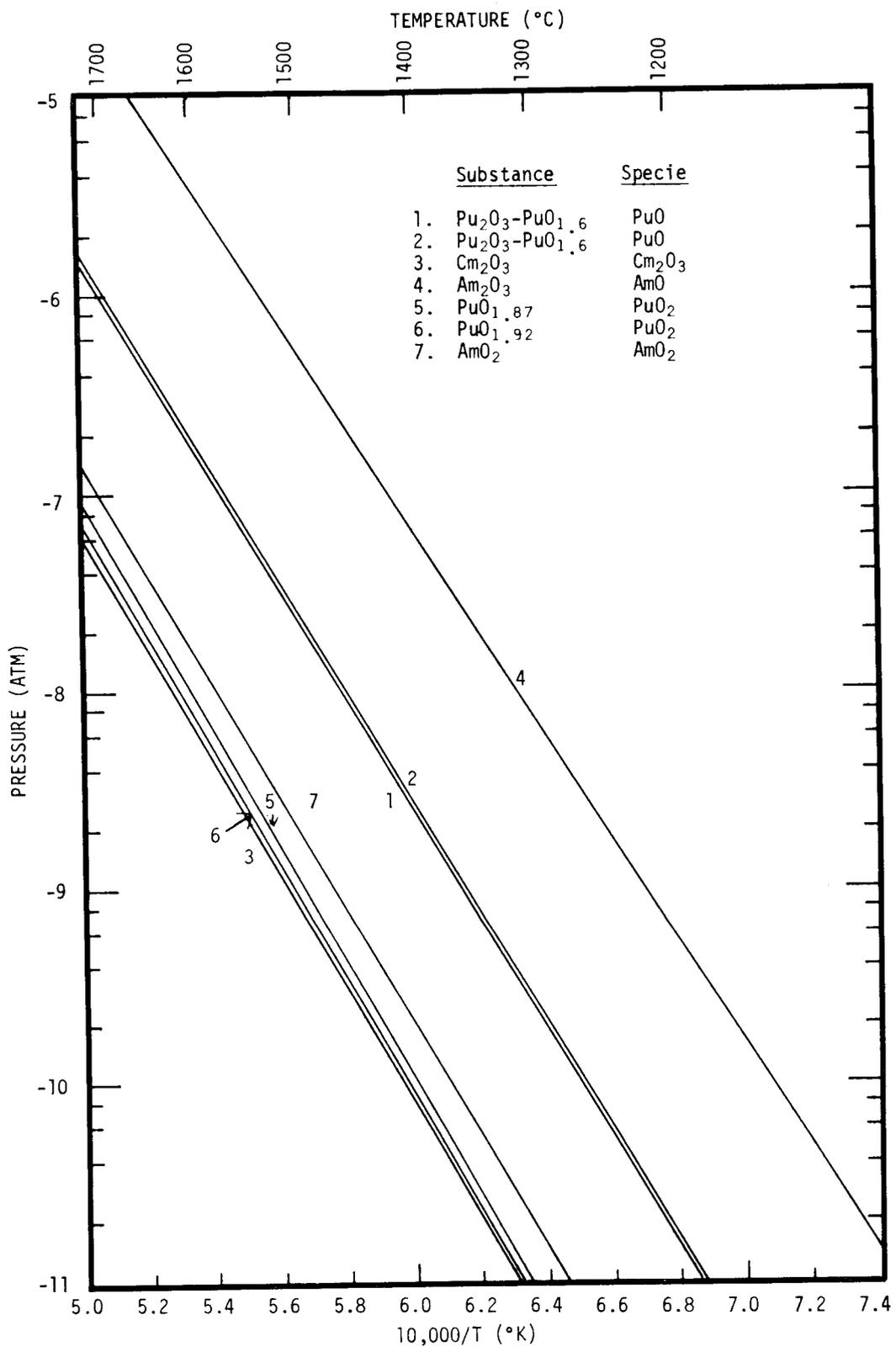


Fig. 1. Vapor Pressure Versus 1/T °K.

From the data presented it can be seen that the reported vapor pressure for AmO_2 is greater than that of PuO_2 or Cm_2O_3 , and that for Am_2O_3 is much higher than the vapor pressure of either Cm_2O_3 , PuO_2 , or $\text{Pu}_2\text{O}_3\text{-PuO}_{1.6}$. Thus a large content of americium oxide in curium oxide fuel may be detrimental from the vaporization standpoint in relationship to various capsule designs and time at temperature.

The vapor pressure reported for the $\text{Pu}_2\text{O}_3\text{-PuO}_{1.6}$ system by Ackerman *et al.*,¹³ and Phipps *et al.*,¹² agree quite well. The vapor pressure for this system is also higher than that of Cm_2O_3 or PuO_2 . The vapor pressure of pure Pu_2O_3 has not yet been measured and may be quite different from that of the $\text{Pu}_2\text{O}_3\text{-PuO}_{1.6}$ system.

Theoretically Pu_2O_3 would be formed as the ^{244}Cm decays in an initially pure Cm_2O_3 fuel form in an environment where excess oxygen would not be available. The vapor pressure data for the $\text{Pu}_2\text{O}_3\text{-PuO}_{1.6}$ system was obtained using a tantalum Knudsen cell in both the work of Ackerman *et al.*,¹³ and Phipps *et al.*,¹² The initial material loaded into the tantalum cell was PuO_2 . Thus reduction of the PuO_2 had occurred. The final stoichiometry of the vaporizing sample could not be determined with great accuracy in this method.

From work reported by Ackerman *et al.*,¹³ and Mulford and Lamar,¹⁵ it is seen that the vapor pressure of PuO_2 tends to increase as the stoichiometry of the sample decreases. The activation energy for the vapor pressure of both the $\text{PuO}_{1.92}$ reported by Ackerman *et al.*,¹³ and that for $\text{PuO}_{1.87}$ by Phipps *et al.*,¹² is greater than that reported by Smith and Peterson¹⁴ for the activation energy for the vapor pressure of Cm_2O_3 . In using the vapor pressures reported by Ackerman *et al.*,¹³ for $\text{PuO}_{1.92}$ and by Smith and Peterson¹⁴ for that of Cm_2O_3 , the temperature at which the vapor pressure for $\text{PuO}_{1.92}$ becomes less than that for Cm_2O_3 is 1166°K. This is a temperature which is nearly 500°C lower than the lowest temperature at which the vapor pressures of $\text{PuO}_{1.92}$ and Cm_2O_3 were determined. A 500°C extrapolation may result in rather large errors. The temperature of 1166°K may also vary because of the errors associated in the experimental measurements from which the vapor pressure equation was obtained. In addition the vapor pressure equation for Cm_2O_3 was calculated using Cm_2O_3 as the vaporizing specie. The vapor pressure for Cm_2O_3 would be increased if the vaporizing specie is in reality CmO . If this were the case, the vapor pressure for Cm_2O_3 would be higher than that of PuO_2 .

It appears from the data reported that the true vapor pressure of PuO_2 and Cm_2O_3 are somewhat similar in magnitude and activation energy. Also the vapor pressure of Pu_2O_3 will probably be larger than that of Cm_2O_3 although the vapor pressure for Pu_2O_3 is not yet measured. The amount of AmO_2 or Am_2O_3 initially present in the fuel form and the ingrown Pu_2O_3 (if its vapor pressure is near that of the $\text{Pu}_2\text{O}_3\text{-PuO}_{1.6}$) may have significant effect on the amount of alpha-emitting material volatilized from the fuel.

X-Ray Diffraction Unit (*P. Angelini*)

The air leaks in the x-ray process glove box have been sealed. The oxygen content in the box can be held to less than 50 ppm with the low argon purge flow of 0.5 ft³/min. For the initial purge, up to 4 ft³/min of argon may be used to lower the oxygen concentration to 50 ppm in a period of less than 1 hr. The glove box is of the stainless steel type with safety glass windows.

A Plexiglas entry glove box could not be adequately sealed from air leaks. In addition, safety regulations now require stainless steel glove boxes with safety glass windows. Thus, a new entry box also satisfying the new regulations will be needed. Design of the new glove box has been completed and fabrication of the new unit will begin July 1, 1973.

The x-ray diffraction system is in the process of being aligned. The unit is now approximately 0.3° off in alignment. The final aligning procedure with the furnace hot stage in place has yet to be performed.

The first experiment planned with the system is to perform a scan on the first pellet used in the ²⁴⁴Cm₂O₃ solubility experiments. This may indicate whether the pellet has undergone any chemical change during those experiments.

Emissivity of ²⁴⁴Cm₂O₃ (*P. Angelini*)

A new flange has been fabricated and tested on the vapor pressure furnace. The flange operates as expected and will enable easier loading of the emittance assembly onto the furnace. The spectroradiometer unit will be tested before the glove box becomes contaminated with radioactive materials.

Heat Capacity (*P. Angelini*)

Curium sesquioxide (²⁴⁴Cm₂O₃) prepared from material freshly separated from the ²⁴⁰Pu daughter will be utilized in this determination in order to define the heat capacity of pure Cm₂O₃. The heat capacity of various mixtures of ²⁴⁴Cm₂O₃ and ²⁴⁰Pu₂O₃ can then be calculated. The thermocouple material to be pressed in the ²⁴⁴Cm₂O₃ fuel pellet is W5Re-W26Re.

Dimensional Stability (*T. A. Butler*)

In preparation for initiation of experimental measurements of the dimensional stability of hot-pressed ²⁴⁴Cm₂O₃ pellets, a resistance furnace, measuring test stand, and die bodies are being assembled for installation in the SFF hot cells.

Rate of Solution of $^{244}\text{Cm}_2\text{O}_3$ (*J. C. Posey*)

The first test of the rate of solution of hot-pressed $^{244}\text{Cm}_2\text{O}_3$ (SRL-18 oxide) was completed. The test was ended 336 hr after spontaneous disintegration of the pellet took place, and it is believed that adequate observation had been made of the effect of disintegration.

In this test a steady stream of fresh, air-saturated distilled water at 22°C was passed over a hot-pressed $^{244}\text{Cm}_2\text{O}_3$ pellet. The stream of water was sampled periodically after it had passed over the pellet. Solution rates were calculated from the ^{244}Cm concentrations in the samples, the flow rates, and the surface area of the pellet. (The experimental procedure was described in more detail in last month's report.)

The results are shown graphically in Fig. 2. The initial unfiltered sample indicated a much higher rate than the subsequent samples. This is attributed to the washing of loose particulate material from the surface of the pellet. The rate then became relatively constant. After 345 hr, a light grey material was observed to be settling in the outlet tube. After 432 hr, the pellet was observed to be disintegrating. Much higher rates of solution were then observed as might be expected from the large increase in surface area. The rates of solution shown on the graph are based on the original surface area of the pellet. The upward trend of the rate suggests progressing breakup of the pellet.

Because of an electrical power outage over the weekend, the flow of water was interrupted for a considerable period of time prior to the first observation of disintegration. This may have allowed an increase in the pellet temperature and hastened the reaction. On the other hand, the appearance of material in the outlet tube suggests that decomposition may have started before the power outage.

Knowledge concerning the conditions under which a pellet disintegrates has greater practical importance than knowledge of the absolute rate of solution from an intact surface. Therefore, a series of aging experiments is planned in which pellets will be placed in beakers of water and held at constant elevated temperature. The times to visible disintegration will be noted. Exploratory work will be started with a pellet in distilled water at a temperature near 100°C. If rapid disintegration occurs, a need for further testing of the effect of temperature would be indicated. A more complete program would also involve the effects of pellet age, density, plutonium content, and water impurities.

The average rate of solution of ^{244}Cm from the intact pellet was $9.3 \mu\text{g}/\text{cm}^2 \cdot \text{hr}$. This value is based on 18 rates observed before the first appearance of sediment in the outlet tube. The first rate and four rates based on filtered samples were excluded in calculating the average. These samples are believed to have been contaminated by particulate material from the first sample which was deposited on the filter and in the filtration equipment. These rates are not shown in Fig. 2. Their inclusion in the average would raise the value to $11.0 \mu\text{g}/\text{cm}^2 \cdot \text{hr}$.

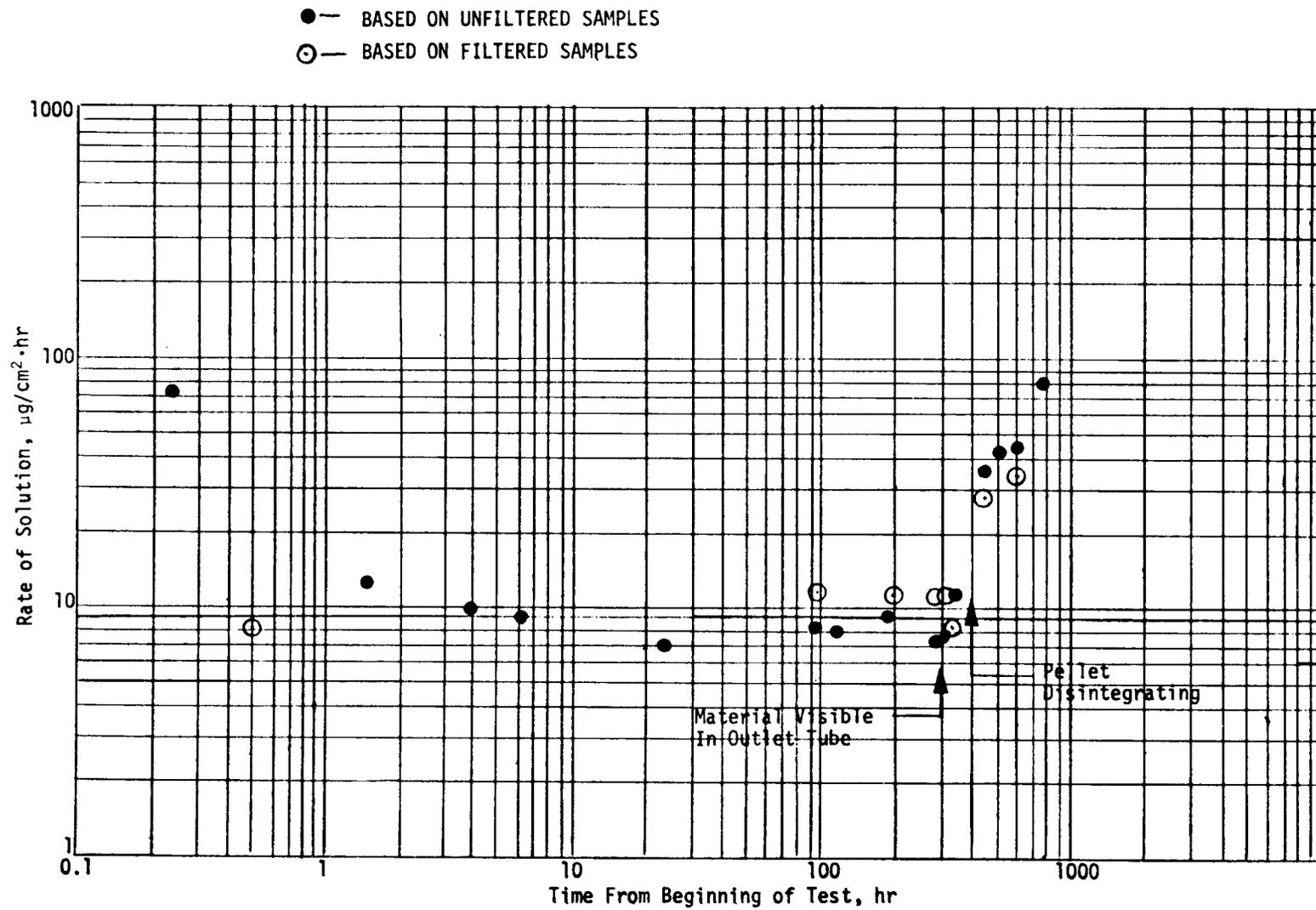


Fig. 2. Rate of Solution of ^{244}Cm From Hot-Pressed Cm_2O_3 Pellet.

After these filtered samples of high ^{244}Cm content were observed, a policy of using a new filter for each sample was adopted.

A test of the rate of solution of Cm_2O_3 in seawater has been started. The procedure is the same as that used with distilled water. No analytical results have been received as yet.

Impact Testing of Heat Source Materials (*D. W. Ramey*)

The modifications to the impact gun for hot cell operations are ~95% complete. Glove box modifications are ~75% complete. The light path housing of the microscope has been sealed with RTV silicon rubber to provide a leak-free glove box system. The microscope has been placed in the glove box and calibrated. Microscope slide preparation equipment has been designed and will be fabricated when funds become available.

Curium Data Sheets (*T. A. Butler*)

Final revisions were made to the draft copy of the *Curium Data Sheets* which was supplied to contractors last month. The major change resulted from a decision to use the isotopic composition of curium expected from the operation of light-water power reactors as a reference heat source rather than the Savannah River product. The effect of this change is to reduce the maximum heat content of the product by ~3.5%. Publication of the data sheets is expected next month.

$^{244}\text{Cm}_2\text{O}_3$ Radiation Measurements (*T. A. Butler and K. W. Haff*)

The encapsulated source containing 61.3 W_t was transferred to the Tower Shielding Facility in June, and the radiation measurements were completed. The analysis of the data is expected to be done in July.

A complete assay was made of ^{244}Cm oxide from batch SRL-17 which was used to prepare the source for the radiation measurements.

The isotopic abundances of the two principal elements, curium and plutonium, are given in Table 7.

Table 7. Isotopic Abundances of Curium and Plutonium in SRL-17 Oxide

Curium		Plutonium	
Mass No.	Isotopic Abundance (atom %)	Mass No.	Isotopic Abundance (atom %)
244	94.28	238	0.083
245	0.87	239	0.024
246	4.73	240	99.87
247	0.078	241	0.002
248	0.044	242	0.019
		244	0.005

The curium and plutonium content of SRL-17 was determined by radiochemical analysis for ^{244}Cm and ^{240}Pu and the total element weight calculated by use of the isotopic abundances given in Table 7. The results are shown in Table 8.

Table 8. Curium and Plutonium Content in SRL-17 Oxide

Sample No.	Weight (mg)	Curium (mg/g)	Plutonium (mg/g)	Cm_2O_3 (mg/g)	PuO_2 (mg/g)
Cm17-1	8.50	738	101	811	114
Cm17-2	9.61	738	103	811	117
Average		738	102	811	116
Adjusted Average ^a		791	109	869	124

^aBased on calorimetric value of 2.11 W of ^{244}Cm per gram.

The radioactive impurities were determined by standard germanium crystal gamma spectrometry and are listed in Table 9.

Table 9. Radioactive Impurities in SRL-17 Oxide

Nuclide	Curies/g
Ruthenium-103	$\leq 5 \times 10^{-6}$
Ruthenium-106	$\leq 2 \times 10^{-5}$
Cesium-134	$\leq 4 \times 10^{-6}$
Cerium-144	$\leq 4 \times 10^{-4}$
Praseodymium-144	$\leq 4 \times 10^{-4}$
Zirconium-95	$\leq 8 \times 10^{-6}$
Niobium-95	$\leq 3 \times 10^{-6}$
Europium-154	3.1×10^{-5}
Americium-243	6×10^{-3}

The elemental impurities were determined by spark source mass spectrometry and are listed in Table 10. Conversion of the major metallic impurities (>10 ppm) to fully oxidized forms equates to 7.7 mg/g.

Table 10. Elemental Impurities in Batch SRL-17 Curium Oxide

Element	Wt (ppm of Cm)	Element	Wt (ppm of Cm)
Aluminum	50	Lead	40
Arsenic	<10	Platinum	500
Boron	10	Silicon	100
Calcium	100	Tantalum	200
Cobalt	10	Titanium	10
Chromium	400	Zinc	10
Copper	50	Zirconium	250
Iron	2000	Americium	3600
Potassium	10	Chlorine	20
Magnesium	30	Fluorine	10
Manganese	50	Sulfur	80
Molybdenum	100	Lanthanum	40
Sodium	50	Cerium	40
Nickel	100	Other rare earths	100

In summary, the composition of SRL-17 curium oxide is:

<u>Material</u>	<u>mg/g</u>	<u>Percent</u>
Cm ₂ O ₃	869	86.8
PuO ₂	124	12.4
Impurities	7.7	0.8

Radioactive impurities are at or below the limits of detection with the exception of ¹⁵⁴Eu (3.1×10^{-5} Ci/g) and ²⁴³Am (6×10^{-3} Ci/g).

Curium Oxide Purification (*T. A. Butler*)

Arrangements have been made with the ORNL TRU facility to reprocess a batch (No. 72-Cm-4) of curium oxide recovered from the Kilowatt Heat Source Test containing about 50 g of ²⁴⁴Cm. The purpose of the reprocessing is to remove the ~15% PuO₂ content which has accumulated as a result of decay of ²⁴⁴Cm. This will provide ~45 g of initial product-quality Cm₂O₃ on which to make characterization studies and relate them to property measurements made with variable levels of PuO₂ content. The reprocessed material is expected to be available by August.

Curium Source Fabrication Facility Operation

(*C. L. Ottinger*)

The two 1.35-cm-diam ²⁴⁴Cm pellets prepared in May for radiation measurements were encapsulated into a test source, and the source was delivered to the Tower Shielding Facility. Significant data for these pellets are given below:

	Pellet <u>SE-1</u>	Pellet <u>SE-2</u>	Total <u>(average)</u>
Height (cm)	1.11	1.15	2.26
Weight (g)	15.62	16.21	31.83
Density (g/cm ³)	9.8	9.9	(9.85)
Watts (direct assay)	32.5	34.8	67.3
Power Concentration (W/g)	2.08	2.14	(2.11)
Power Density (W/cm ³)	20.4	21.1	(20.75)

During the pellet preparation and source assembly, the cell atmospheres were argon with oxygen content <200 ppm except for the residual carbon removal operation, which was done in argon at 2500 ppm oxygen by heating at 1000°C for 8 hr. When pellet SE-2 was removed from the furnace after the carbon removal, a hairline crack was noted across the diameter of the top surface. The pellets were assayed individually by calorimetry. Inspection of the pellets after calorimetry showed that pellet SE-2 had separated into two pieces and that pellet SE-1 had developed a hairline crack across the diameter of the top surface. The pellets, still in their platinum calorimeter cups, were stored overnight in vacuum, and pellet SE-1 also separated into two pieces.

Each pellet piece was visually inspected with a 6X monocular through the cell window. The exposed surfaces were smooth, uniform, and fine-grained; there was no evidence of chipping or flaking. In both cases the fracture was along the vertical axis, dividing the pellet into essentially equal pieces. The two halves of each pellet were fitted together with forceps and inserted into the 1.41-cm-diam inner capsule without difficulty. No material loss was detected either by weighing or by calorimetry of the empty storage cups. The inner capsule was welded by the GTA process in argon; then it was inserted into the outer capsule which was welded by GTA in air.

Fuel batch SRL-17 was used for these test pellets. This material was processed in November 1969. Assays in June 1973 showed a power concentration of 2.04 W/g in the CmO₂ form and 2.11 W/g in the Cm₂O₃ form (from pellet data); the ²⁴⁴Cm/total curium ratio is 0.943. From these data the pellet composition would be 86.8% Cm₂O₃, 11.6% PuO₂, and 1.6% other impurities (analytical results are reported in ²⁴⁴Cm₂O₃ Radiation Measurement section). These results are in good agreement with the preparation history of this fuel batch and the analytical results.

The most recently processed fuel batch, SRL-31 (January 1971), was opened and some of the material removed for tests. The fuel, in the form of granular powder, came out of the annular shipping can easily. Some fractions of the powder were stored in platinum containers for observation. A 30-g fraction in a layer ~7.5-cm diameter by 0.5-cm deep remained in the powder form when stored in air for five days. A similar fraction, 20 g in a layer 5-cm diameter by 0.5-cm deep, was calcined to the Cm₂O₃ form and only a light crust formed. However, a 12-g fraction in a layer ~2-cm diameter by 2-cm deep formed into a hard mass while being assayed on the calorimeter. These observations are in accord with previous experience in that the fuel must be handled in relatively thin layers to prevent agglomeration.

Two runs of pellets, pressed from batch SRL-31 on the 0.46-cm, ten-place multiple die, yielded 19 pellets. These were stored overnight in vacuum and one batch of ten pellets disintegrated to powder. Both batches had been pressed under the same conditions. The batch which disintegrated had been held in the die body for 10 hr prior to ejection; also, these pellets had been stored in a platinum wire basket and the others in a ceramic dish. It is not known whether either of these differences could account for the breakage. Since the breakage occurred before density measurements were made, it may be that this was originally a poor quality batch, and the breakage was simply mechanical. Another pressing was made which yielded ten good pellets. After residual carbon oxidation, the ends of the pellets were polished and the pellets stored in individual containers. The average density of the 19 pellets was 9.9 g/cm³. This is significantly better than the average densities realized on pellets of the same nominal size made from batches SRL-17 (8.4 g/cm³) and SRL-18 (8.8 g/cm³). Samples of batch SRL-31 were submitted for analysis. Five SRL-31 pellets and one SRL-17 pellet were transferred to experimental facilities.

APPENDIX
Curium-244 Inventory

	<u>²⁴⁴Cm Status (g)</u>		
	<u>6-1-73</u>	<u>Change</u>	<u>7-1-73</u>
<u>Receipts from SRL</u>			
Allocated to 04 Heat Source Program	1,902		1,902
Allocated to 05 Target Program	<u>302</u>		<u>302</u>
Total Receipts from SRL	2,204		2,204
<u>Withdrawals from 04 Program</u>			
Analytical samples	2		2
Shipped to Lovelace Foundation	9		9
Shipped to SRL	2		2
Discarded to ORNL waste	6		6
Unaccounted for	<u>80</u>		<u>80</u>
Total Withdrawals from 04 Program	99		99
<u>Balance Remaining in 04 Program</u>			
Stored residues for recovery	322		322
In-use material	146		146
Stored raw material	<u>1,335</u>		<u>1,335</u>
Total Balance in 04 Program	1,803		1,803
<u>Withdrawals from 05 Program</u>			
Transferred to TRU	146		146
Shipped to other sites	44		44
Transferred to Target Group	<u>5</u>		<u>5</u>
Total Withdrawals from 05 Program	195		195
<u>Balance Remaining in 05 Program</u>			
	107		107

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