ORNL ISOTOPIC POWER FUELS
QUARTERLY REPORT FOR
PERIOD ENDING MARCH 31, 1974

C. L. Ottinger

MASTER

OAK RIDGE NATIONAL LABORATORY

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C. L. Ottinger
Isotopes Division

JUNE 1974

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SUMMARY

Examination of the 49 compatibility test couples which were taken off test in December 1973 was started. Non-radioactive control couples representative of these 49 specimens were examined. Development of the techniques required for fabrication of the 11-couple combined compatibility/tensile strength test matrix continued. Free energy calculations were made covering possible reactions of $^{244}\text{Cm}_2\text{O}_3$ fuel with six potential encapsulants.

Helium release experiments at 500, 650, and 800°C were completed. These tests indicated that the controlling mechanism for helium release from $^{244}\text{Cm}_2\text{O}_3$ is different at different temperatures, with a change in mechanism occurring in the region of 600-700°C. Vapor pressure measurements were made on $^{244}\text{Cm}_2\text{O}_3$. A 25-W $^{244}\text{Cm}_2\text{O}_3$ pellet was exposed to dry air; it exhibited a similar edge-fracturing effect as that observed in a previous test. A leach rate study was done on a sample of air-oxidized $^{244}\text{Cm}_2\text{O}_3$ fuel.

Evaluation of the criticality aspects of three reference ^{244}Cm -fueled source assemblies was completed; the results indicated that no criticality problems would be expected. A re-orientation of the ^{244}Cm development program from emphasis on experimental properties measurements to emphasis on laboratory-scale development required some changes in the utilization of facilities and modification of some experimental plans. Plans were initiated for a ^{244}Cm recovery process development experimental program.

CURIUM-244 FUEL DEVELOPMENT

(Division of Space Nuclear Systems Program LR 30 01 03 3)

 $^{244}\text{Cm}_2\text{O}_3$ Compatibility ProgramCompatibility Couple Tests (*T. A. Butler and J. R. DiStefano*)

Examination of the compatibility couples from the FY 1973 matrix shown in Table 1 was delayed for approximately two months while the examination facility was shut down for equipment reworking and maintenance. The nonradioactive control exposures for the 900 and 1400°C tests were completed, and the specimens were examined. A summary of the results of the 900 and 1400°C control test examinations is given in Table 2. Some conclusions that can be drawn are (1) the precious metals were unaffected by exposure to helium, vacuum, or graphite under the test conditions; (2) the superalloys reacted with graphite at 900°C but did not bond to the graphite when in contact; (3) molybdenum and tantalum reacted with graphite at 1400°C when there was surface contact; and (4) the molybdenum/graphite reaction was worse than the tantalum/graphite reaction, with both reactions worse under vacuum conditions than under helium.

After completion of the maintenance work at the examination facility in March, examination of the couples from sets 1, 2, 7, 8, 9, and 10 (see Table 1) was resumed. The noble metals and noble metal alloys from sets 1 and 2 were selected for examination on a first priority basis. Top disk samples were removed for chemical analysis; the results are shown below:

<u>Material</u>	<u>Oxygen Concentration (ppm)</u>	
	<u>Set 1</u>	<u>Set 2</u>
Iridium	<10	<10
Platinum	<10	<10
Pt-20% Rh	<10	<10
Pt-26% Rh-8% W	24	17

Only the Pt-26% Rh-8% W (Pt-2608) alloy picked up oxygen. In the 1100°C tests, Pt-2608M (containing 0.5% Ti) had been found to pick up oxygen (23-107 ppm).¹

Preliminary examination of the samples from sets 1 and 2 indicated that the unalloyed platinum reacted slightly with the Cm_2O_3 , but the other materials appeared to be unaffected. At 1100°C unalloyed platinum reacted with Cm_2O_3 to form a Pt-Cm compound,¹ but little or no interaction occurred between the fuel and the other test materials (Pt-20% Rh was not tested at 1100°C).

Table 1. Record of FY 1973 Compatibility Matrix Exposures

Set ^a	Start of Test	Thermal Cycles	Cumulative Hours	End of Test
1	5-3-73	1	5021	12-3-73
2	5-3-73	1	5021	12-3-73
3	4-16-73	3	2560	8-6-73
4	4-16-73	3	2560	8-6-73
5	4-17-73	2	2510	8-9-73
6	4-17-73	2	2510	8-9-73
7	5-3-73	2	4892	11-27-73
8	5-3-73	2	4892	11-27-73
9	5-3-73	2	5016	12-4-73
10	5-3-73	2	5016	12-4-73

^aSet identifications:

1. 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.
2. 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.
3. 1100°C; 2500 hr; graphite, helium atmosphere; Ir, Pt, Pt₃Ir, and Pt-26% Rh-8% W-0.5% Ti.
4. 1100°C; 2500 hr; dynamic vacuum; Ir, Pt, Pt₃Ir, C, and Pt-26% Rh-8% W-0.5% Ti.
5. 1100°C; 2500 hr; helium atmosphere; Ir, Pt, Pt₃Ir, C, and Pt-26% Rh-8% W-0.5% Ti.
6. 1100°C; 2500 hr; graphite, dynamic vacuum; Ir, Pt, Pt₃Ir, and Pt-26% Rh-8% W-0.5% Ti.
7. 1400°C; 5000 hr; graphite, helium atmosphere; Ir, C, Mo, Mo-46% Re, Ta, T-111, W, and W-26% Re.
8. 1400°C; 5000 hr; dynamic vacuum; Ir, Mo, Mo-46% Re, Ta, T-111, W, and W-26% Re.
9. 1400°C; 5000 hr; helium atmosphere; Ir, Mo, Mo-46% Re, Ta, T-111, W, and W-26% Re.
10. 1400°C; 5000 hr; graphite, dynamic vacuum; Ir, C, Mo, Mo-46% Re, Ta, T-111, W, and W-26% Re.

Table 2. Summary of Results on Control Tests for $^{244}\text{Cm}_2\text{O}_3$ Compatibility Tests

Material	Visual Observations		Weight Change (g)
	Capsule	Specimen	
<u>Conditions: 900°C; 5000 hr; static helium; Al₂O₃ capsule holder; Hastelloy X outer container</u>			
Hastelloy C-276	Gray-black-gold film on outer surface, especially on end touching Al ₂ O ₃	Dull	0
Haynes 188	Same as above, except gold film on top end not touching Al ₂ O ₃	Dull	0
Haynes 25	Same as Hastelloy C-276	Dull	0
Hf-1% Pt-0.5% Pd	Dull, alumina-colored layer on outside surface, gold-colored layer below	Dull, black on surface touching capsule bottom	-0.0021
Graphite	No change on outside, but metallic layer on inside	Metallic layer on all surfaces except bottom where in contact with graphite capsule	0
Pt-20% Rh	Slight dull appearance on outside	Bright, except bottom surface touching capsule	0
Pt-26% Rh-8% W	Slight dull appearance on outside	Bright	0
<u>Conditions: 900°C; 5000 hr; static helium; graphite intermediate capsule; graphite capsule holder; Hastelloy X outer container</u>			
Hastelloy C-276	Gray-black layer on outer surface	Black	+0.0008
Haynes 188	Gray-black layer on outer surface	Black	+0.0006
Haynes 25	Light-gray layer on outer surface	Black	+0.0007
Hf-1% Pt-0.5% Pd	Gray-gold layer on outer surface	Dull, very light gold layer in some areas	0
ThO ₂	Surface spotted gray-black-white	Surface spotted gray-black-white	0
Platinum	Etched appearance	Bright, but etched appearance	0
Pt-20% Rh	Bright	Dull	0
Pt-26% Rh-8% W	Bright	Bright, one dark spot	0
Iridium	Bright	Bright	0
<u>Conditions: 1400°C; 5000 hr; static helium; graphite intermediate capsule; graphite capsule holder; tantalum outer container</u>			
Molybdenum	Bonded to graphite intermediate capsule, could not be separated	Etched but bright appearance	0
Tantalum	Dull on outer surface	Bright, large grains visible	0
T-111	Dull on outer surface	Dull	0
Tungsten	Shiny	Bright	a
W-26% Re	Shiny	Dull to shiny	a
Iridium	Shiny, etched	Bright, etched	a
Graphite	Light gray	No change	0
<u>Conditions: 1400°C, 5000 hr; dynamic vacuum; graphite intermediate capsule; graphite capsule holder; tantalum outer container</u>			
Molybdenum	Bonded to graphite intermediate capsule; inside surface irregular; graphite appeared to have penetrated to inside; capsule broke when we attempted to remove specimen; cleavage-type fracture	Could not be removed; reacted with graphite and capsule	a
Mo-46% Re	Bonded to graphite; could not remove	Bright	+0.0014
Tantalum	Bonded to graphite; could not remove	Bright	0
T-111	Shiny	Shiny	0
Tungsten	Bright	Bright	a
W-26% Re	Dull to shiny	Shiny	0
Iridium	Bright, etched	Stuck to capsule; could not remove; shiny	a
Graphite	Unchanged	Unchanged	0

^aNot obtained; specimen damaged when capsule was opened.

FY 1974 Compatibility Matrix (*J. R. DiStefano and C. L. Ottinger*)

The materials and exposure conditions for the FY 1974 compatibility matrix are shown below:

5000 hr, 900°C Helium	5000 hr, 1100°C Vacuum	10,000 hr, 1400°C Vacuum
Haynes 188	Pt-30% Rh-8% W	Mo-46% Re
Ta-10% W	Ta-10% W	W-26% Re
Mo-46% Re	Mo-46% Re	
TZM		
ZrO ₃		
Si ₃ N ₄		

Except for the ZrO₂ and Si₃N₄, these test couples will include specimens which will be used to test tensile strength. The tensile strength specimens will be in contact with ²⁴⁴Cm₂O₃ fuel pieces in the form of flat bars (approximately 0.5 × 0.125 × 0.050 in.). The ZrO₂ and Si₃N₄ couples will use cylindrical pellets and disk-shaped specimens.

All the required materials for this matrix were received from suppliers. Material and labor to produce the finished test specimens of Ta-10% W, Haynes 188, TZM, and W-26% Re were provided by the Metals Division of the Thermo Electron Company; the Si₃N₄ materials were provided by General Atomic. No reasonable bids for fabrication of the ZrO₂ specimens were received from commercial vendors, so the design was modified so that commercially available ZrO₂ inserts will be used in graphite outer containers. The Mo-46% Re and Pt-30% Rh-8% W were provided from ORNL stocks. Fabrication of the tensile strength specimens was started.

The rectangular ²⁴⁴Cm₂O₃ test fuel form presents an unusual in-cell fabrication problem. The procedure currently being tested involves a slotted die and punch assembly which is retained in a graphite adapter during hot pressing. After some technique development, pressings of Gd₂O₃ were done successfully in cold runs; demonstration runs with ²⁴⁴Cm₂O₃ were scheduled for April. The main expected problem is the removal of the ²⁴⁴Cm₂O₃ piece from the slotted die. Assembly of the compatibility couples is scheduled for late May.

Thermodynamic Calculations (*E. E. Ketchen*)

Calculational studies of potential reactions of encapsulant materials with ²⁴⁴Cm₂O₃ fuels were continued. Six materials, five alloys and Si₃N₄, were investigated from a thermodynamic viewpoint. Samples of all of these materials are currently being tested in the FY 1973 compatibility matrix or are scheduled for testing in the FY 1974 matrix. In studies of the alloys, common assumptions were that there would be no compound formation between constituents, that the most favorable oxides of the alloy constituents would be formed, and that oxygen solubility in the alloy would not be considered. Since free energy values for Cm₂O₃

are not available, the values for Pu_2O_3 were used as stand-ins. Partial molar free energy calculations were made by the method described previously.¹ Free energies of formation were calculated from the data of Glassner² and Oetting.³ Since possible reactions with Si_3N_4 involve products other than oxides, a different approach was used; this is described in detail under "Silicon Nitride" below. A reference fuel consisting of 95% Cm_2O_3 and 5% PuO_2 was assumed in all cases.

Reactions With Hastelloy C-276 — The composition of Hastelloy C-276 in atom percent is: Ni, 57.95; Cr, 19.21; Mo, 10.41; Fe, 6.15; W, 1.36; Co, 2.65; Mn, 1.14; V, 0.37; C, 0.52; Si, 0.11; P, 0.081; and S, 0.058. The calculated partial molar free energies of mixing for these constituents from 600 to 1300°C are given in Table 3.

Table 3. Partial Molar Free Energies of Mixing of the Constituents in Hastelloy C-276

Components	$-\Delta\bar{G}_m$ (cal/mole)				
	600°C	800°C	1000°C	1200°C	1300°C
Ni	920	1,130	1,350	1,570	1,670
Cr	2,620	3,280	3,930	4,590	4,920
Mo	3,880	4,780	5,680	6,580	7,030
Fe	4,830	5,940	7,050	8,160	8,710
W	7,380	9,090	10,750	12,510	13,360
Co	6,300	7,740	9,190	10,630	11,350
Mn	7,710	9,490	11,270	13,050	13,940
V	9,730	11,960	14,180	16,410	17,530
C	9,030	11,120	13,210	15,300	16,350
Si	11,790	14,490	17,200	19,900	21,250
P	12,340	15,170	18,000	20,830	22,690
S	12,880	15,840	18,800	21,760	23,240

The free energies of formation for the oxides considered in the $^{244}\text{Cm}_2\text{O}_3$ Fuel/Hastelloy C-276 reaction calculations are given in Table 4.

Table 4. Gibbs Free Energy of Formation of Oxides
Involved in Hastelloy C-276/Curium Fuel Reactions

Constituents	$-\Delta G_f$ (kcal/mole)				
	600°C	800°C	1000°C	1200°C	1300°C
NiO	39.06	35.01	31.01	27.10	25.15
Cr ₂ O ₃	203.92	189.81	175.72	161.67	154.63
MoO ₂	95.60	87.91	80.36	72.94	69.27
Fe ₃ O ₄	199.79	185.20	170.88	156.61	149.47
WO ₂	101.16	93.85	86.78	79.96	76.80
CoO	39.46	35.37	31.02	27.08	24.96
MnO	76.82	73.30	69.76	66.23	64.27
V ₂ O ₃	242.27	230.90	219.82	209.03	203.72
CO ₂	94.55	94.36	94.24	94.02	94.00
SiO ₂	172.92	164.60	156.33	148.10	144.00
P ₂ O ₃	212.19	200.88	189.69	178.62	173.16
SO ₂	65.74	63.80	61.86	59.93	58.97
Pu ₂ O ₃	352.12	339.32	326.94	314.98	309.15
PuO ₂	215.55	207.05	198.70	190.53	186.50

The free energies from Tables 3 and 4 were used to calculate the free energies for the reactions given in Eqs. 1-24 below.

The results of the calculations for the reactions involving Cm_2O_3 are given in Table 5; the results for the reactions involving PuO_2 are given in Table 6.

Table 5. Free Energies of Reaction
for Hastelloy C-276/ Cm_2O_3 Reactions

Equation	ΔG_r (cal/mole Cm_2O_3)				
	600°C	800°C	1000°C	1200°C	1300°C
1	237,680	237,700	237,950	238,390	238,720
3	153,450	156,070	159,090	162,490	164,360
5	209,310	208,170	207,260	206,560	206,300
7	213,140	213,790	214,640	215,870	216,650
9	211,460	212,190	212,900	213,800	214,000
11	252,650	256,440	261,430	265,640	268,320
13	144,790	147,880	151,460	155,430	158,170
15	129,300	132,330	135,490	138,770	140,480
17	223,840	214,470	205,400	196,900	192,680
19	110,420	114,160	118,240	122,680	125,020
21	-47,590	-32,090	-16,430	-590	8,220
23	272,820	267,370	262,340	257,720	255,550

Since the free energy of Eq. 21 is negative over the 600–1200°C temperature range, the reaction of Cm_2O_3 with phosphorus of the alloy would be predicted. Likewise the free energy of Eqs. 20 and 22 are negative, and the reaction of PuO_2 with silicon and phosphorus of the alloy is predicted. Since phosphorus is so reactive, it is highly likely that it may be involved in a compound formation with one of the other constituents of the alloy which could change the thermodynamic picture. However, the small percentage of silicon is also expected to react. Experimental verification of the small interaction of Hastelloy C-276 with the curium product is needed.

Table 6. Free Energies of Reaction
for Hastelloy C-276/PuO₂ Reactions

Equation	ΔG_r (cal/mole PuO ₂)				
	600°C	800°C	1000°C	1200°C	1300°C
2	20,410	20,450	20,400	20,270	20,190
4	6,370	6,840	7,260	7,630	7,800
6	16,560	16,600	16,570	16,450	16,380
8	16,320	16,460	16,520	16,520	16,510
10	16,040	16,200	16,230	16,180	16,070
12	22,910	23,570	24,320	24,820	25,120
14	4,930	5,480	5,990	6,450	6,760
16	2,350	2,890	3,330	3,620	3,820
18	18,110	16,580	14,980	13,360	12,520
20	-800	-140	450	990	1,240
22	-27,130	-24,520	-21,990	-19,560	-18,230
24	26,270	26,390	24,470	23,500	22,990

Reactions With W-26% Re — The calculated partial molar free energies of mixing for the two constituents in W-26% Re (74.24 atom % W and 25.76 atom % Re) are given in Table 7 for the temperature range from 600 to 1400°C.

Table 7. Partial Molar Free Energies of
Mixing of the Components of W-26% Re Alloy

Temperature (°C)	$-\Delta \bar{G}_m$ (cal/mole)	
	W	Re
600	520	2350
800	640	2890
1000	750	3430
1200	840	3970
1300	930	4240
1400	990	4510

The free energies of formation for the oxides considered in the ²⁴⁴Cm₂O₃ Fuel/W-26% Re alloy reaction calculations are given in Table 8.

Table 8. Gibbs Free Energy of Formation of Oxides Involved in W-26% Re Alloy/Curium Fuel Reactions

Temperature (°C)	$-\Delta G_f$ (kcal/mole)			
	WO ₂	ReO ₂	Pu ₂ O ₃	PuO ₂
600	101.16	66.80	352.12	215.55
800	93.85	58.83	339.32	207.05
1000	86.78	51.10	326.94	198.70
1200	79.95	43.60	314.98	190.53
1300	76.80	40.34	309.15	186.50
1400	74.28	37.78	303.41	182.52

The values from Tables 7 and 8 were used to calculate the free energies for Eqs. 25-28 (shown below) over the 600-1400°C temperature range. Results of these calculations are given in Table 9.

Table 9. Gibbs Free Energy of Reaction for Eqs. 25-28

Temperature (°C)	ΔG_r (cal/mole of Cm ₂ O ₃ or PuO ₂)			
	Eq. 25	Eq. 26	Eq. 27	Eq. 28
600	201,150	14,320	255,450	23,370
800	199,500	14,080	255,420	23,400
1000	197,900	13,730	255,440	23,320
1200	196,300	13,260	255,540	23,130
1300	195,350	12,960	255,000	22,900
1400	193,480	12,490	253,520	22,490

Since the free energies are all positive for Eqs. 25-28, no reaction is predicted between W-26% Re alloy and curium oxide sources between 600 and 1400°C.

Reactions With Mo-46% Re (69.50 atom % Mo, 30.50 atom % Re) — The partial molar free energy of mixing values for molybdenum and rhenium from 600 to 1400°C are shown in Table 10; the free energies of formation of MoO₂, ReO₂, Pu₂O₃, and PuO₂ are shown in Table 11.

Table 10. Partial Molar Free Energies of Mixing of the Components of Mo-46% Re Alloy

Temperature (°C)	$-\Delta\bar{G}_m$ (cal/mole)	
	Molybdenum	Rhenium
600	450	1620
800	590	2090
1000	740	2570
1200	880	3040
1300	960	3270
1400	1030	3510

Table 11. Gibbs Free Energies of Formation of MoO₂, ReO₂, Pu₂O₃, and PuO₂

Temperature (°C)	$-\Delta G_f$ (kcal/mole)			
	MoO ₂	ReO ₂	Pu ₂ O ₃	PuO ₂
600	95.60	66.80	352.12	215.55
800	87.91	58.83	339.32	207.05
1000	80.36	51.10	326.94	198.70
1200	72.94	43.60	314.98	190.53
1300	69.27	40.34	309.15	186.50
1400	65.64	37.78	303.41	182.52

The free energies from Tables 10 and 11 were used to calculate the free energies for Eqs. 29-32 over the 600-1400°C temperature range. Results are shown in Table 12.

Since the free energies are all positive for Eqs. 29-32, no reaction is predicted between Mo-46% Re alloy and the Cm₂O₃ product between 600 and 1400°C.

Table 12. Gibbs Free Energy of Reaction for Eqs. 29-32

Temperature (°C)	ΔG_r (cal/mole of Cm_2O_3 or PuO_2)			
	Eq. 29	Eq. 30	Eq. 31	Eq. 32
600	209,400	15,700	254,350	23,190
800	208,340	15,660	254,220	23,200
1000	207,510	15,330	254,140	23,100
1200	206,900	15,030	254,130	22,900
1300	206,680	14,850	253,540	22,660
1400	206,500	14,660	252,010	22,240

Reactions With Haynes 25 — The partial molar free energies of mixing for the constituents in Haynes 25 alloy are given in Table 13. The composition of Haynes 25 in atom % is Co, 52.31; Ni, 10.64; Si, 2.22; Mn, 1.71; C, 0.52; P, 0.06; and S, 0.059. The calculated free energies of formation of the various oxides are shown in Table 14.

Table 13. Partial Molar Free Energies of Mixing of the Constituents in Haynes 25 Alloy

Components	$-\Delta \bar{G}_m$ (cal/mole)				
	600°C	800°C	1000°C	1200°C	1300°C
Co	1,060	1,320	1,580	1,830	1,960
Ni	3,880	4,780	5,670	6,560	7,000
Cr	2,200	2,760	3,330	3,890	4,180
W	4,860	6,050	7,230	8,410	9,000
Fe	5,890	7,240	8,590	9,940	10,610
C	9,040	11,130	13,220	15,310	16,350
Si	6,330	7,840	9,360	10,870	11,630
Mn	6,980	8,600	10,220	11,830	12,640
P	12,840	15,790	18,730	21,680	23,150
S	12,880	15,840	18,800	21,750	23,230

The free energies from Tables 13 and 14 were used to calculate the free energies for Eqs. 33-52. Results are shown in Tables 15 and 16.

Table 14. Gibbs Free Energy of Formation of Oxides
Involved in Haynes 25/Curium Fuel Reactions

Constituents	$-\Delta G_f$ (kcal/mole)				
	600°C	800°C	1000°C	1200°C	1300°C
CoO	39.46	35.37	31.02	27.08	24.96
NiO	39.06	35.01	31.01	27.10	25.15
Cr ₂ O ₃	203.92	189.81	175.72	161.67	154.63
WO ₂	101.16	93.85	86.78	79.96	76.80
Fe ₃ O ₄	199.79	185.20	170.88	156.61	149.47
CO ₂	94.55	94.36	94.24	94.02	94.00
SiO ₂	172.92	164.60	156.33	148.10	144.00
MnO	76.82	73.30	69.76	66.23	74.27
P ₂ O ₃	212.19	200.88	189.69	178.62	173.16
SO ₂	65.74	63.80	61.86	59.93	58.97
Pu ₂ O ₃	352.12	339.32	326.94	314.98	309.15
PuO ₂	215.55	207.05	198.70	190.53	186.50

Table 15. Free Energies of Reaction
for Haynes 25/Cm₂O₃ Reactions

Equation	ΔG_r (cal/mole Cm ₂ O ₃)				
	600°C	800°C	1000°C	1200°C	1300°C
33	236,940	237,160	238,600	239,930	240,150
35	246,580	248,620	250,890	253,360	254,710
37	152,590	155,030	157,870	161,100	162,870
39	207,680	207,620	207,620	207,660	207,460
41	215,520	216,710	218,100	219,880	220,920
43	223,850	214,480	205,420	196,910	192,690
45	102,230	104,190	106,490	109,130	109,580
47	142,600	145,210	148,310	151,790	154,290
49	-46,580	-30,850	-14,970	1,110	9,040
51	272,820	267,370	262,340	257,710	255,540

Table 16. Free Energies of Reaction
for Haynes 25/PuO₂ Reactions

Equation	ΔG_r (cal/mole PuO ₂)				
	600°C	800°C	1000°C	1200°C	1300°C
34	20,290	20,360	20,510	20,420	20,430
36	21,900	22,270	22,560	22,770	22,850
38	6,230	6,670	7,060	7,390	7,550
40	15,410	15,430	15,350	15,150	14,980
42	315,880	299,080	281,880	264,310	255,420
44	18,110	16,580	14,980	13,360	12,520
46	-2,160	-1,800	-1,510	-1,390	-1,170
48	4,570	5,030	5,460	5,840	6,120
50	-26,970	-24,310	-21,750	-19,270	-18,070
52	26,270	25,390	24,470	23,490	22,990

Since the free energy of Eq. 49 is negative over the 600–1175°C range, the reaction of Cm₂O₃ with phosphorus of the alloy would be predicted. Likewise the free energy of Eqs. 46 and 50 are negative and the reaction of PuO₂ with the silicon and phosphorus of the alloy is predicted. Although it was assumed that no compound formation between the fuel and the constituents of the alloy would occur, phosphorus is so reactive that it is highly likely that it may be involved in a compound formation with one of the other constituents of the alloy, and this could change the thermodynamic picture. However, the small percentage of silicon is also expected to react.

Reactions With Pt-2608M — The composition of Pt-2608M in atom percent is Pt, 52.27; Rh, 39.33; W, 6.77; and Ti, 1.63. The partial molar free energies of mixing for Pt, Rh, W, and Ti were calculated; the results are shown in Table 17.

Table 17. Partial Molar Free Energies of Mixing of Components of Pt-26% Rh-8% W-0.5% Ti

Temperature (°C)	$-\Delta\bar{G}_m$ (cal/mole)			
	Pt	Rh	W	Ti
600	1040	1570	4420	6,980
800	1300	1940	5490	8,620
1000	1560	2320	6560	10,260
1200	1820	2690	7630	11,890
1300	1950	2870	8160	12,710

The calculated free energies of formation of Pt_3O_4 , Rh_2O , WO_2 , TiO , Pu_2O_3 , and PuO_2 are shown in Table 18. Platinum will not react with oxygen at 600–1300°C, but rhodium, tungsten, and titanium will react with oxygen at 600–1300°C.

Table 18. Gibbs Free Energy of Formation of Pt_3O_4 , Rh_2O , WO_2 , TiO , Pu_2O_3 , and PuO_2

Temperature (°C)	ΔG_f (cal/mole)					
	Pt_3O_4	Rh_2O	WO_2	TiO	Pu_2O_3	PuO_2
600	10,300	-11,350	-101,160	-103,780	-352,120	-215,550
800	26,400	-9,090	-93,850	-99,380	-339,320	-207,050
1000	42,080	-6,940	-86,780	-95,080	-326,940	-198,700
1200	57,330	-4,900	-79,960	-90,870	-314,980	-190,530
1300	64,790	-3,910	-76,800	-88,810	-309,150	-186,500

The free energies from Tables 17 and 18 were used to calculate the free energies for Eqs. 53–58. Results are shown in Table 19.

Table 19. Gibbs Free Energy of Reaction for Eqs. 53-58

Temperature (°C)	ΔG_r (kcal/mole of Cm_2O_3 or PuO_2)					
	Eq. 53	Eq. 54	Eq. 55	Eq. 56	Eq. 57	Eq. 58
600	327.49	35.38	207.01	15.30	61.72	-8.92
800	323.69	34.78	206.78	15.30	67.04	-8.00
1000	320.04	34.09	206.61	15.18	72.48	-7.18
1200	316.42	33.28	206.49	14.96	78.04	-6.45
1300	315.07	32.85	206.19	14.77	80.85	-6.12

Since the free energies are positive for Eqs. 53, 55, and 57, Cm_2O_3 is not expected to react with the alloy. However, the reaction of titanium with PuO_2 has a negative free energy, hence the PuO_2 of the curium product is expected to react with the titanium of the alloy.

In conclusion, it appears from thermodynamic considerations that the Pt-26% Rh-8% W-0.5% Ti alloy will react with the Cm_2O_3 fuel containing 5% PuO_2 at 600-1300°C.

Silicon Nitride — Several possible reactions of Si_3N_4 with the curium heat source product are conceivable. Some of the possible products are CmN , N_2 , SiO_2 , CmSi , Cm_2Si_3 , and CmSi_2 . The thermodynamic data needed for the calculating of the free energies of reaction to produce curium silicides are not available. Hence, the free energy calculations were made on the CmN , N_2 , and SiO_2 only. Since the actinide silicides are probably among the weaker compounds, they may not be important anyway.

The free energies of formation of Si_3N_4 , CeN , SiO_2 , Pu_2O_3 , and PuO_2 were calculated from a data calculation by O. Kubaschewski *et al.*,⁴ a compilation by Glassner,² a survey by K. A. Gschneidner,⁵ and a review article by Oetting.³ The results are shown in Table 20.

Table 20. Gibbs Free Energy of Formation of Si_3N_4 , CeN , SiO_2 , Pu_2O_3 , and PuO_2

Temperature (°C)	$-\Delta G_f$ (kcal/mole)				
	Si_3N_4	CeN	SiO_2	Pu_2O_3	PuO_2
600	240.79	56.18	172.92	352.12	215.55
800	260.99	51.18	164.60	339.32	207.05
1000	282.05	46.18	156.33	326.94	198.70
1200	303.97	41.18	148.10	314.98	190.53
1300	315.14	38.68	144.00	309.15	186.50

The data from Table 20 were used to calculate the free energies of Eqs. 59 and 60. The CeN was used as a stand-in for CmN and Pu_2O_3 was used as a stand-in for Cm_2O_3 . Results are shown in Table 21.

Table 21. Gibbs Free Energy for Eqs. 59 and 60

Temperature (°C)	ΔG_r (cal/mole of Cm_2O_3 or PuO_2)	
	Eq. 59	Eq. 60
600	156,960	16,320
800	171,740	17,980
1000	187,300	19,660
1200	203,640	21,350
1300	212,040	22,190

Since the free energies of Eqs. 59 and 60 are positive, the Si_3N_4 should not react with the curium oxide heat source product to produce CmN, N_2 , or SiO_2 . Nothing definite can be said about the reactions of Si_3N_4 with the curium oxide product to give a silicide but this is not expected since the silicides are probably weaker compounds than the nitrides. From the standpoint of thermodynamic calculations, the Si_3N_4 should not react with the curium oxide product. Compatibility studies are needed to verify the conclusions.

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

Helium Release (*P. Angelini*)

The three helium release experiments initiated in December 1973 were completed. Experimental procedures and initial data were reported previously.¹ The plots of helium release rate versus time for samples A (500°C), B (800°C), and C (650°C) are presented in Fig. 1. During each incremental measuring time, the release rate is recorded and integrated such that the amount of helium emitted over that incremental time is obtained. The abscissa of Fig. 1 represents the time from initial heating of the sample to the end of the incremental measuring time for the release rate.

The experiments were continued uninterrupted up to time period J (see Fig. 1). At time J the temperature of a specific sample was decreased, and the sample unloaded in an inert atmosphere glove box. The sample pellet was then photographed, and its dimensions and mass measured. It was then cracked with approximately one-half of the sample used for an x-ray diffraction study and the remainder reweighed and reloaded into the

Fig. 1. Helium Release Rate vs Time for $^{244}\text{Cm}_2\text{O}_3$ Samples.

furnace and reheated to the same previous temperature. The time period necessary to perform these operations was approximately six hours per sample. The x-ray diffraction scans were performed usually a day after the unloading procedure. The three samples were unloaded on different days in order to keep their exposure at ambient temperature to a minimum.

The mass and dimensional data for each sample measured at the beginning of the experiment (time 0) and at time J are presented in Table 22.

Table 22. Mass and Dimensional Data

Sample	Temperature (°C)	Time 0			Time J		
		Mass (g)	Height (mils)	Density (g/cm^3)	Mass (g)	Height (mils)	Density (g/cm^3)
A	500	0.2278	52.3	10.44	0.228	52.2	10.47
C	650	0.2374	53.4	10.66	0.238	53.5	10.67
B	800	0.2291	53.7	10.23	0.229	52.6	10.44

The mass measurements are within experimental error. No increase or decrease in mass occurred in any of the samples during the more than 1100 hr at temperature. If there was any oxidation or reduction of the samples during this time, a change in mass would have occurred and been measured. Thus, the samples did not change stoichiometry during the test. The measurement of height for pellets A (500°C) and C (650°C) showed no differences at time J. A significant height change occurred in sample B (800°C). The sample increased in density during the time period J. This is a significant difference between the lower temperature experiments (500 and 650°C) and the 800°C experiment and is an additional phenomenon which shows that a different mechanism for helium release in Cm_2O_3 occurs at temperatures lower than 650°C.

Prior to unloading of the samples, it was thought that perhaps some macroscopic damage had occurred to sample pellets A and C due to their emission of a large fraction of their helium inventory during an earlier time in the experiment. In inspecting the sample pellets during the unloading period, no major macroscopic defects could be seen in any of the pellets. The pellets were photographed (Fig. 2), and no anomalous expansion occurred in any of the pellets. It can be seen from the photographs that there is a slight difference in surface appearance of the 500 and 650°C samples and the 800°C sample. The pellets were broken using a mortar and pestle. Sample A (500°C) broke into many pieces and was the most easily broken of the three pellets. The 800°C pellet was the hardest to break. This would indicate that some macroscopic structural damage did occur to the lower temperature pellets A and C.

X-ray diffraction scans made from 10 to 80°2 θ showed that the lower the sample temperature the larger the monoclinic cell parameters and the broader the diffraction peaks. Also the diffraction peaks above 60°2 θ were not observed for the 500 and 650°C samples. The pattern obtained from the 800°C sample indicated that the monoclinic cell parameters were larger than those obtained for a standard Cm_2O_3 monoclinic sample. X-ray diffraction peaks up to 80°2 θ were measured for the 800°C sample. These results show that the crystallites in the 500 and 650°C samples were smaller than those of the 800°C sample. The absence of the high angle lines indicates additional damage to the crystal structure of the 500 and 650°C samples.

The evidence of the dimensional differences, the surface appearance, the mechanical strength of the pellets, and the differences observed in the x-ray diffraction scans show that the lower temperature pellets did undergo greater crystallite and structural damage than the 800°C pellet. The data reinforce the theory of a different helium release mechanism operating at the lower temperatures.

After the samples were weighed and reloaded into the furnaces, the helium release experiment continued until the helium release rate of the samples was equal to the helium generation rate. At a time labeled I on Fig. 1, the samples were transferred to the high-temperature vacuum furnace and degassed to a temperature of 1900°C. The results of the helium inventory measurements are presented in Table 23.

Sample A, 500°C, 1230 hr

Sample B, 800°C, 1150 hr

Sample C, 650°C, 1175 hr

Fig. 2. $^{244}\text{Cm}_2\text{O}_3$ Pellets After Helium Release Experiment.

Table 23. Helium Inventory Measurements

Sample	Temperature (°C)	Helium Inventory (cm ³ He/g Cm ₂ O ₃)	Diffusion Parameter D' (1/sec)
A	500	0.262	2.26×10^{-8}
C	650	0.194	3.04×10^{-8}
B	800	0.0582	1.07×10^{-7}

The diffusion parameter data are plotted on Fig. 3 with the previous data obtained for $^{244}\text{Cm}_2\text{O}_3$.⁶ The D parameters for the 650 and 500°C samples are near the extrapolated curve. On observing the three samples during this experiment, various nonsteady state situations could be seen in each. The diffusion parameter probably varied in absolute value during the course of the experiment for each sample but much more drastically for the 500 and 650°C samples. In observing the results in Fig. 1, an

Fig. 3. Helium Diffusion Parameters for $^{244}\text{Cm}_2\text{O}_3$.

anomaly was noted in that after the reloading period the helium release rate for the three samples decreased from its previous steady-state value. As time progressed, the type of release changed for the A (500°C) and C (650°C) samples. The burst-type helium release again became prominent during the remainder of the experiment for samples A and C. The A (500°C) and C (650°C) experiments showed that there is an additional helium release mechanism at these temperatures. Additional experiments would be necessary in this temperature range in order to better understand the phenomena occurring at these temperatures. At these temperatures there are many factors which could influence the helium release characteristics of samples, and these coupled with the long time period necessary for a steady-state condition to develop greatly increase the problem of clarifying the helium release phenomena near the 650°C temperature range.

Four isochronal helium release experiments were performed using the remainder of the $^{244}\text{Cm}_2\text{O}_3$ fuel from helium release experiment C (650°C). These were performed to provide additional information as to the types of helium release mechanisms operating in the 500 and 800°C temperature range.

The experimental conditions of the four experiments are presented in Table 24.

Table 24. Experimental Conditions of the
Isochronal Anneal Experiments for $^{244}\text{Cm}_2\text{O}_3$

Experiment Number	Initial Annealing Temperature (°C)	Time Period at Ambient Temperature (days)
1	800	3
2	800	20
3	1100	20
4	1100	4

In these experiments the initial annealing temperature was held for approximately 1 hr. The sample was then cooled over a 3-hr period to ambient temperature with the sample held at ambient temperature for the desired time period as shown in Table 24. The concentration of helium in the sample increased at ambient temperature during the desired time period. During each of the isochronal anneal experiments, the sample was maintained at the desired temperature for one half hour with the sample's temperature increased in 100°C intervals.

The data obtained during the experiments are presented in Fig. 4. In observing the data from experiment 1, the onset of a definite change in helium release characteristics of the sample occurred near the 600°C temperature range. In experiment 2 the sample was maintained at ambient temperature for 20 days (approximately seven times longer than experiment 1). Again the onset of the measurable change of the helium release

Fig. 4. Isochronal Anneal Experiments for $^{244}\text{Cm}_2\text{O}_3$.

characteristics occurred near the 600°C temperature. Thus the initial helium concentration in the sample within the concentration range obtained in the present experiments does not significantly change the temperature at which there is a definite change in the helium release mechanism.

The experimental conditions were changed such that the initial annealing temperature was increased from 800 to 1100°C. The data from experiment 3 (20-day period at ambient temperature) indicate that the onset of measurable change in the helium release characteristics again occurred near the 600°C temperature. In this experiment, burst-type helium release was observed to begin at 300°C, to peak at 800°C, and to continue to 1100°C. In experiment 4 (4-day period at ambient temperature) the onset of the

change in the helium release again occurred near 600°C. In addition there was no burst-type helium release observed during the experiment. Thus changing the initial annealing temperature from 800 to 1100°C in the present experiments does not significantly change the temperature at which the onset of the helium release mechanism operative above the 600°C temperature range is initiated. The 600°C temperature is indicated to be the minimum temperature at which the helium release mechanism operating in the 600-1300°C temperature range is measurably observed in the present experiments.

The burst-type helium release in experiment 3 occurred over the 300 to 1100°C temperature range. This type of helium release decreased as time progressed in the 800°C steady-state helium release experiment; it increased with increasing time in the 500 and 650°C steady-state experiments. The results from these experiments show that the burst-type helium release is related to the helium concentration in the sample over the 300 to 1100°C temperature range and is the major helium release mechanism operating below the 650°C temperature range.

As shown by the gradual disappearance of the burst-type helium release in the 800°C experiment, this type of release becomes secondary during steady-state experiments above the 650°C temperature range.

The gradual increase in the burst-type helium release at temperatures below 650°C indicates that as the concentration of helium increases in a radiation damaged fuel form the single helium atoms form clusters. As time progresses the concentration of the clusters increase such that they interact in providing an interconnected microstructure through which the clusters may be released. Above the 650°C temperature range, the experiments indicate that the clusters or dislocation loops formed by radiation damage become significantly more mobile and migrate to releasing areas. The rate of annealing for this process at temperatures greater than 650°C is such that coalescence of large numbers of helium-filled clusters or dislocation loops is effectively reduced. The helium release rate becomes more uniform with the burst-type helium release almost eliminated as the sample's temperature is maintained for long periods of time at temperatures above 650°C.

Vapor Pressure (*J. C. Posey*)

The vapor pressure of Cm_2O_3 is being measured using the Knudsen cell method. Several preliminary values have been determined and compared to the earlier work of Smith and Peterson.⁷ Current work has been directed primarily toward the elimination of possible systematic errors and the reduction of random error. The data determined so far in the current work are shown in Fig. 5 along with a part of the data of Smith and Peterson. The two groups of data can be compared at about 1600°C where their temperature ranges touch. The ORNL data are lower than those determined by Smith and Peterson in Run 2 but agree well with those determined in Run 1. Smith and Peterson, however, believed the Run 2 data were their best because of the presence of about 12.5 mole % impurities in the Cm_2O_3 used in Run 1.

They also conducted two other runs which gave badly scattered higher data. Our methods are being examined for possible systematic error.

Fig. 5. Vapor Pressure of Cm_2O_3 .

All of the data are presented as if the Cm_2O_3 were present in the vapor state as Cm_2O_3 molecules. (It is necessary to assume a molecular weight to calculate vapor pressure from Knudsen cell data.) Smith and Peterson presented their data in this form because the actual vapor species had not been proven. They, however, deduced from thermodynamic considerations that Cm_2O_3 probably vaporized according to the following disproportionation reaction:

Plans call for the determination of the vapor species by mass spectrometer in the future.

In our work a known fraction of the Cm_2O_3 leaving the Knudsen cell impinges on a target plate at the top of the furnace. The amount of curium on the target is determined by an alpha counting procedure, and the amount of Cm_2O_3 leaving the Knudsen cell is calculated from this value. This calculation assumes that all of the molecules striking the target stick, but this could not be assumed with certainty. In some similar reported cases, the condensation coefficient is much less than one.^{8,9} (The condensation coefficient is the fraction of the molecules striking the surface which stick.) The size of the condensation coefficient is strongly influenced by the nature of the surface. High values occur when the condensing molecules readily fit into the crystalline lattice of the surface.

Several targets with differing surfaces were prepared and exposed in the vapor pressure apparatus. The results are given in Table 25.

Table 25. Effect of the Nature of Target Surface
on the Amount of Curium-244 Collected

Exposure Temperature (°C)	Exposure Time (hr)	Curium-244 Deposited (μg)	Nature of Surface
1535	0.500	10.9×10^{-5}	Stainless steel
1535	0.500	9.84×10^{-5}	Oxidized stainless steel
1535	0.500	9.35×10^{-5}	Nd_2O_3 deposited on stainless steel
1535	0.500	8.29×10^{-5}	Lead electroplated on stainless steel and lightly oxidized
1535	0.500	9.27×10^{-5}	Platinum
Average deposit		9.53×10^{-5}	$S(x) = 0.95 \times 10^{-5}$
1492	1.00	7.80×10^{-5}	Stainless steel
1490	1.00	7.32×10^{-5}	Oxidized stainless steel
1490	1.00	7.80×10^{-5}	Nd_2O_3 deposited on stainless steel
1492	1.00	8.70×10^{-5}	Lead electroplated on stainless steel and lightly oxidized
Average deposit		7.90×10^{-5}	$S(x) = 0.58 \times 10^{-5}$

Any influence of surface composition is entirely obscured by the random scatter of the data. The standard deviation of points about the mean was 0.95×10^{-5} μg or 10% for the 1535°C data and 0.58×10^{-5} μg or 7.3% for the 1490°C data. Stainless steel gave the highest value in the 1535°C tests but was below average in the 1490°C test; lead gave the lowest value in the 1535°C test but gave the highest value in the 1490°C test. It was concluded that the condensation coefficient is little influenced by the nature or the composition of the surface of the target. It is not likely that five different substances would exhibit essentially equal condensation coefficients unless the coefficients were all near unity. The point could be proven rigorously by means of a hollow target which would operate in a manner analogous to a black body hole as used in the measurement of temperature by optical pyrometer. Since this proof would involve substantial time and expense, it is not planned.

The original temperature control equipment functioned poorly in the lower temperature range. The temperature tended to drift in an erratic manner. This made the long runs required at the lower temperatures nearly impossible and limited the temperature range. A proportional controller was designed, fabricated, and installed on the furnace power supply. The controller is different from the previous one in that it maintains a desired constant power input to the furnace whereas the previous one maintained a constant current input to the furnace. The present controller can also linearly ramp the power level from any two positions over the entire furnace temperature range, and the ramping time can be varied linearly from one-half to six hours. The present controller should maintain a more constant operating temperature over the complete temperature range. In an experiment with the new controller at a furnace temperature of 1260°C, the temperature was maintained essentially constant over a 72-hr period.

In order to test the temperature uniformity of the Knudsen cell used in the Cm_2O_3 vapor pressure experiments, a second Knudsen cell of identical physical dimensions has been placed in the glove box. This second cell has two additional black body holes; one located immediately above the present one on the base and the other located on the upper piece near the top surface. The temperature calibrations will show if any thermal gradients exist along the cell. If a significant temperature difference is found, the cell can be oriented such that the temperature difference will be minimized.

In preparation for a re-run on several data points of the vapor pressure, new target holders were fabricated. The use of a fresh target holder for each cycle of measurements should reduce the likelihood of incidental contamination on the targets; this is especially important at the low-temperature end of the range since the amount of ^{244}Cm collected is so small. In combination with the improved temperature control reported last month, this technique should provide better data.

Dimensional Stability (*C. L. Ottinger*)

The 25-W pellet of purified Cm_2O_3 (PCM-P1) which had been exposed to dry air for ~4 months was broken up in order to use the $^{244}\text{Cm}_2\text{O}_3$ for other experiments. Although the material which had flaked off from the ends of this pellet was a coarse powder, the remaining bulk pellet was quite hard and difficult to fracture. It was finally broken up by placing it in a cylindrical well of a chill block and using a striking rod to impact the pellet. The other purified $^{244}\text{Cm}_2\text{O}_3$ pellet (PCM-P2), which had been stored under argon, was exposed to dry air and observed. In contrast to PCM-P1, there was little flaking of material from the edges of this pellet during the first few days. However, multiple small cracks appeared in the edge zones, indicating that a similar phenomenon was occurring. Observation of this pellet will continue.

Solubility of Stored Curium Oxide Powder in Air-Saturated Distilled Water (*J. C. Posey*)

A test was made of the solution behavior of curium oxide powder from the stored inventory of curium oxide. This powder has a composition falling between $^{244}\text{Cm}_2\text{O}_3$ and $^{244}\text{CmO}_2$. A 0.0858-g sample of the powder was placed in 150 ml of distilled water contained in a stainless steel beaker. The beaker was covered to reduce evaporation. The mixture was agitated by a teflon covered magnetic stirrer. The heat of decay of the ^{244}Cm and the energy of stirring caused the temperature to be 38°C although the room temperature was approximately 25°C . Samples were withdrawn at intervals through 10- to 20- μm sintered glass filter sticks and their ^{244}Cm contents were determined by an alpha counting procedure.

The solution concentration as a function of time is shown in Fig. 6. The reason for the series of peaks is not known. It is possible that different chemical compounds were formed as time progressed. Curium forms four known anhydrous oxides, $\text{CmO}_{1.5}$, $\text{CmO}_{1.71}$, $\text{CmO}_{1.83}$, and CmO_2 . Little is known concerning the hydrated oxides or hydroxides.

Fig. 6. Solution of CmO_x .

At 338 hr, an olive green color was observed and the volume of powder appeared to increase. This may have been caused by corrosion of the beaker.

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

In a previous report¹ the calculated abundances of the principal isotopes of curium were shown to vary depending on the type of commercial power reactor and composition of the fuel. The abundance of the sum of the fissile isotopes ^{243}Cm and ^{245}Cm varied in the range 6.4 to 12.2 atom %. This contrasts with <1 atom % of the fissile isotopes in Savannah River product ^{244}Cm , which is currently being used for fuel characterization, and raised the question of criticality safety of some heat source designs. The following criticality evaluation was prepared by the ORNL Neutron Physics Division.

A study of the criticality parameters of three ^{244}Cm -fueled heat sources using the KENO Monte Carlo code has been made. Heat source designs considered, designated A, B, and C, are described in Table 26. Cross sections used were from the 100 group set processed from data in the ENDF/B data file, except those for ^{245}Cm , which were compiled by O. L. Smith as part of a study for the ORNL Reactor Division. All calculations assumed water or graphite between units in the arrays studied and 15-cm water reflection external to the arrays. Curium isotope abundances were taken from those for PWR (U + Pu) fuel, since the highest percent (12.2%) of ^{245}Cm occurred here. Cross sections for ^{244}Cm and ^{245}Cm only were used in the calculation. Curium-243 was included with ^{245}Cm , and ^{246}Cm was included with ^{244}Cm . Because of the small amounts of ^{243}Cm and ^{246}Cm present, this approximation should not introduce any significant error, and based on available data, it should result in a high estimate of k_{eff} .

Table 26. Curium-244 Heat Source Descriptions

Design	Unit Description	No. of Units	Total Watts
A	Fourteen $^{244}\text{Cm}_2\text{O}_3$ pellets totaling 400 W; arranged uniformly within a graphite sphere; encapsulated in metal and graphite concentric shells; overall diameter 3.5 in.	6	2400
B	Two pencil-type $^{244}\text{Cm}_2\text{O}_3$ sources in thin metal capsules totaling 300 W; arranged side-by-side in a rectangular graphite body $3 \times 3 \times 1.5$ in.	28	8400
C	$^{244}\text{Cm}_2\text{O}_3$ pellets totaling 4400 W stacked to form a column 1.1-in. diameter by 15-in. high; encapsulated in metal cladding (no graphite)	2	8800

For all the systems studied, the geometries were represented as accurately as was deemed reasonable for a survey study. Any approximations made were made so as to increase the multiplication of the systems.

The effect of resonance corrections for ^{244}Cm and of various cross section compilations for ^{245}Cm was considered. The effect of these two factors was found not to be significant for these systems.

Design A

Source design A was approximated by three concentric spherical annular regions consisting of void, homogenized fuel with graphite, and a region of low density graphite. Several thin layers consisting of Haynes 188, TZM, and graphite surrounded this core. A $2 \times 2 \times 2$ water-moderated array was used, with six of the units containing spheres and with the outside layers in contact, and the other two units containing water. This arrangement resulted in a k_{eff} of 0.234 ± 0.005 .

In order to test how well this configuration represented the actual geometry, another geometry was used in which the fuel-graphite region was divided into two regions, one with graphite only and the other with higher than average density fuel mixed with the rest of the graphite. This new arrangement more closely approximates the actual geometry of the sphere and gave a k_{eff} of 0.233 ± 0.005 , indicating no significant effect.

It was noted during the course of the calculations that the fission cross sections for the ^{245}Cm set generated at ORNL were somewhat different from a set which had been compiled at the Savannah River Plant. In view of possible uncertainties in these cross sections, a new set was generated which contained the higher value of fission cross sections from these two sets for all energies. Scattering and capture cross sections from the ORNL set were used. Such a set should significantly reduce the possibility of underestimating the criticality of the ^{244}Cm heat sources. The use of this cross-section set for the spheres described above gave a k_{eff} of 0.244 ± 0.005 , which is only a relatively small increase.

Design B

Source design B was represented by a $3 \times 3 \times 4$ water-moderated array, with the bottom 3×3 (27 units) and one central unit at the top containing fuel pellets. The remaining eight units on the top contained water. For no separation between units, this arrangement gave a k_{eff} of 0.402 ± 0.005 . In order to test the effect of varying amounts of water between the units, the edge-to-edge spacing was varied by 1-cm increments. It was found that the highest k_{eff} , occurring at 2-cm separations, was 0.441 ± 0.008 .

In the above calculations, no allowance had been made for the effect of self-shielding in the resonance capture cross sections of ^{244}Cm . An additional calculation at 2-cm separations which included the effects of the resonance corrections gave a k_{eff} of 0.453 ± 0.008 , which is only a small increase over the previous result. In addition, a calculation

which used the modified fission cross section described previously, as well as the resonance correction, yielded a k_{eff} of 0.471 ± 0.007 . This is the highest k_{eff} obtained for any of the calculations in this study.

Since all of the units contain graphite, the possibility of graphite moderation between elements of the array was considered. The arrays were water reflected. Design B was chosen for this study, since it had the highest k_{eff} for water moderation. For various spacings between the units, the highest value of k_{eff} with graphite moderation was 0.421 ± 0.006 at 0-cm separation between units.

Design C

Source design C consisted of two adjacent rods of fuel, with several layers of various cladding. This arrangement, with water moderation, resulted in a k_{eff} of 0.331 ± 0.007 .

Summary of Results

The results of ^{244}Cm heat source calculations are summarized in Table 27. The effect of varying the separations between adjacent units is demonstrated in the design B values. Since the k_{eff} values here are higher than for the A and C designs, it appears unlikely that the highest k_{eff} for design B results will be exceeded for any spacing of the other designs. If the maximum number of units are not exceeded and no other major changes in design are encountered, the heat sources appear to have no criticality problem.

Table 27. Results of Criticality Evaluation of Curium-244 Sources

Design	No. of Units	Edge-to-Edge Spacing (cm)	k_{eff}	Remarks
A ^a	6	0	0.234 ± 0.005	
		0	0.233 ± 0.005	Extra region in sphere
		0	0.244 ± 0.005	Revised ^{245}Cm fission cross sections
B ^a	28	0	0.402 ± 0.005	
		1	0.431 ± 0.007	
		2	0.441 ± 0.008	
		2	0.453 ± 0.008	Resonance corrected ^{244}Cm
		2	0.471 ± 0.007	Resonance corrected ^{244}Cm and revised ^{245}Cm fission cross sections
B ^b	28	3	0.405 ± 0.008	
		0	0.421 ± 0.006	Resonance corrected ^{244}Cm and revised ^{245}Cm fission cross sections
		1	0.399 ± 0.006	Same
		3	0.353 ± 0.006	Same
		5	0.334 ± 0.007	Same
C ^a	2	0	0.331 ± 0.007	

^aWater-moderated, water-reflected.

^bGraphite-moderated, water-reflected.

Effects of Plutonium In-Growth (*C. L. Ottinger*)

Current experimental work with ^{244}Cm utilizes for the most part "stock" ^{244}Cm oxide resulting from a processing campaign carried out at SRL during the period 1968-1971. A small fraction of ^{244}Cm was recovered from waste residues at ORNL in 1973 to provide some low-plutonium material for experiments, but except for this fraction materials available contain plutonium concentrations ranging upwards from ~10%. Although these are referred to as "production-grade," this term is not intended to imply that they are identical to the ^{244}Cm products that would be expected from a by-product ^{244}Cm recovery plant.

Among the as yet unanswered questions in the development of ^{244}Cm for heat source use are those related to the effects of impurities. The impurities which will be present in practical ^{244}Cm fuels are of two types — process contaminants and plutonium. Process contaminants are those which are not totally removed during the ^{244}Cm separations process or which are introduced as a result of the process; these may include any of a large variety of impurities at various levels. Since the development of process flow-sheets is still only in the study stage, evaluation of the likely process impurities can be only an educated guess at present. Based on previous processing experience, it can be inferred that americium will be the primary process contaminant, and that it will be present in concentrations of about 1-2 wt %. For study purposes, an initial ratio of process impurities to curium of 0.03 has been assumed, but no assumed distribution of impurities has been established. Possible influences of process impurities include effects on fabricability of fuels to compatibility, vaporization characteristics, thermophysical properties, and others in addition to the obvious effect on power density. It will be necessary to evaluate these effects both by simulation and eventually by practical demonstration when typical fuels are available.

While the types and amounts of process impurities cannot be accurately predicted at present, the amount of plutonium can be since it varies only with the time since separation of the ^{244}Cm . (It can be confidently assumed that the plutonium content will be insignificant as of separation time.) In any processing/fuel fabrication/source encapsulation system which includes a few months of storage and/or shipment time for the products, plutonium will be the major contaminant in the fuel as of time of source fabrication. Also, the "curium" materials used in experimental work are of course mixtures of curium and plutonium (at least), and the interpretation of experimental results must take this into account. Not only the concentration of plutonium but also its chemical form can influence the characteristics of the fuel.

It has been generally assumed that a ^{244}Cm recovery system would process the ^{244}Cm to the CmO_2 form for storage and that it would be converted to the Cm_2O_3 form immediately prior to encapsulation. During the period between chemical separation and encapsulation, any plutonium resulting from decay would thus be in the dioxide form. The procedures normally used for conversion of the CmO_2 to Cm_2O_3 (typically calcination at 1000°C in an oxygen-free atmosphere) will not convert the PuO_2 to the

sesquioxide form. As of the time of encapsulation, the fuel will be composed of Cm_2O_3 and PuO_2 plus the oxides of the process impurities. After encapsulation there will be no free oxygen available for oxidation of the decay-produced plutonium, and the mixed oxide system will become more complex.

One approach to dealing with the question of the chemical form of the decay-produced plutonium would be to establish curium process systems to provide Cm_2O_3 as the product form. The Cm_2O_3 could be stored under oxygen-free conditions and all subsequent operations carried out in inert-atmosphere enclosures. Both the curium and the decay-produced plutonium oxides would then remain in the most reduced state. While the Pu_2O_3 may exert significant influences on the characteristics of the fuel, the types and magnitudes of such influences could be determined systematically. Also, thermodynamic calculations indicate that PuO_2 may react with components of several potential encapsulants, so elimination of PuO_2 from the fuel may be attractive in this regard.

The recent re-orientation of the ^{244}Cm development program requires that most of the ^{244}Cm now in experimental facilities be encapsulated for long-term storage. These materials include batches ranging in plutonium content from less than 5% to nearly 20%. Selected fractions will be converted to the Cm_2O_3 form prior to encapsulation so that samples will be available in the future for examination.

General Operations (*C. L. Ottinger*)

The furnace and associated in-cell equipment which had been used for ceramic compatibility work were disassembled and discarded. Cell services were removed and decontamination was started in order to release the cell for other operations. A considerable quantity of solid waste was removed from the Curium Souce Fabrication Facility cells and the equipment was checked out in preparation for $^{244}\text{Cm}_2\text{O}_3$ pelletization work.

Curium-244 Recovery Development

(*C. L. Ottinger and J. C. Posey*)

A program has been initiated to investigate various processes having potential applicability for the recovery of ^{244}Cm from the wastes resulting from processing of power reactor fuels. The ultimate goal of this program is the demonstration of one or more flowsheets adaptable to production-scale processing. If ^{244}Cm is to be utilized in significant quantities for power generation or other applications, a system must be developed which is attractive when compared to alternative sources of power. Comparisons between ^{244}Cm power sources and other potential sources will be based on several criteria, including relative safety, applicability, system weights (for space applications), availability, and, of course, cost. The cost of recovery and purification will be a significant factor in any analysis, and process development information will be required in order to predict these costs.

Since any ^{244}Cm recovery process must eventually be incorporated into a system which includes not only the separations process itself, but also receipt of feed material and preparation of solid wastes for storage, certain limitations are imposed on the ^{244}Cm process. In addition to meeting the normal criteria of technical feasibility, safety, and economics the process must be designed to limit the volume of solid waste to the lowest practical value. The process should also be as versatile as possible in order to accommodate changes in feed composition. Future feed supplies (i.e., reactor fuel wastes) are expected to fall into two general categories: 1) feeds containing essentially fission products with relatively small amounts of other contaminants; and 2) feeds in which a large fraction of the elemental content results from process chemicals added during fuel reprocessing operations. Two reference fuel compositions will be defined to represent these two categories, and the necessary modifications to processes related to this variation will be investigated.

Processing of reactor fuel wastes for recovery of ^{244}Cm will involve four distinct but inter-related phases:

1. Feed Conditioning: Modification of the stored reactor fuel waste to provide a solution ready for ^{244}Cm processing.
2. LN/AN Separation: Processing to provide a ^{244}Cm stream which is composed essentially of those lanthanides (LN) and actinides (AN) that are analogs of curium in classical processes.
3. AN Separation: Fractionation of the LN/AN stream to provide a ^{244}Cm stream containing americium as the primary contaminant.
4. Purification: Final separation of the ^{244}Cm from the americium and the remaining other contaminants.

Each of these phases may incorporate several unit processes or operations, but this division provides a convenient description of the required group operations. The initial area of concentrated effort in this program will be Phase 3, although some work will be done on other phases concurrently. Solvent extraction, in particular differential extraction, appears to offer several advantages as applied to the separation of actinides from lanthanides, and this process will be evaluated.

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