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**ORNL Isotopic Power Fuels
Quarterly Report
for Period Ending June 30, 1974**

C. L. Ottinger

OAK RIDGE NATIONAL LABORATORY

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ISOTOPES DEVELOPMENT CENTER

ORNL ISOTOPIC POWER FUELS QUARTERLY REPORT
FOR PERIOD ENDING JUNE 30, 1974

C. L. Ottinger

Isotopes Division

DECEMBER 1974

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

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SUMMARY

Examination of $^{244}\text{Cm}_2\text{O}_3$ compatibility couples continued with inspection of materials exposed at 900°C and at 1400°C. All of the test materials exposed to $^{244}\text{Cm}_2\text{O}_3$ at 1400°C for 5000 hr showed some interaction. These included both iridium and graphite, neither of which had shown reaction at lower temperatures. Attempts to fabricate thin rectangular pellets of $^{244}\text{Cm}_2\text{O}_3$ for use in combined compatibility/tensile strength tests were unsuccessful, and this phase of the compatibility work was terminated. The calculational thermodynamic reaction study phase was completed.

Total normal emittance measurements were made on a $^{244}\text{Cm}_2\text{O}_3$ pellet in the temperature range from 725°C to 1175°C. Normal spectral emittance values were determined on the same pellet in the 3.0-5.5- μ wavelength range at three temperatures. Heat capacity measurement work was initiated. Some nonradioactive demonstration runs of a technique for hot pressing metal-jacketed pellets were made.

Literature surveys, calculations, and preliminary experimental work on ^{244}Cm recovery from fuel reprocessing wastes continued. The first step, feed conditioning, was investigated experimentally; and a study was performed of the applicability of the TALSPEAK process and its modifications to the ^{244}Cm recovery problem. Design of experimental equipment was started.

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 (*J. R. DiStefano and C. L. Ottinger*)FY 1973 Compatibility Matrix

Metallographic examination of the $^{244}\text{Cm}_2\text{O}_3$ -fueled compatibility samples shown in Table 1 continued. The results of the examination of the 5000-hr, 900°C couples (sets 1 and 2, Table 1) are summarized in Table 2. The noble metals and graphite showed little evidence of interaction, while the superalloys all showed some evidence of interaction ranging from slight surface roughening to 1-2 mil grain boundary attack. Hafn alloy 105 and ThO_2 may have interacted with graphite since dark gray layers were found on their surfaces only in samples from set 2. The other differences between sets 1 and 2 can probably be attributed to variations in surface contact. No gross evidence of interaction was seen, indicating good compatibility for all of these materials under the test conditions.

Table 1. $^{244}\text{Cm}_2\text{O}_3$ Compatibility Test Conditions

Set Number	Test Materials and Conditions
1	900°C; 5000 hr; helium atmosphere; Ir, C, Pt, Hf-1% Pt-0.5% Pd, Hastelloy C-276, Haynes alloy 25, Haynes alloy 188, ThO_2 , 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 alloy 25, Haynes alloy 188, ThO_2 , Pt-20% Rh, and Pt-26% Rh-8% W
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 Metallographic Observations
for Material Exposed to $^{244}\text{Cm}_2\text{O}_3$ for 5000 hr at 900°C

Material	Set 1	Set 2
Platinum	Irregular surface on Pt; metallic outer layer on Cm_2O_3 with dark and light gray subsurface layers	Slight surface roughening
Pt-20% Rh	Slight surface roughening	Slight surface roughening
Pt-26% Rh-8% W	No significant change	No significant change
Iridium	No significant change	No significant change
Haynes alloy 25	Very slight surface attack (~ 0.1 mil)	Surface roughening and some grain boundary attack ($\sim 1-2$ mils)
Haynes alloy 188	Grain boundary attack (~ 1 mil)	Very slight surface roughening
Hastelloy C-276	Grain boundary attack (~ 2 mils)	Grain boundary attack (~ 1 mil)
Hafn alloy 105	Surface roughening and very slight grain boundary attack	Dark gray layer on surface; some surface cracks
ThO_2	Irregular surface; Cm_2O_3 cracked	Dark gray layer on surface; layer cracked in some areas
Graphite	No significant change	

Results of the examinations on two of the 5000-hr, 1400°C sets (7 and 8) are shown in Table 3. All of the materials showed some interaction with $^{244}\text{Cm}_2\text{O}_3$. Reactions between iridium and $^{244}\text{Cm}_2\text{O}_3$ and between graphite and $^{244}\text{Cm}_2\text{O}_3$ were noted for the first time. No such reactions had been observed at 900°C or at 1100°C. The iridium showed small surface and subsurface voids while the graphite appeared to have reacted to form a corrosion product. The top graphite specimen could not be removed for chemical analysis; and during the polishing, the $^{244}\text{Cm}_2\text{O}_3$ (or perhaps $^{244}\text{Cm}_2\text{O}_3 + \text{C}$) reacted with water and/or air until it disintegrated.

Table 3. Results of $^{244}\text{Cm}_2\text{O}_3$ Compatibility
Tests at 1400°C for 5000 hr

Material	Set 7	Set 8
Iridium	Grain boundary attack to depth of <0.5 mil. Some surface and sub-surface voids; Ir specimen bonded to capsule.	Same as results in set 7.
Tantalum	Irregular surface with layer of Cm_2O_3 tightly adhering. Small voids connected to surface and just below surface (<0.3 mil) white (oxide?) phase in Ta next to Cm_2O_3 ; metal particles in Cm_2O_3 .	Same as results in set 7.
T-111	Grain boundary attack to 2-3 mils. Attack area void near surface but contains gray (Cm_2O_3) phase deeper in T-111.	Same as results in set 7.
Molybdenum	Capsule stuck to graphite; Mo-C reaction visible in some areas. Very shallow grain boundary grooves at surface in contact with Cm_2O_3 ; metal particles in Cm_2O_3 .	Same as results in set 7 except no Mo-C reaction.
Mo-46% Re	Capsule stuck to graphite; Mo-C reaction visible in some areas and capsule wall cracked. Precipitate in Mo-46% Re. Irregular surface at Cm_2O_3 interface; metal particles in Cm_2O_3 .	Same as results in set 7 except no Mo-46% Re-graphite reaction.
Tungsten	Capsule cracked. Irregular specimen surface and some surface grains missing (<0.5 mil) which would indicate grain boundary attack.	Same as results in set 7.
W-26% Re	Irregular surface and grain boundary attack to ~0.1 mil.	Same as results in set 7.
Graphite	Graphite specimen could not be removed. Reaction product (perhaps an oxy-carbide of curium) at graphite- Cm_2O_3 interface. Graphite specimens had very irregular surfaces.	No graphite test in set 8.

Results of tantalum and T-111 are similar to those previously reported.¹ Attack was less than had been found at 1650°C but slightly more than was noted at 1250°C.

Molybdenum and Mo-46% Re capsules stuck to the graphite intermediate capsules in which they were contained. Although the metallographic samples did not show bonding, there was evidence of interaction, especially along grain boundaries of the metal capsules. In addition, the capsule walls were cracked in some areas. Very limited attack by $^{244}\text{Cm}_2\text{O}_3$ was noted, but the presence of metal particles in the fuel is evidence that some dissolution did occur.

Tungsten and W-26% Re alloy both showed irregular surfaces. Some surface grains of tungsten were missing, indicative of selective grain boundary attack. The tungsten capsule wall was quite brittle and several cracks were noted in the samples from both sets 7 and 8.

Inspection of the FY 1973 matrix couples was not completed during this quarter as originally scheduled. Remaining work includes 20 etched pictures, 4 microprobe analyses, and 34 microhardness measurements plus the preparation of 34 composite metallographic photographs. This work will continue and should be completed during the first quarter of FY 1975.

FY 1974 Compatibility Matrix

The capsule and test couple components for the FY 1974 matrix were received or fabricated and all of the mechanical work completed on them in preparation for fueling.

Attempts to prepare the required rectangular pellets of $^{244}\text{Cm}_2\text{O}_3$ to the proper specifications were unsuccessful. In 28 attempts using slotted graphite dies (with some variations in exact design), only one pellet meeting exact specifications was produced. There were some pellets only slightly out of specifications and some which were broken in such a way that they might have been fitted together and used. However, the procedure was not adaptable to in-cell operation for production of the multiple identical pellets required. The main problem was that the pellets stuck in the die channel, probably on account of the large surface area contact relative to thickness; and breakage occurred during attempts to remove the pellets. Some modifications to the die design were tried but none produced an acceptable technique.

Alternative techniques such as use of a double-ended graphite die or high-pressure compaction in a segmented steel die were considered. Either of these would have some potential, and there are others which could be investigated. However, such investigation and the demonstration of the selected process would involve experimental time, manpower, and facility commitment outside the scope of the reduced ^{244}Cm program for FY 1975. Work on this phase of the ^{244}Cm program was stopped in June.

Thermodynamic Calculations (*E. E. Ketchen*)

The calculations described below complete the thermodynamic calculations program which was started in FY 1973. During this program, 25 potential encapsulants were considered and calculations made of their possible reactions with $^{244}\text{Cm}_2\text{O}_3$ fuel material.

Possible reactions of $^{244}\text{Cm}_2\text{O}_3$ fuel with materials being considered for use as encapsulants were investigated from a thermodynamic viewpoint. Six pure metals (Ir, Pt, Mo, W, Ta, and Ru) and three alloys (Pt_3Ir , Pt-20% Rh, and Ru-2% Rh) were considered. In all cases a reference fuel consisting of 95% $^{244}\text{Cm}_2\text{O}_3$ and 5% PuO_2 was assumed. Calculations were made in the temperature range from 600 to 1300°C, and formation of the most favorable oxides for this temperature range was assumed. No account was taken of possible oxygen solubility nor of compound formations between elements. Free energies of formation for the oxides were calculated from the data of Glassner² and Oetting.³ For the alloys, free energies of mixing were calculated by the method described previously.⁴

Pure Metals (Ir, Pt, Mo, W, Ta, and Ru)

Unalloyed Ir, Pt, Mo, W, and Ta have all been suggested as possible encapsulants for $^{244}\text{Cm}_2\text{O}_3$. Another candidate which has not been considered previously is ruthenium. Ruthenium has many characteristics similar to iridium, which is receiving much attention as a source container.

The calculated free energies of the oxides of the six metals and of the plutonium oxides involved in the calculations are shown in Table 4. Since free energy data for Cm_2O_3 are not available, those for Pu_2O_3 were used as stand-ins. The free energies of formation for Rh_2O are also included in Table 4; these were used in the calculations described under "Alloys" below.

Table 4. Gibbs Free Energy of Formation
of Ir_2O_3 , Pt_3O_4 , MoO_2 , WO_2 , Ta_2O_5 , RuO_4 , Rh_2O , Pu_2O_3 , and PuO_2

Constituents	ΔG_f (kcal/mole)				
	600°C	800°C	1000°C	1200°C	1300°C
Ir_2O_3	13.90	2.45	-8.61	-19.49	-24.04
Pt_3O_4	10.30	26.40	42.08	57.33	64.79
MoO_2	-95.60	-87.91	-80.36	-72.94	-69.27
WO_2	-101.16	-93.85	-86.78	-79.96	-76.80
Ta_2O_5	-395.69	-374.82	-354.18	-333.75	-323.63
RuO_4	-30.18	-23.03	-15.97	-8.50	-5.02
Rh_2O	-11.35	-9.09	-6.94	-4.90	-3.91
Pu_2O_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 Table 1 were used to calculate the free energies of Eqs. 1-12. Results are shown in Tables 5 and 6.

Table 5. Gibbs Free Energy of Reaction
for Eqs. 1, 3, 5, 7, 9, and 11

Temperature (°C)	ΔG_r (kcal/mole Cm_2O_3)					
	Eq. 1	Eq. 3	Eq. 5	Eq. 7	Eq. 9	Eq. 11
600	366.02	359.85	412.44	24.32	114.71	329.48
800	341.77	359.12	414.91	28.89	114.43	322.04
1000	318.33	358.50	412.80	33.30	114.43	314.97
1200	395.49	357.98	411.14	37.55	114.73	308.61
1300	285.09	357.74	410.49	39.38	114.97	305.38

Table 6. Gibbs Free Energy of Reaction
for Eqs. 2, 4, 6, 8, 10, and 12

Temperature (°C)	ΔG_r (kcal/mole PuO_2)					
	Eq. 2	Eq. 4	Eq. 6	Eq. 8	Eq. 10	Eq. 12
600	41.80	40.77	15.59	14.20	-0.08	35.71
800	37.79	40.69	15.41	13.92	-0.10	34.51
1000	33.80	40.50	15.15	13.54	-0.19	33.24
1200	29.79	40.21	14.81	13.30	-0.34	31.98
1300	27.92	40.03	14.61	12.71	-0.43	31.30

Since the free energies of Eqs. 1, 3, 5, 7, 9, and 11 are all positive, the Cm_2O_3 is not expected to react with Ir, Pt, Mo, W, Ta, or Ru over the 600-1300°C temperature range. Since only tantalum (Eq. 10) is negative, tantalum should be the only metal to react with PuO_2 of the curium oxide product over the 600-1300°C temperature range. It appears from

thermodynamic considerations that of the metals Ir, Pt, Mo, W, Ta, and Ru, only tantalum should react with the $^{244}\text{Cm}_2\text{O}_3$ product over the 600–1300°C temperature range. Recent experimental evidence⁵ showed no reactions with iridium at 1100°C, but there was evidence of reaction with platinum. The Cm/Pt reaction is thought to be an intermetallic compound formation, which is not considered in the above calculations. In some previous experiments¹ tantalum showed limited reaction with $^{244}\text{Cm}_2\text{O}_3$ fuel at 1250°C, some interdiffusion at 1650°C, and some mass transfer at 1850°C (10,000-hr exposures in all cases).

Alloys (Pt₃Ir, Pt–20% Rh, and Ru–2% Rh)

Two of the alloys studied, Pt₃Ir (74.72 atom % Pt, 25.28 atom % Ir) and Pt–20% Rh (67.85 atom % Pt, 32.15 atom % Rh), are included in current experimental compatibility work; the Ru–2% Rh (98.03 atom % Ru, 1.97 atom % Rh) is not presently scheduled for testing. The partial molar free energy of mixing values for these alloys are given in Table 7.

Table 7. Free Energies of Mixing for Pt₃Ir, Pt–20% Rh, and Ru–2% Rh

Temperature (°C)	–ΔG (cal/mole)					
	Pt ₃ Ir		Pt–20% Rh		Ru–2% Rh	
	Pt	Ir	Pt	Rh	Ru	Rh
600	360	1980	640	1890	30	2810
800	470	2530	790	2340	40	3450
1000	590	3080	950	2790	50	4100
1200	700	6320	1100	3240	60	4750
1300	750	3900	1180	3470	60	5070

Free energy values from Tables 4 and 7 were used to calculate the free energies for Eqs. 13–20. Since the free energy of formation for platinum oxide is positive over the 600–1300°C temperature range (see Table 4), platinum should not react with oxygen at the temperatures of interest. However, iridium, rhodium, and ruthenium can all react with oxygen in this temperature range.

The results of the calculations of the free energies for Eqs. 13-20 are shown in Table 8.

Table 8. Gibbs Free Energy of Reaction for Eqs. 13-20

Temperature (°C)	ΔG_r (kcal/mole of Cm_2O_3 or PuO_2)							
	Eq. 13	Eq. 14	Eq. 15	Eq. 16	Eq. 17	Eq. 18	Eq. 19	Eq. 20
600	369.8	42.4	329.4	35.7	329.4	35.7	301.2	31.0
800	346.4	38.6	326.1	35.2	322.0	34.5	291.3	29.4
1000	323.9	34.7	322.9	34.6	314.9	33.2	281.5	27.6
1200	302.0	30.9	319.7	33.8	308.6	32.0	271.8	25.8
1300	292.0	29.1	318.2	33.4	305.3	31.3	267.0	24.9

Since all of the free energies for Eqs. 13-20 are positive, no reaction would be predicted for $^{244}\text{Cm}_2\text{O}_3$ fuel containing 5% PuO_2 with any of the three alloys.

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

Emissivity (*P. Angelini*)

Emittance, one of the physical properties to be determined for $^{244}\text{Cm}_2\text{O}_3$ fuel material, relates the thermal radiative power emitted by a surface to the thermal radiative power emitted by a black body of the same area and at the same temperature. Radiant energy transfer is a major process which affects the temperature profile in a fuel form and its surroundings. Emittance values for a given material may differ according to the type of surface of the body. Using a pellet of $^{244}\text{Cm}_2\text{O}_3$ fabricated by procedures which have been used to prepare pellets for heat sources and other experiments, measurements were made of both the total normal emittance and the spectral normal emittance at various wavelengths. The total normal emittance was determined at 725, 795, 885, 1005, 1115, and 1175°C. Spectral normal emittance values were obtained at 725, 885, and 1115°C for the wavelength range from 3.0 to 5.5 μ in 0.5- μ increments.

A $^{244}\text{Cm}_2\text{O}_3$ pellet was prepared by hot-pressing using a graphite die and punch assembly. The stationary (bottom) punch had a 1/32-in.-diam by 3/32-in.-long projection centered on it. After being loaded and pressed by standard procedure, the pellet was ejected, breaking off the projection and leaving it incorporated in the pellet. Since the normal graphite oxidation process (4-hr heating at 1000°C in argon containing 2500 ppm oxygen) is designed to remove only traces of graphite, it was decided to oxidize the carbon by heating the pellet in air. The first pellet was taken from the argon atmosphere of the pressing cell to a tube furnace in an air-atmosphere cell and heated to 1000°C in a period of ~1-1/2 hr. The temperature was maintained at 1000°C for 16 hr; then the furnace was cooled and the pellet inspected. The pellet appeared to be intact and

the graphite had been completely burned away. The pellet was sealed in argon, but after a 4-day storage period it had disintegrated. A second pellet was fabricated by the same procedure except that the atmosphere of the furnace cell was kept inert (argon at ~ 100 ppm oxygen) until the pellet had been heated to 1000°C ; then air was introduced. After 16 hr at 1000°C in air, the argon atmosphere was reestablished before the furnace was cooled. An excellent pellet resulted and was used in the emissivity experiment without further surface treatment. The pellet was prepared from $^{244}\text{Cm}_2\text{O}_3$ fuel which was purified in July 1973.⁶ The diam, height, and density were 0.953 cm, 0.318 cm, and 10.1 g/cm^3 , respectively.

The emittance determination apparatus is presented in Fig. 1. A sample specimen was loaded on the unit and the apparatus connected to the viewing port flange of the high-temperature vacuum furnace used previously in the Cm_2O_3 vapor pressure experiments. The sample is located in the furnace heat shield area and is heated by thermal radiation from the furnace heating element. The surface used to obtain the emittance values does not receive direct thermal radiation from the heating element or from the heat shields. This reduces the error in emittance values caused by thermal radiation reflected from the measured surface.

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Fig. 1. Emittance Determination Apparatus.

A thermistor thermal radiation detector was used to measure the radiative power emitted by the sample's surface. The detector responded linearly to power and its responsivity was nearly uniform for thermal radiation in the 0.5- to 30.0- μ wavelength range. A constant voltage source supplied the biasing voltage to the detector. The rotary filter holder contained one open position for total thermal radiation transmission and six infrared bandpass filters of 3.0-, 3.5-, 4.0-, 4.5-, 5.0-, and 5.5- μ wavelengths. The incident thermal radiation to the detector was mechanically chopped at a frequency of 2.66 hz. The signal from the thermal radiation detector was measured using a lock-in amplifier. Light from a small bulb was also chopped by the wheel prior to being detected by a photo electric detector. This provided the reference signal to the lock-in amplifier. The lock-in amplifier was operated in its tuned mode and was tuned to the same frequency, 2.66 hz, as its input and reference signal. A two-pen recorder was used to record the output of the lock-in amplifier. One of the two lock-in amplifier output signals was filtered through a 10-sec filter so that a smoother signal would be recorded.

A 0.953-cm-diam by 0.318-cm-thick disk of pyrolytic graphite was fabricated. A black body hole of the same dimensions as the one in the Cm_2O_3 pellet was drilled in the disk. The flat surface exposed to the thermal radiation detector was that along the c-plane. It has been shown that the normal emittance and normal spectral emittance for this plane at temperatures and wavelengths similar to those used in the present experiment are nearly unity.^{7,8} A calibration curve of surface temperature and black body hole temperature versus furnace power supply dial setting was obtained. The brightness pyrometer used for temperature readings had been previously calibrated with compensating glass plates identical to the furnace window and glove box window. In all cases, the black body hole temperature and the surface temperature of the graphite were measured to be equal within experimental error. The thermal radiation detector was then mounted on the unit, and calibration experiments of temperature versus detector output for various spectral filters were performed.

Readings were obtained at 725, 795, 885, 1005, 1115, and 1175°C with the filter wheel in the total thermal radiation mode and at 725, 885, and 1115°C with the filter wheel in the spectral mode.

A second pyrolytic piece of graphite having no black body hole was installed in the unit, and the complete procedure described above performed. No difference in signal strength that was outside experimental error was determined for the two pieces of graphite. This result shows that the surface of the pyrolytic graphite pieces was emitting essentially with an emittance value of one in the present temperature and spectral range.

The Cm_2O_3 pellet was loaded into the unit. Preliminary results for the normal emittance of $^{244}\text{Cm}_2\text{O}_3$ at temperatures of 795, 885, 1005, 1115, and 1175°C are presented in Fig. 2. The normal spectral emittance of $^{244}\text{Cm}_2\text{O}_3$ at 3.0-, 3.5-, 4.0-, 4.5-, 5.0-, and 5.5- μ wavelength and at temperatures of 725, 885, and 1115°C are presented in Fig. 3. A photograph of the $^{244}\text{Cm}_2\text{O}_3$ pellet is presented in Fig. 4. The black body hole

is clearly visible and the surface of the pellet appeared to be quite smooth. The broken pellet surface near the edges was caused in prying the last tantalum pellet holder from the pellet. The broken surface was not seen by the thermal radiation detector. The sample's surface affecting the thermal radiation detector was centered in the pellet and was about 0.25 in. in diam. This provided a large pellet surface area for which emittance values were determined.

Fig. 2. Total Normal Emittance of $^{244}\text{Cm}_2\text{O}_3$.

Fig. 3. Normal Spectral Emittance of $^{244}\text{Cm}_2\text{O}_3$.

Fig. 4. $^{244}\text{Cm}_2\text{O}_3$ Pellet for Emittance Measurement.

The normal spectral emittance results for $^{244}\text{Cm}_2\text{O}_3$ show that the surface emits in a fairly uniform manner throughout the 3- to 5.5- μ wavelength region. The emittance values for $^{244}\text{Cm}_2\text{O}_3$ in this range generally increase with increasing wavelength. The results also show that the surface does not exist as an ideal black or gray body with respect to wavelength.

Experiments were also performed on Er_2O_3 and Gd_2O_3 pellets in order to test the accuracy of the method; the data obtained were similar to those reported by others.⁹ These experiments were performed on cold-pressed pellets which had been fired in air at 1200°C for 16 hr. No other surface preparation was performed on the pellets. The pellets were fabricated with a black body hole located in one end in a manner similar to the $^{244}\text{Cm}_2\text{O}_3$ pellets. The dimensions and densities of the pellets are shown below:

	Diameter (cm)	Thickness (cm)	Density (g/cm ³)
Er ₂ O ₃	1.059	0.410	4.59
Gd ₂ O ₃	0.915	0.438	5.80

The pellets were loaded into the glove box, and the experiments performed using the same procedure as used in the Cm₂O₃ experiment.

The emittance data for Er₂O₃ and Gd₂O₃ are presented in Figs. 5 and 6. In Fig. 5 is presented the total normal emittance versus temperature and in Fig. 6 is presented the spectral normal emittance values versus wavelength with the samples held at different temperatures. The total normal emittance results show that this quantity is not very temperature dependent in the 700 to 1150°C temperature range. The spectral emittance results show that the spectral emittance of Er₂O₃ and Gd₂O₃ tend to increase with increasing wavelength.

Fig. 5. Total Normal Emittance Versus Temperature.

Fig. 6. Spectral Normal Emittance Versus Wavelength.

The accuracy of the overall method for the total normal emittance values is approximately $\pm 3\%$ at all temperatures and for all materials covered. The spectral emittance values of Ce_2O_3 , Er_2O_3 , and Gd_2O_3 have an accuracy of $\pm 3\%$ for temperatures greater than 850°C . The smallest measured voltage output from the thermal radiation detector occurred in the 725°C Gd_2O_3 spectral emissivity experiment at the $3.0\text{-}\mu$ wavelength. The voltage measured was $1.60\text{ }\mu\text{V}$. The root-mean-square noise value of the signal was approximately $\pm 0.1\text{ }\mu\text{V}$. The standard deviation for the emittance value was approximately ± 0.03 in this case. Other values possessed standard deviations less than the above; however, a conservative estimate of the standard error for the majority of the Er_2O_3 , Gd_2O_3 , and Ce_2O_3 725°C spectral emittance values is ± 0.02 .

Heat Capacity (*P. Angelini*)

After considerable reorientation, repairs, and checks of the heat capacity measuring equipment, radioactive operations were initiated. A $^{244}\text{Ce}_2\text{O}_3$ test pellet was hot pressed with a thermocouple wire embedded in it. The pellet was transferred to the heat capacity equipment cell, but the thermocouple wire separated from the pellet during handling. Since the experiment could not be conducted as planned, it was decided to use an alternative method. The $^{244}\text{Ce}_2\text{O}_3$ fuel material will be crushed to powder form then packed into a molybdenum capsule of known weight. A thermocouple wire will be embedded in the center of the powder and will lead out through the cap to the connector. Measurement of the heat capacity of this assembly will be done, and correction for the molybdenum effect will be made to provide a value for the $^{244}\text{Ce}_2\text{O}_3$. This experiment will be conducted early in FY 1975.

Source Capsule Development (*P. Angelini*)

A fabrication method has been tested which permits the simultaneous hot pressing of a metal capsule about a ceramic body. The procedure was used to fabricate an iridium metal capsule about Gd_2O_3 and a ruthenium metal capsule about Gd_2O_3 . In Fig. 7 are presented three pellets. These pellets were cut by a diamond abrasive wheel. The dark color of the ceramic body resulted during the polishing of the pellets. The pellets shown are $1/2$ in. in diam and vary from $1/8$ to $1/2$ in. in height. Figure 8 shows the reverse side of the pellets. The crack in the ruthenium capsule developed during the cutting of the pellet. The pellets showed intimate contact between the metal capsule and the ceramic body; this contact would tend to minimize temperature gradients within the source. The density of both the metal and the ceramic was greater than 98% of theoretical density. This procedure could eliminate welding problems encountered in present methods of source encapsulation.

PHOTO 1920-74

Fig. 7. Ir Encapsulated Gd_2O_3 Pellet, Ru Encapsulated Gd_2O_3 Pellet, and Ru Pellet (left to right).

PHOTO 1892-74

Fig. 8. Ir Encapsulated Gd_2O_3 Pellet, Ru Encapsulated Gd_2O_3 Pellet, and Ru Pellet (left to right).

The procedure can be used to provide different metal capsule thicknesses. Special vents in the capsule can be fabricated at time of hot pressing or later by drilling through the metal capsule. It should be feasible to vary the density of the metal such that one may produce a capsule permeable to helium. The procedure is applicable to forming source units of complicated geometry. It is anticipated that spherical source units can be fabricated by this method. It may become advantageous to cold or hot press the metal capsule and ceramic body in separate steps and to later encapsulate the ceramic body in the capsule by hot pressing.

The hot-pressing characteristics of iridium and ruthenium were very similar. This was expected since the properties of ruthenium are very similar to those of iridium. Both have stress properties greater than tungsten for temperatures up to $2000^{\circ}C$, and both have melting points above $2300^{\circ}C$. The oxidation resistance of ruthenium is better than that of iridium for temperatures lower than $1100^{\circ}C$. The density and cost of ruthenium are approximately one-half and one-third, respectively, of iridium. Thus on an equal volume basis, the mass of a ruthenium capsule would be one-half the mass of an iridium capsule. Also the cost of the ruthenium capsule material would be less than one-sixth that of the iridium capsule.

Curium-244 Process Development

Studies and calculations related to ^{244}Cm recovery from reactor fuel reprocessing wastes continued. Some preliminary experimental work on the first stage of the proposed separations sequence, feed conditioning, was done. The main thrust of experimental effort in the next few months will be concerned with the third phase, the lanthanide/actinide fractionation. Studies and calculations relative to the use of a solvent extraction process for the separation of an actinide (curium) fraction from the mixed lanthanide/actinide fraction were begun.

Feed Conditioning (A. F. Rupp)*

The initial processing step (after clarification) on the ^{244}Cm feed will probably be a reduction of the HNO_3 content. Formic acid reduction has been suggested by several workers and has good potential. While direct treatment of relatively concentrated (4-5 M HNO_3) feeds with formic acid does present some hazards, it should be useful with proper safety precautions. An alternative process is evaporation to dryness followed by leaching to remove the ^{244}Cm . In tests with simulated feed (see Table 9) the solution was evaporated to dryness, lightly calcined to decompose most of the nitrates, then leached with 0.5 M HNO_3 . The rare earths were recovered in solution with about a 90% yield, while most of the iron and zirconium remained with the residue. However, the zirconium hydrated oxide tends to form a colloid that is hard to cope with.

Table 9. Composition of Simulated Waste

Component	Grams/Liter	Gram-Atoms per Liter $\times 10^3$
Alkali Metals	4.96	197
Alkaline Earths	0.46	3.9
Lanthanides/Actinides	3.77	25
Noble Metals	0.79	7.6
Uranium	1.78	7.5
Zirconium	0.66	7.1
Molybdenum	0.64	6.6
Iron	3.55	63
Technetium	0.15	1.4
Chromium, Nickel	0.05	0.9
Phosphate	0.36	—
Nitric Acid	284	(4.5 M)

*ORNL Consultant.

A combination process involving both evaporation and formic acid reduction might be preferred. Figure 9 shows distillation curves for the sequential distillation of the simulated feed. The solution would not be taken to dryness, but water would finally be added to take up the pot contents to $\sim 2 M$ in HNO_3 for the formic acid reduction step. There is sufficient spread between the evaporation temperature of 60-70% HNO_3 ($\sim 120^\circ\text{C}$) and the initial nitrate decomposition temperature ($\sim 200^\circ\text{C}$) to allow easy control. This would permit recovery of the HNO_3 , save process time, reduce costs for formic acid, and allow a lower volume of off-gas. The nitrogen oxides from the formic acid reduction step could also be recovered as HNO_3 if desired.

Fig. 9. Distillation of Simulated Waste.

The formic acid in this application is unusually helpful in that many services are performed by one reagent:

1. The excess HNO_3 is eliminated.
2. The progressive pH and free acid adjustment allow homogeneous precipitation of fine-grained hydrous oxides of iron and zirconium without precipitation of the rare earths.
3. Easily reducible elements such as Te, Ru, Rh, and Pd are precipitated as metals.
4. Other compounds such as zirconium molybdate and iron phosphate tend to precipitate.

Variations in the $\text{HCOOH}/\text{HNO}_3$ ratio and reaction time could be used to regulate the amount of dross precipitated versus the ^{244}Cm lost to the precipitate. Workers at Karlsruhe¹⁰ pointed out that the alkaline and alkaline earth nitrates are poorly decomposed. This would be a disadvantage for feeds containing high concentrations of sodium. Large amounts of sodium would also interfere with subsequent processing, particularly if oxalate precipitation were used.

Solvent Extraction Studies (*J. C. Posey*)

Various possible processes for the recovery of ^{244}Cm from fission-product waste materials have been studied in order to select the most promising and to determine the principal gaps in the known technology. It was assumed that the purpose of the process would be curium production rather than waste decontamination, and that consequently high recovery would not be necessary. Much of the technology could, however, be applied to waste decontamination. It has also been assumed that the process would be applied to a waste containing large amounts of iron, sodium, and gadolinium. The most difficult problem is the separation of the curium from the much larger quantity of lanthanides which are present in the waste (as much as ~1300:1). A reasonably pure lanthanide/trivalent actinide fraction can be separated by any of several well known methods such as oxalate precipitation or TBP extraction.

TALSPEAK Process

The process showing the greatest promise is the TALSPEAK process developed by Weaver and Kappelman of ORNL.¹¹ In this process the lanthanides are extracted away from americium and curium by HDEHP [di(2-ethylhexyl)phosphoric acid]. The trivalent actinides are held in solution by the complexing action of DTPA (diethylenetriaminepentaacetic acid). Lactic acid is used as a buffer. Weaver and Kappelman tested other extractants, complexing agents, and buffering acids; several were found to be effective but the above combination was considered the best. Weaver is currently carrying out research on the use of the process for the decontamination of nuclear wastes.¹² The TALSPEAK process was demonstrated on a

laboratory scale by Weaver and Kappelmann and more recently by workers at Karlsruhe, Germany.^{10,13} The Karlsruhe process differed from that of Weaver and Kappelmann in the use of a different method of feed preparation and in the use of an aliphatic diluent with added TBP. Weaver and Kappelmann used an aromatic diluent. The aliphatic diluent is cheaper and has a lower density, but gives poorer separation.¹¹ The TBP was added to stabilize the organic phase during an alkaline clean-up process for the HDEHP. According to Weaver¹² the TBP is not required for this process if an aromatic diluent is used. The TBP tended to reduce the extraction of europium, and it is probable that it would have a similar or greater effect on the extraction of gadolinium.

Chemistry of TALSPEAK Process

The size of the distribution coefficients in the TALSPEAK extraction are the net result of two different equilibrium reactions,

and

[HY has been substituted for the conventional HDEHP as a symbol for di(2-ethylhexyl)phosphoric acid in order to simplify the presentation of equations. The HY exists as a dimer $(\text{HY})_2$ in the organic phase. It reacts as a singly ionized dimer, HY_2^- .¹⁴ The M represents any trivalent lanthanide or actinide.]

Both the aqueous phase DTPA complex and the organic phase HDEHP complex are in equilibrium with the free ion M^{3+} in the aqueous phase. The equilibrium equation for Eq. 21 can be written as follows:

$$K_m = (\text{M}^{3+})(\text{DTPA}^{5-})/(\text{MDTPA}^{2-}) \quad (23)$$

The second equilibrium is expressed in terms of E_A^0 which is the distribution coefficient in the absence of an aqueous phase complexing agent.

$$E_A^0 + [\text{M}(\text{HY}_2)_3]/(\text{M}^{3+}) \quad (24)$$

Equations 23 and 24 can be combined algebraically to form Eq. 25 if it is assumed that M^{3+} makes a negligible contribution to the total aqueous phase concentration of M. This is true at a pH of 3 or higher.

$$K_m E_A^0 / (\text{DTPA}^{5-}) = [\text{M}(\text{HY}_2)_3] / (\text{MDTPA}^{2-}) = E_A^0 \text{ (TALSPEAK)} \quad (25)$$

Equation 25 shows that the TALSPEAK distribution coefficient for any given trivalent actinide or lanthanide is proportional to $K_m E_A^0$ for that element.

The absolute value also is inversely proportional to DTPA^{5+} which is a function at the (DTPA^{5-}) and hydrogen ion concentrations. Furthermore the absolute values of E_A^0 are approximately proportional to the cube of the HDEHP concentration and inversely proportional to the cube of the hydrogen ion concentration. They can be made to vary over a very high range;

however, these factors affect all of the values of E_A^0 in the same manner, and the values of E_A^0 for the different elements maintain the same approximate ratio to each other.

When several of these ions are present in the same solution, all of the factors affecting (DTPA⁵⁻) and the absolute values of E_A^0 will be the same for all of the ions. Consequently the ratio of the TALSPEAK distribution coefficient of one ion to that of any of the other ions can be calculated, providing values of K_m and relative values of E_A^0 are known for the two ions. Most of these values are available in the literature. The absolute values can be adjusted by varying the concentrations of HDEHP and DTPA. The hydrogen ion concentration is not freely adjustable. The pH must be held in the range of 3.0 to 3.5 for good process operation to be achieved.

Using Eq. 25 the relative values of the TALSPEAK distribution coefficients were calculated using values of K_m and E_A^0 found in the literature.¹⁵⁻¹⁹ The results of the calculations (See Appendix 1) are shown in Fig. 10 along with experimental values taken from Weaver and Kappelmann.¹¹ Also shown are values of E_A^0 for the simple HDEHP versus perchlorate system and values of K_m . All values are given as ratios to the value for curium.

Fig. 10. TALSPEAK Distribution Coefficients.

The agreement between the measured values and the calculated values is good considering that data by six different investigators went into the calculation. The calculations also assume that essentially all of the metal ions in the aqueous phase are in the form of the DTPA complex. Actually a small fraction will be present as free ions or as lactic acid complexes (if this buffering acid is used).

These calculations confirm the mechanism of the TALSPEAK separation and give good estimates of the separation factors for those lanthanides for which no experimental data are available. The gadolinium-to-curium distribution coefficient ratio is shown to be about 100. Thus, the added gadolinium of the waste can be separated from curium, although the volume of extractant required is increased by this addition.

Use of TALSPEAK With Differential Extraction

The separations which could be achieved were calculated for a single differential extraction. It was assumed that the TALSPEAK distribution coefficients had the ratios given in Fig. 10. The distribution coefficients used were 15.9 for gadolinium, 6.4 for neodymium, and 0.156 for curium. The lanthanides, gadolinium and neodymium, were used in this calculation because gadolinium is the most plentiful lanthanide and neodymium is the most difficult to separate. The ratios of gadolinium and neodymium to curium are those expected to be present in the waste. The results are given in Table 10.

Table 10. Removal of Gadolinium and Neodymium From Curium Solution by Differential Extraction Using TALSPEAK Chemistry

Fraction of Curium Remaining	Neodymium Remaining		Gadolinium Remaining	
	Fraction	Mole Nd/ Mole Cm	Fraction	Mole Gd/ Mole Cm
1.00	1.00	291	1.00	596
0.99	0.678	199	0.412	248
0.95	0.186	57.4	0.011	6.91
0.90	0.0170	5.50	9.3×10^{-5}	0.0616
0.85	0.00187	0.646	6.3×10^{-7}	4.4×10^{-4}
0.80	1.78×10^{-4}	0.0649	2.9×10^{-9}	2.2×10^{-6}
0.75	1.41×10^{-5}	0.00547		
0.70	9.6×10^{-7}	4.0×10^{-4}		

The optimum end point for the differential extraction is dictated by the nature of the next process step. It is anticipated that this will be the ion-exchange separation of curium from americium. Excellent decontamination with respect to neodymium and the lower lanthanides is expected in this step. Thus, the extraction need remove them only to a level at which they do not make a large contribution to the total volume of material to be processed. On the other hand, gadolinium is not easily separated in

the ion-exchange process. Consequently, an essentially complete removal in the extraction step is desirable. Both of these objectives are met at about 85% curium recovery. These calculations assume that optimum conditions for separation are maintained throughout the process. They represent the best results which might be anticipated.

But what if these distribution coefficient ratios are not reached because of failure to reach equilibrium or for any other reason? The calculations were repeated assuming distribution coefficient ratios only 50% as great as those shown in Fig. 10. The distribution coefficients used were numerically 10.2 for gadolinium, 4.53 for neodymium, and 0.22 for curium. These calculations and those above assumed a 1% holdup of dispersed extractant in the differential extraction apparatus.

Results of these calculations are shown in Table 11. The same product purity could be achieved as in the ideal case, but the curium recovery would be lowered to 70-75%.

Table 11. Removal of Neodymium and Gadolinium
From Curium at 50% of Theoretical Efficiency

Fraction of Curium Remaining	Neodymium Remaining		Gadolinium Remaining	
	Fraction	Mole Nd/ Mole Cm	Fraction	Mole Gd/ Mole Cm
1.00	1.00	291	1.00	596
0.99	0.820	241	0.656	396
0.95	0.364	111	0.116	72.8
0.90	0.125	40.4	0.0120	7.96
0.85	0.0408	14.0	0.00109	0.765
0.80	0.0124	4.54	8.5×10^{-5}	0.0634
0.75	0.00345	1.43	5.4×10^{-6}	0.00430
0.70	8.9×10^{-4}	0.37	3.1×10^{-7}	2.64×10^{-4}
0.65	2.02×10^{-4}	0.093	1.32×10^{-8}	1.21×10^{-5}
0.60	4.36×10^{-5}	0.021	4.90×10^{-10}	4.50×10^{-7}
0.55	4.90×10^{-6}	0.0026		
0.50	1.20×10^{-6}	7.0×10^{-4}		

The curium extracted along with the lanthanides could be recovered easily by back extraction using the TALSPEAK chemistry. This step could be carried out using the extraction equipment which would be required for solvent recovery. Thus, no additional units of extraction equipment would be required. The total volume of aqueous solution to be processed would, however, be increased. An economic evaluation of this step cannot be made with the present data.

Problem Areas

The TALSPEAK process is known to have two principal weaknesses. The extraction kinetics are comparatively slow for the higher lanthanides,^{11,13} and comparatively large extractant volumes are required. It is believed that the process can be improved in both respects.

Extraction Kinetics — Karpacheva and Ilozheva²⁰ studied the kinetics of the extraction of Am^{3+} from perchlorate solution by HDEHP. It is likely that other trivalent actinides and lanthanides follow the same mechanism. They concluded that the Am^{3+} ion first reacts with a trace of HDEHP dissolved in the aqueous phase. This reaction occurs in three successive steps in each of which one HDEHP unit is added. The product of the third step is neutral and dissolves in the organic phase. The third addition was rate controlling under the conditions of their work. They showed that the forward extraction rate was described by Eq. 26

$$d(\text{Am}^{3+})/dT = k[(\text{Am}^{3+})(\text{HDEHP})^{1.5}/(\text{H}^+)^2] \quad (26)$$

where T is time and k is a constant.

This equation can apply only under conditions in which the extraction rate is not diffusion controlled. These conditions will occur when agitation is sufficiently vigorous.

It should be noted that the time required to reach equilibrium depends on the distribution coefficient as well as on the rate constant when the rate is first order with respect to the metal ion concentration. The higher distribution coefficients are associated with longer equilibrium times when the rate constants are equal.

The kinetics of the TALSPEAK extraction are more complicated than those of the simple extraction from perchlorate solution. The work of Karpacheva and Ilozheva does, however, show that the extraction rate can be affected by the metal ion concentration, the HDEHP concentration, the hydrogen ion concentration, and the solubility of HDEHP in the aqueous phase. The available rate information for the TALSPEAK extraction is in qualitative agreement with Eq. 26.

Both the Karlsruhe and ORNL groups found that the higher lanthanides were slower to extract than the lower ones. As can be seen in Fig. 10, the instability constants of the DTPA complexes of the lanthanides increase with increasing atomic number up to dysprosium. Consequently, the fraction of the element present in free ionic form will decrease with increasing atomic number and the extraction rate will also decrease for it is proportional to the concentration of free ion. Using the data of Appendix 1, it could be predicted that cerium would extract 78-fold faster than europium.

The instability constants for americium and curium are lower than those of any of the lanthanides. Thus, better than equilibrium separation factors could occur in a real process. This effect would be much more pronounced for the lower lanthanides. For the higher lanthanides, the values of K_m are closer than those of curium and americium, and the small increase in K_m is probably more than counteracted by the fact that the distribution coefficients of the lanthanides are higher than those of the actinides, and other things being equal, a higher distribution coefficient will require a longer equilibrium time.

Weaver and Kappelmann¹¹ found that extraction rates were much slower when the aqueous phase contained only Na_5DTPA than they were when a lactic acid buffer was also present. The Na_5DTPA solution had been adjusted by nitric addition to the same pH as the buffered solution. Weaver¹² later found that the substitution of glycolic acid for lactic acid caused a further increase. These results indicate that factors other than the free ion concentration affect the rate in the TALSPEAK process and suggest that further improvement is possible.

Weaver¹² has found that the extraction rates are increased when the temperature is increased and that the temperature increase has little effect on the ratios of the distribution coefficients. The temperature increase did lower all of the distribution coefficients; however, this can be counteracted by increasing the HDEHP concentration. An increase in the HDEHP concentration would have other desirable effects. It is believed that further investigation of temperature effects might be very rewarding.

No study of back-extraction rates has been found in the literature. It is likely that these rates will also be a function of the free ion concentrations since the extracted elements must pass through this form. If this is true, the extraction rate constant will decrease as the atomic number of the lanthanide increases and the extractions will become slower as the pH increases.

Solution Volumes and Solvent Capacity — The loading capacity of the solvent for lanthanides is approximately proportional to the HDEHP concentration. Each lanthanide ion reacts with six HDEHP formula units. Thus, the theoretical molar capacity is one-sixth the HDEHP molarity. In practice, a jelly-like precipitate starts to form as the theoretical limit is approached.¹⁴ Weaver¹² found the practical limit to be about 60% of the theoretical limit when 0.5 M HDEHP was used.

In the TALSPEAK process the maximum HDEHP concentration is limited by the distribution coefficients of americium and curium at low solvent loading. Since these elements should remain in the aqueous phase, distribution coefficients below one are desirable. The distribution coefficients are adjusted to the proper level by adjusting the HDEHP concentration. Both Weaver and Kappelmann¹¹ and the Karlsruhe groups^{10,13} chose 0.3 M. Changes in the system which allow a higher HDEHP concentration are desirable provided the distribution coefficients of americium and curium under conditions of low loading are not increased excessively.

The total volume of extractant required is approximately inversely proportional to the HDEHP concentration. The proper choice of diluents and operation at somewhat elevated temperature should aid in this respect.

The maximum aqueous phase concentrations are limited by the solubilities of DTPA and the DTPA-metal complexes. Data concerning these factors are incomplete. Weaver and Kappelmann chose a 0.1 M DTPA solution. The Karlsruhe group chose 0.05 M DTPA. They stated that DTPA precipitated from 0.1 M solution after prolonged standing. They did not state the conditions under which this took place. One would expect both pH and temperature to influence such a precipitation.

Mechanical Equipment

Differential extraction has been chosen as the most attractive method for using the TALSPEAK process on a commercial scale. The capital costs are lower than those of countercurrent multiple-stage extraction and the equipment is more versatile.

When used in developmental work, differential extraction has additional attractions. There is no long waiting period for the achievement of steady-state operation. The equipment is compact enough for operation in a glove box or hood, and the contact time and vigor of agitation are easily adjusted.

Flow Sheets

Although this work deals principally with the separation of americium and curium from the lanthanides, the procedure will be strongly influenced by the preceding and following steps in the flow sheet. One possible flow sheet will contain the following steps immediately prior to the TALSPEAK separation:

1. An oxalate precipitate of the trivalent actinides and lanthanides will be converted to the oxide.
2. The oxide will be dissolved in lactic or glycolic acid.
3. DTPA will be added. It is assumed that the moles of DTPA must at least equal the total moles of lanthanides plus actinides. The DTPA must contain at least 2 moles of sodium per mole of DTPA if the solution pH recommended by Weaver and Kappelmann (3.0-3.5) is to be obtained.

The lanthanides can be extracted from this solution leaving the americium and curium. The calculated results have been given in Tables 10 and 11.

A second possible flow sheet assumes that a pure lanthanide actinide fraction is obtained by TBP extraction. The metal will be stripped from the TBP by water. The resulting solution will contain nitric acid.

This acid could be removed by evaporation to dryness or destroyed by reaction with formic acid. A better approach, however, is available. The lanthanides and actinides will be extracted from the nitric acid solution by HDEHP. The actinides will then be removed from the HDEHP using a reverse TALSPEAK extraction. Calculations indicate that, at 99% curium recovery for the step, the curium-to-lanthanide ratio will be about 12-fold more favorable in this solution than in the original solution. The remainder of the lanthanides can then be extracted from this solution in the usual manner.

This modification of the process should require much less DTPA than the method described previously. The amount of added sodium or ammonium ion would also be much less.

The following procedure should be investigated for the TBP extraction of the trivalent actinides and lanthanides from the waste. The sizable amounts of NaNO_3 and $\text{Fe}(\text{NO}_3)_3$ present are utilized as salting agents:

1. The uranium, neptunium, and plutonium are extracted directly from the waste by 19% TBP. This waste is expected to be 4.5 M in nitric acid and 8.9 M in total nitrates. Consequently, these elements are expected to have high distribution coefficients. The distribution coefficient of zirconium is estimated to be in the range of 2 to 4. Much of the zirconium is extracted in this operation.
2. The acid concentration is lowered to 0.1-0.2 M.
3. The americium, curium, and lanthanides are extracted using 100% TBP. The distribution coefficient of americium is estimated to be in the range of 5 to 11 under these conditions. Either of these values is high enough for successful differential extraction or multiple-stage counter-current extraction. Distribution coefficients for curium are generally higher than those of americium in TBP extractions. This estimate was made using an equation developed by Walsh²¹ from data obtained using solutions containing both NaNO_3 and HNO_3 . It is assumed that the other nitrate ions in the waste will be as effective as those in NaNO_3 as salting agents.

Iron may precipitate before the acid concentration is low enough to allow extraction. This is believed to be the possible stumbling block in this procedure.

Process Development Plans

The work of previous investigators proves that curium and americium can be separated from the lanthanides by the TALSPEAK process. Most of the reported data, however, were obtained at low concentrations and at room temperature. Perhaps 90% of the data were obtained using cerium, europium, and americium tracers. Weaver and Kappelman¹¹ did show that the distribution coefficient of curium differs very little from that of americium and obtained some data for La, Pr, Nd, Pm, Sm, Tm, and Y. No data are available for gadolinium.

The principal deficiencies in the published information include lack of data at elevated temperature and at high concentrations. The limited rate data available for the TALSPEAK system do not include measurement of the effects of the vigor of agitation, phase loading, or temperature. None of these data were obtained using multicomponent systems.

These variables will be evaluated under conditions such as would occur in an industrial process. The work will, in so far as practical, be carried out in small-scale models of actual production equipment. Four small-scale differential extraction units will be constructed. Two will be designed for aqueous-to-organic extractions, and two for organic-to-aqueous extractions. One of each type will be used in an alpha glove box. The other two will be used in a hood. The units will be instrumented to obtain data which can be used in the design of larger units.

Emphasis will be placed on data obtained under conditions which will be involved in large-scale processes. These conditions will include high solvent loading and elevated temperature. Extractions from multicomponent systems will be carried out in order to evaluate the effects of varying rates of extraction.

Conventional batch distribution coefficient data will be required in certain cases. These include the distribution coefficient of gadolinium and the distribution coefficients of other representative lanthanides and curium at elevated temperatures and under conditions of heavy organic and aqueous phase loading. These data are necessary for comparison with the data obtained with the differential extraction units in order to establish the degree of equilibration which is achieved.

Other methods of separation should be investigated experimentally if the available information indicates that a superior process is possible. In most cases this should involve only a few exploratory experiments.

The design of the experimental equipment needed for the planned differential solvent extraction tests was initiated. Two laboratory-scale contactors will be fabricated, one for "cold" tests and one for tracer-level tests. The agitators for these experimental contactors will be equipped with variable-speed motors and replaceable blade assemblies so that the effects of agitator head design and of mixing speed can be evaluated. Procurement of equipment parts and of the chemicals needed for simulated waste makeup was begun.

Paramagnetic Separation of Curium (*J. C. Posey*)

Preliminary studies indicate that a basically different type of process is possible. It takes advantage of the very high paramagnetic susceptibility of the Cm^{3+} ion. This susceptibility exceeds that of all other aqueous ions except Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , and Er^{3+} . These are minor components in fission-product mixtures, but Gd^{3+} may be present in large amounts if used as a nuclear poison in fuel reprocessing.

The process is based on the fact that, when a solution of paramagnetic ions is placed in a nonhomogeneous magnetic field, the paramagnetic ions tend to migrate toward the region of greatest magnetic field intensity. The method was investigated by Noddack, Noddack, and Wich.²² They partially separated a group of the more paramagnetic lanthanides from the less paramagnetic lanthanides and analyzed the process mathematically. The driving force for migration is proportional to the paramagnetic susceptibility of the ion (χ), to the magnetic field strength (H), and to the magnetic field strength gradient ($dH/d\chi$). The maximum separation occurs when the magnetically induced migration equals the rate of back diffusion. They achieved a one-stage enrichment ratio of 1.14 for Gd^{3+} with respect to the less paramagnetic rare earths. This was accomplished with a field strength of 7800 Gauss and a gradient of 1400 Gauss/cm. The mathematically predicted enrichment ratio was 1.350. (The paramagnetic susceptibilities of Gd^{3+} and Cm^{3+} are nearly identical.²³) Greater enrichment ratios were exhibited by Tb^{3+} , Dy^{3+} , Ho^{3+} , and Er^{3+} . Presumably a stronger magnetic field should have increased the separation.

The process would be easy to operate. A stream of solution would pass slowly through a magnetic field. The liquid would emerge from the stage in two streams. One would be withdrawn from the point of maximum Cm^{3+} enrichment, the other would be withdrawn from the point of maximum Cm^{3+} depletion. Stages could be combined easily to form a cascade or counter-current multiple stage unit.

A series of stages could also be combined to operate as a chromatographic column. The solution would pass through a series of magnetic fields located along a single tube. Each field would tend to hold back the paramagnetic ions while allowing the diamagnetic ions to pass. The rate of movement of different kinds of ions would be an inverse function of their magnetic susceptibility.

In so far as is known at present, the process could be applied to almost any solution. There are few impurities which would seriously interfere with the process. Most ions are diamagnetic and would be impelled weakly toward the weaker part of the field. Some impurities such as iron, nickel, and the lanthanides are paramagnetic. Their paramagnetic susceptibilities, however, are in most cases substantially lower than that of curium and separation should be possible. Some of the lanthanides heavier than europium would go with the curium but could be separated easily by solvent extraction. The americium would not be removed with the curium.

Although the data of Noddack *et al.* indicate that a process is possible, we have not experimentally verified their results or shown that it can be applied to curium. The process does seem to be worth exploratory investigation.

The possibility of developing a practical process will hinge on two things:

1. How much can the stage separation factor be increased by increasing the magnetic field strength?

2. How large a rate of flow can be used while maintaining good separation? This flow rate will depend on the rate of ion migration and on the design of suitable equipment in which migration distances are minimized.

The process could be applied to wastes which contain essentially only fission products, but would be less appropriate for wastes containing large amounts of added gadolinium.

General Operations

Since ^{244}Cm work during FY 1975 will involve very small amounts of actual fuel material, most of the fuel material inventory at the CSFF will be returned to long-term storage status. A full inventory of all ^{244}Cm materials was initiated. All experimental materials except the heat capacity pellet and the FY 1973 Compatibility Couples were transferred from the experimental facilities to the CSFF. Canning of the ^{244}Cm inventory for storage was started. A relatively small amount of $^{244}\text{CmO}_2$ will be kept at the CSFF for distribution as required to other experimenters. The bulk of the ^{244}Cm inventory will be encapsulated in welded containers which will be transported to the Fission Products Development Laboratory for storage. When the storage operation is complete, all experimental equipment in the CSFF will be disassembled, and the facility will be placed in standby condition.

APPENDIX 1. DATA USED IN TALSPEAK CALCULATIONS

Values of K_m , the instability constant for the DTPA complex, have been determined ¹⁴ for all of the lanthanides except promethium by Moeller and Thompson¹⁵ and for the transplutonium elements by Baybarz.¹⁶ Pierce and Peck¹⁷ measured the distribution coefficients of all of the lanthanides between HDEHP in toluene and perchlorate solution. The perchlorate anion was used because it has less tendency to form complex compounds than any other common anion. Pierce and Peck reported their data as relative values. That is, they gave the ratio of the distribution coefficient of each lanthanide to the distribution coefficient of each other lanthanide but did not give absolute values.

The value of E_A^0 for curium was calculated using a formula given by Baes¹⁸ for americium, and the ratio of 1.4 for E_A^0 of curium to that of americium as measured by Horwitz *et al.*¹⁹

Experimental values of the TALSPEAK distribution coefficient ratios were calculated from distribution coefficients read from Fig. 1 of ref. 11. These distribution coefficients were measured using an aqueous phase 0.05 M in the pentasodium salt of DTPA (Versonex-80) and 1 M in lactic acid. The organic phase was 0.3 M HDEHP in diisopropyl benzene.

Data and Results for the Calculation of TALSPEAK Separation Factors

Ion	$K_m \times 10^{23}$	Relative E_A^0 HDEHP-ClO ₄ ⁻	$K_m \times$ $E_A^0 \times 10^{20}$	$\frac{[E_A^0 (M^{3+})]}{[E_A^0 (Cm^{3+})]}$		
				HDEHP- ClO ₄ ⁻	TALSPEAK Calculated	TALSPEAK Measured
La ³⁺	3310	1	3.31	0.198	644	370
Ce ³⁺	316	2.98	0.913	0.590	177	126
Pr ³⁺	85.1	6.09	0.519	1.203	101	57
Nd ³⁺	25.2	8.42	0.212	1.670	41	39
Pm ³⁺		18.2		3.60		
Sm ³⁺	4.57	55.4	0.253	10.98	49	48
Eu ³⁺	4.07	105	0.427	20.80	83	107
Gd ³⁺	3.47	151	0.525	29.9	102	NA
Tb ³⁺	1.95	743	1.450	147.0	282	NA
Dy ³⁺	1.51	1,560	2.36	308.5	459	NA
Ho ³⁺	1.66	3,030	5.04	600	978	NA
Er ³⁺	1.82	6,840	12.42	1,352	2,420	NA
Tm ³⁺	1.91	17,000	32.50	3,462	6,700	7,040
Yb ³⁺	2.40	52,500	126	10,400	24,500	NA
Lu ³⁺	3.63	97,800	354	19,400	69,000	NA
Y ³⁺	8.91	50,000	44.6	990	8,660	670
Am ³⁺	1.20	3.63	0.00435	0.719	0.89	0.89
Cm ³⁺	1.02	5.05	0.00515	1.00	11.00	1.00

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