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SIMULTANEOUS RECOVERY AND PURIFICATION OF Pm, Am and Cm
BY THE USE OF ALTERNATING DTPA AND NTA CATION-EXCHANGE FLOWSHEETS

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SIMULTANEOUS RECOVERY AND PURIFICATION OF Pm, Am and Cm
BY THE USE OF ALTERNATING DTPA AND NTA CATION-EXCHANGE FLOWSHEETS

Recently at Hanford, approximately 140 grams of promethium, 50 grams of curium-244 and 1000 grams of a mixture of americium-241 and -243 were recovered from 13-1/2 tons of Shippingport Reactor Blanket elements and purified. In this presentation I plan to give

- a brief description of the processes used in isolating and purifying these valuable isotopes,
- highlights of some of the chemistry, and
- possible long range implications for future recovery of these elements from power reactor fuels.

We believe that the work to be described is noteworthy because

- it is the first demonstration on an appreciable scale, of the recovery of americium, curium (and promethium) from material typical of spent power reactor fuels,
- the technology used represents an advancement in the state of the art, and
- all process steps were carried out in existing process equipment using chemicals compatible with stainless steel.

The undertaking was a joint effort by Atlantic Richfield Hanford Company and Battelle-Northwest, both prime contractors to the AEC at Hanford and, respectively, operators of the chemical processing and laboratory operations at the site.

G. L. Ritter and A. L. Bolt, chemical engineers with Atlantic Richfield, prepared a paper describing their companies work, but due to a crowded program, this contribution was not included. I have, therefore, taken the liberty to summarize their work.

This separations campaign is summarized in Slide No. 1. The five boxes on the right represent the separate steps involved in the recovery process. Step I represents the prime power reactor fuel reprocessing step in which uranium, plutonium and neptunium were recovered from the dissolved fuel and americium, curium and the rare earths were discarded in the high-salt raffinate (or waste solution). In Step II (at the Redox Plant) and Step III (at the Semiworks Plant) Am, Cm, and the rare earths were recovered from the high-salt

SHIPPINGPORT REACTOR

BLANKET FUEL
ELEMENTS

I
U Pu Np
REMOVAL

II
RE Am Cm
CONCENTRATION

III
RE Am Cm
PURIFICATION

IV
RE / Am Cm
PARTITION AND
Pm PURIFICATION

V
Am / Cm
PARTITION AND
PURIFICATION

REDOX
PLANT

ATLANTIC RICHFIELD
HANFORD COMPANY

SEMIWORKS
PLANT

BATTELLE-NORTHWEST

HIGH LEVEL
RADIOCHEMISTRY
FACILITY

waste solution, separated from nonlanthanide-actinide elements and concentrated into a shippable volume. In Step IV, americium and curium were isolated from the rare earths and then, by a continuation of the same process, pure promethium was recovered and the other rare earths rejected to waste. Step No. V illustrates the final separation of americium and curium from each other.

Now, let us briefly examine some of these process steps to get a better idea of the quantities of material involved, the concentrations of components of interest, the equipment used, and the chemistry. Slide No. 2 provides some information on the Shippingport blanket fuel which was processed in the Redox Plant. From this data, one would expect to find over a kilogram of americium and 60 grams of curium in the 13.5 ton batch. The fuel had remained in the reactor for years as several core loadings were burned out. The high concentration of americium and curium are a result of this high integrated neutron flux.

Slide No. 3 details the processing steps performed by Atlantic Richfield. In Step I the fuel bundles were disassembled, the Zircaloy cladding was penetrated with a Zirflex dissolution ($5.5 \text{ M NH}_4\text{F}$, $0.5 \text{ M NH}_4\text{NO}_3$), and the uranium dioxide dissolved with a nitric acid leach. Uranium, plutonium and neptunium were separated from the aluminum nitrate salted dissolver solution by counter current extraction with hexone (methyl isobutyl ketone). This is the standard Redox Process, in use since 1953. The raffinate was then thermally concentrated to 4300 gal.

Step II utilizes an adaptation of a process demonstrated by Henry at Savannah River (DP-972, August 1965). The raffinate (or waste solution from Step I) was subjected to a batch extraction with 50% tributyl phosphate (TBP) in a hydrocarbon diluent. The rare earths, americium and curium extract (along with some other impurities). This step is much easier to describe than it was to perform. Because the equipment was merely a large stirred tank, considerable entrainment occurred. Under the high salting conditions, distribution coefficients for americium and curium were quite high - ranging from 45 to 86 - so the extractant was contacted successively, from one to three times, with equal volumes of the Redox waste solution from Step I. Some difficulty was experienced with emulsions

SHIPPINGPORT BLANKET DATA

QUANTITY

13.5 TONS URANIUM

COMPOSITION
(AVERAGE VALUES)

Pu

4,740 gm/TON URANIUM

Np

45 gm/TON URANIUM

Am

94 gm/TON URANIUM

Cm

5 gm/TON URANIUM

EXPOSURE

10,500 MWD/T (AVERAGE)

36,000 MWD/T (PEAK)

TIME SINCE DISCHARGE

APPROX. 3 YEARS

ATLANTIC RICHFIELD HANFORD COMPANY RECOVERY OF SHIPPINGPORT PRODUCTS

SHIPPINGPORT BLANKET FUEL ELEMENTS

and phase disengaging times of 6 to 20 hours were found necessary in the extraction cycle. Disengaging during the back extraction occurred readily in the first two of the three back extractions used; however, in the third, extensive emulsification occurred that defied several remedial actions. Finally, time (45 hours) solved the problem. The emulsification and poor disengaging is believed linked to ZrO_2 solids carried over into the Step II feed solution from the Zircaloy decladding operation. The failure to get good phase separation in the decanting operation resulted in considerable contamination of the product with "unextractable" salts. However, the primary objective of reducing the volume to a manageable quantity was achieved. About 92% of the americium-curium was recovered in this step. The principal losses were 3.3 percent to the organic and 1.8 percent to the process tank.

Following cask transfer to the Semiworks, a counter current solvent extraction process was used to separate americium, curium and the rare earths from the contained impurities. In this process step, americium, curium and the rare earths are extracted as solvated salts of di-[2-ethylhexyl]-phosphoric acid. Aluminum and iron are prevented from being extracted by the addition of the complexant, nitrilotriacetate, and a proper pH adjustment. This D2EHPA-TBP extraction process was derived from well established process technology developed primarily by L. A. Bray at Hanford and tested in the Semiworks for the Hanford Waste Management Program. Thermal concentration, followed by sugar denitration, further reduced the volume, lowered the nitric acid concentration to approximately 0.5 M and yielded a product very suitable as feed for the follow-on ion-exchange steps. These process steps in the Semiworks went extremely well. Material balances were good and recoveries exceeded 95 percent.

The results obtained in the three process steps performed by Atlantic Richfield are summarized in Slide No. 4. The column headed "Shippingport Waste" describes the waste solution from the counter current hexone processing. To appreciate the full impact of this solvent extraction effort, I must point out that this 4300 gallon solution was 1.6 M $Al(NO_3)_3$, 1.5 M $NaNO_3$ and contained only 4 milligrams of curium per liter. Note the nearly 30-fold decrease in volume and the near elimination of all impurities except sodium. Sodium extracts into the organic phase at the pH used for the

SUMMARY OF ARHCO PROCESSING

	<u>SHIPPINGPORT WASTE</u>	<u>REDOX PRODUCT</u>	<u>SEMIWORKS PRODUCT</u>
VOLUME	4300 GAL	275 GAL	150 GAL

CATION COMPOSITION
(WT% EXCLUDING H⁺)

Cm	0.0034	0.093	0.18
Am	0.062	1.70	3.22
RARE EARTH	1.4	45.2	85.8
Na	43.0	7.0	10.6
Al, Fe, Cr	54.0	27.0	0.14
U	1.7	19.0	0.0057

Semiworks processing and is quantitatively back extracted by 2 M HNO_3 .

For your interest, I have included a photograph of one of the remotely operated and maintained Redox process cells (Slide No. 5). Slide No. 6 is a photograph of the 30-ton cask used for transporting the product of Step II from Redox to the Semiworks.

The Semiworks product was transferred by a 20-ton shielded cask to the High Level Radiochemistry Facility operated by Battelle-Northwest where the two steps shown in Slide No. 7 were performed. Steps IV and V are cation exchange processes similar to those used for the commercial separation of the rare earth elements from each other. In a typical separation scheme, the mixture of rare earths is absorbed on a bed of cation exchanger (such as Dowex 50). The randomly loaded mixture of ions is then eluted down additional resin beds with a buffered complexant such as ethylenediaminetetraacetic acid (EDTA) which forms complexes of differing stability with each rare earth and therefore sorts the rare earths into discrete bands during the elution process. As the rare earth band moves down additional resin, readsorption is forced by preloading the elution resin beds with an ion which forms a stronger complex than any of the rare earths. Zn^{+2} served as this restraining ion in our work. As you can observe on the slide, we used two different complexing agents. In the remaining time, I will review the research which lead to the ion-exchange process and the application of this work to the purification of americium, curium and promethium from the Shippingport concentrate.

Using macro quantities of specific rare earths to provide reference points and tracer amounts of americium and curium, a number of separations were performed with the eluting agents ethylenediaminetetraacetic acid (EDTA), hydroxyethylethylenediaminetriacetic acid (HEDTA), diethylenetriamine-penetaacetic acid (DTPA), nitrilotriacetic acid (NTA), and α hydroxyisobutyric acid. In each experiment, only enough work was done to determine the elution sequence. The DTPA and NTA results proved to be the most interesting and are shown in Slide No. 8.

BATTELLE - NORTHWEST PURIFICATION OF SHIPPINGPORT PRODUCTS

HIGH LEVEL RADIOCHEMISTRY FACILITY

ION-EXCHANGE ELUTION SEQUENCE

WITH DTPA

Zn^{+2} , Pb^{+2} , Er^{+3} - Ho^{+3} - Dy^{+3} , Gd^{+3} , Eu^{+3} , Sm^{+3} , Y^{+3} , Pm^{+3} , Nd^{+3} , Pr^{+3} , Ce^{+3} , La^{+3}

          ↑   ↑
       Cm^{+3} Am^{+3}

WITH NTA

Zn^{+2} , $(Cm^{+3}-Y^{+3})$, Gd^{+3} , (Eu^{+3}, Am^{+3}) , Sm^{+3} , Pm^{+3} , Nd^{+3} , Pr^{+3}

These sequences predict that Cm and Am will proceed ahead of the RE band and in a region where essentially no fission product rare earths exist. Thus with DTPA, a relatively clean Am-Cm cut could be expected with especially good separation from europium and yttrium. On the other hand, NTA promised better separation of Cm and Am from each other in the laboratory experiments but, of course, required good prior separation from Y and Eu. Thus, the DTPA and NTA flowsheets tended to complement each other. These elution sequences warned that great care should be taken in the DTPA cycle to avoid contamination of the americium-curium concentrate by europium, since the ensuing NTA elution cycle could not be expected to provide significant europium decontamination.

Slide No. 9 shows idealized elution curves for the two ion-exchange steps. The first step utilizes the standard DTPA-Zn flowsheet used during the past two years for the separation of pure promethium. It yields a curium-americium concentrate, and, on continued elution, a pure promethium product and some promethium recycle. Care must be exercised to discontinue the collection of the curium-americium concentrate before breakthrough of europium, since the second cycle does not separate americium from europium. If little or no gadolinium is present, europium will elute directly adjacent to americium and an americium-europium binary solution will be obtained which must be recycled to a subsequent DTPA separation.

In the second step, the americium-curium concentrate is acidified, reabsorbed onto a bed of resin and eluted down several smaller sized columns of Zn^{+2} form resin with NH_4OH buffered NTA. The second step yields a pure curium product, a pure americium product and some recycle.

The two step elution process was used about as shown on the slide for final processing of the Shippingport concentrate obtained from Semiworks. The only significant difference was the apparent absence of significant amounts of gadolinium. The separations were performed in the same equipment used routinely for the separation of pure promethium. This equipment consists of nine ion-exchange columns ranging in diameter from 14" to 1" and having resin depths of 8.5 ft. The columns are water jacketed for heating or cooling and instrumented with an in-line optical absorption spectrophotometer and a gamma ray spectrometer so that effluent streams

TWO-CYCLE FLOWSHEET (SIMULATED ELUTION CURVES)

may be monitored semi-continuously for chemical and radiochemical values. In this step the RE, Am, Cm feed was processed in two batches. No feed adjustment was required prior to absorption. After absorption, the RE AmCm band was eluted with DPTA through 6 columns of decreasing diameter at which time the Am and Cm had accumulated at the bottom of the RE-actinide band adjacent to the zinc barrier ion. This fraction was isolated and reserved for the second ion-exchange cycle. Continued elution removed europium, samarium, yttrium, promethium, neodymium, etc., as successive bands. A "pure" center cut of the promethium band was reserved for an experimental program requiring promethium typical of power reactor origin.

Slide No. 10 shows the americium-curium product elution curve from the second of the two DTPA separation runs. The americium-europium binary from the first DTPA run was back cycled into the feed for the second run. The data points are counting rates at specific gamma energies obtained from the in-cell gamma spectrometer facility.

Only two problems were encountered during the ion-exchange work. One was gas formation, which will be discussed later. The second was Np^{239} , a daughter of Am^{243} . This isotope has a γ spectra almost indistinguishable from the spectra of Cm^{244} . In addition, its chemistry in both the DTPA and NTA systems was such that it moved down-flow from the absorbed band, without noticeable reabsorption at a concentration proportional to the Am^{243} content in the absorbed band. As a result, curium could not be counted at levels lower than those shown in Slide 10. The europium breakthrough was very sharp and continued to increase through two additional orders of magnitude before reaching a plateau value. Fraction A was found by analysis to contain 426 gms Am, 38 gms Cm while fraction B contained 228 gms Am with 0.3 gm Cm; indicating some separation was obtained.

The curium-americium "A" fractions from each of the two DTPA runs were combined and processed through a single NTA final separation. Slide No. 11 shows the elution curve from the final column. The first 17 liters of effluent were collected in liter increments and the remainder in two large fractions.

Slide No 10

Slide No 11

PRODUCT ELUTION CURVE
NTA CYCLE

Before proceeding to the next slide I would like to comment that we did have substantial amounts of radiolytic gas develop in the resin beds, which is not surprising at a power density exceeding 400 watts per liter of resin in the pure curium absorption band. Frequent degassing was required to prevent the resin beds from going dry. The discontinuity in the curium plateau was the result of a rather large amount of gas passing through the gamma detector. Following removal of most of the curium, the final column was twice degassed by a blow-down-refill procedure. Radiolytic gas formation in the resin beds is troublesome, but can be lived with. Higher flow rates and operating pressure would minimize or eliminate this problem.

Slide No. 12 summarizes the americium recovery and product purity. Note that the material balance is across three ion exchange separation runs.

Slide No. 13 summarizes the curium results. The product includes the Zn-Cm binary from the front edge of the absorption band. The zinc was removed from this curium solution by carefully controlled ammonium hydroxide precipitation of the curium.

Slide 14 shows the operating conditions used for the two ion-exchange separations. I will give more details on the use of NTA at paper No. 151 this afternoon.

Slide 15 is a photograph taken through the four-foot thick shielding window using the auto luminescence of the curium product solutions. The light is peach-colored and apparently due to fluorescence of the curium species. (These are two liter bottles contained in stainless steel buckets.)

Slide No. 16 summarizes the technology that has been developed and demonstrated at Hanford to do this kind of work. The recovery described in this paper utilized the processes marked by circled X's.

In conclusion, we feel that the technology demonstrated is the basis for a practical process for the future large scale recovery of these radioisotopes from power reactor fuel wastes. (Certainly Purex process wastes should offer no more problems than the Redox wastes used in this demonstration.) Although extensive uses for americium and curium do not now exist, there is no question that very large quantities of these materials

AMERICIUM RECOVERY

PRODUCT RECOVERY

818 GRAMS

106 LITERS

PRODUCT PURITY

Am 99.4 WT%

Cm 0.5 WT%

RARE EARTHS <0.1 WT%

Na <0.01 WT%

Fe <0.04 WT%

Al <0.01 WT%

FISSION PRODUCTS NOT DETECTABLE

RECYCLE

156 GRAMS

MATERIAL BALANCE

91%

CURIUM RECOVERY

PRODUCT RECOVERY

35 GRAMS

5 LITERS

PRODUCT PURITY

Cm²⁴⁴

> 94 WT%

Am

< 6 WT%

RARE EARTHS

< 0.1 WT%

Na

< 0.01 WT%

Fe

< 0.04 WT%

Al

< 0.01 WT%

FISSION PRODUCTS

NOT DETECTABLE

RECYCLE

13.5 GRAMS

RECYCLE PURITY

Am

74 WT%

Cm

26 WT%

MATERIAL BALANCE

96%

ELUTING CONDITIONS SHIPPINGPORT Am-Cm RECOVERY

	<u>DTPA</u>	<u>NTA</u>
ELUANT CONC.	20.0 gm/l	20.0 gm/l
ELUANT pH	6.50	6.4
FLOW RATE	3.5 ml/min-cm ²	6.0 ml/min-cm ²
TEMPERATURE	60-65°C	60-65°C

AMERICIUM-CURIUM TECHNOLOGY

	BNW		ARHCO
	<u>LAB SCALE</u>	<u>PILOT SCALE</u>	<u>PLANT SCALE</u>
CRUDE RECOVERY			
POWER REACTOR WASTE			
SULFATE PPT	X		
TBP EXT.	X	X	(X)
HANFORD PUREX WASTE			
SULFATE PPT	X	X	X
D2EHPA EXT.	X	X	X
LANTHANIDE-ACTINIDE REFINING			
D2EHPA	X	X	(X)
LANTHANIDE-ACTINIDE SPLIT			
CHROMATOGRAPHIC ION EXCHANGE	X	(X)	
ACTINIDE SEPARATION AND PURIFICATION			
CHROMATOGRAPHIC ION EXCHANGE	X	(X)	

(X) TECHNOLOGY USED FOR SHIPPINGPORT Am-Cm RECOVERY

will become available as the nuclear economy grows. Slide 17 shows a projection of the annual availability of americium and curium over the next 20 years from power reactor fuels.

Please note that the annual availability is plotted on a log scale and includes a 3-year storage for Cm-242 decay. As you can see, these curves predict that the annual availability of americium from this source will exceed 10 kilograms 5 years from now, and curium will reach that same level 4 years later. It will not be long until 10's of kilograms of curium-244 will be available.

ISOTOPES FROM POWER REACTORS