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SUBJECT: Investigation of Paducah Ash and Metal Recovery Waste as a Large-Scale Source of Neptunium-237

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FROM: P. M. Lantz and G. W. Parker

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INVESTIGATION OF PADUCAH ASH AND METAL RECOVERY WASTE

AS A LARGE-SCALE SOURCE OF NEPTUNIUM-237

Examination of Hanford Recovered Uranium and Cyclone Separator Ash for Neptunium Content

In connection with the recent neptunium isolation program at ORNL, a cursory analysis of Savannah River and Hanford Operations last year resulted in the discovery of a moderate amount of neptunium-237 in the uranium oxide[1] at K-25. An initial analysis of Hanford uranium at Paducah in April 1956 revealed that little of the neptunium was contained in the former Redox process material. Subsequently the Hanford Purex Process has been contributing an increasing proportion of the processed uranium.

On or about 3-15-57 Mr. Robert Lavin of the Paducah Technical Development Section informed this group of an apparent discrepancy in plutonium content in their current shipments of uranium oxide to Paducah as reported by Hanford and that determined by the Paducah Laboratory. It was suggested that the difference might be accounted for by the presence of Np^{237} in the higher count as the result of different methods of analysis. At our request samples of the Hanford uranium oxide and Paducah cyclone separator ash were submitted for Np^{237} analysis.

Results of the oxide and separator ash analyses are tabulated in Table I below.

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Table I

Sample Date	Sample Code	Description of Sample	Np^{237} (cc/m/g)	Np^{237} (g/T)
3-16-57	Composite 16 UA	Hanford UO_3	720	0.823
3-16-57	Composite 504	Hanford UO_3	760	0.869
3-16-57	Cyclone Separator	Cyclone Separator Ash (UF_4)	1.4×10^4	16.015

Later, in view of the encouraging results obtained from the above oxides and ash, it was deemed advisable to examine an accumulation of tower, cyclone separator, and filter ash for Np^{237}.

In order to obtain a clearer picture of the distribution of Np^{237} throughout the Paducah plant, samples were requested from the head end, the product, tails and assumed critical points throughout the metal recovery plant. These samples were removed during the same general period of operation, 5-3-57 thru 5-15-57.

The theoretical yield of neptunium in irradiated normal uranium is expected to range from 2.5-3.0 grams of neptunium for each kilogram of plutonium. Assuming the level of Hanford metal to be 600 grams Pu^{239} per ton then the corresponding Np^{237} yield should be in the region of 1.8 grams per ton of uranium or 1320 cc/m/g UO_3. This would indicate that ~50% of the Np^{237} produced was being fed into the Paducah plant with the uranium oxide. As indicated by the specific activity of the cyclone separator ash there is a build up of neptunium at the head end of the plant with the non-volatile uranium tetrafluoride.

The sampling of the stock pile of ash was handled in the following manner: the lot was divided into six groups, a portion was removed from each drum relative to its total weight, the samples from each group were combined, mixed thoroughly, and a composite sample was prepared. Analysis revealed that an excellent source of Np was available for immediate processing with the possibility of a continuous supply. It will be noted in Table II that the Np is predominately in the cyclone separator ash with lots 1, 4, 5, and 6 totaling ~120 grams. This material has been transferred to O.R.N.L. and is currently being processed by the Metal Recovery Plant. Normally the Paducah ash is disposed of at that site by grinding for re-fluorination or dissolution and processing in their Metal Recovery Plant.

Table II

Neptunium Content of Accumulated Ash at Paducah

Date Received	Sample Code	Description of Sample	Approx. Wt. (Tons)	Np^{237} (dc/m/g)	Np^{237} (g/T)	Total Np^{237} (g)
4-30-57	Comp. # 1	Mixed Ash UF_4	4	4.3×10^3	4.9	19.7
5-1-57	Comp. # 2	Mixed Ash UF_4	~5	580	0.66	3.3
5-1-57	Comp. # 3	Mixed Ash UF_4	~5	1.24×10^3	1.41	7.05
5-3-57	Comp. # 4	Cyclone Separator Ash UF_4	2	1.8×10^4	20.6	41.2
6-18-57	Comp. # 5	Separator Ash UF_4	1	5.653	6.47	6.47
6-18-57	Comp. # 6	Separator Ash UF_4	2.5	1.84×10^4	21.05	52.6

Based on a plant profile analysis in the following Table III it is apparent that most of the Np^{237} is stopped by the tower, cyclone separator and barrier filter, thereby depleting the plant product and tails stream.

Table III

Neptunium Distribution in Paducah Diffusion Process

Date Received	Sample Code	Description of Sample	Np^{237} (cc/m/g)	Np^{237} (g/T)
5-3-57	Serial # 192-D	UO_3 Feed	960	1.098
6-18-57	UA-36 150C 21	UO_3 Feed	450	0.514
6-18-57	Tower Ash	Current Tower Ash	66	
5-17-57	N-3241	Sludge From Barrier Filter Cleaning Tank	6,680	7.6
5-17-57	N-1636	Liquid From Barrier Filter Cleaning Tank	0	
5-17-57	N-906	Dry Ash From Barrier Filter # 33457	2,712	3.1
5-17-57	N-801	Dry Ash From Barrier Filter # 26944	3,590	4.1
6-18-57	338251, 338253	U_3O_8 Made From Current Product UF_6	0	
6-18-57	345695, 345749	U_3O_8 Made From Current Tails UF_6	0	

Neptunium in the Paducah Metal Recovery Plant

Since the Paducah metal recovery plant processes all of the waste from the diffusion plant including the ash from the head end this seemed to be a good

phase to examine for Np^{237}. Samples were taken from the mixer-settler and pulse column raffinates and the corresponding uranyl nitrate strips during a period which was considered representative of normal operation. Since the mixer-settler phase operates only 8 hours per day with the raffinate passing into two pulse column units in parallel, operating full time, the pulse column raffinate stream appeared to be the one to consider for possible Np^{237} recovery. On the basis of the analyses in Table IV approximately 0.6 grams Np^{237} per day is available in the pulse column raffinate for recovery and this could probably be increased by tailoring the process to this end. However, the Np^{237} loss to the mixer-settler and pulse column uranyl nitrate would eventually be recovered on re-cycle in the plant.

Summary

An approximate material balance of neptunium-237 occurring in the Paducah operations and originating in the UO_3 from Hanford Purex Process indicates that most of the element is deposited in the nonvolatile ash collected in the plant head end. No neptunium was found in the product uranium and no samples were available from intermediate stages.

On the basis of a Separator Ash Composite collected from March 25, 1957 through June 15, 1957, neptunium is now accumulating at the rate of about 250 grams per year in this portion of the recycle material. In the existing stock pile of 12 tons of ash of mixed origin, about 120 grams of neptunium was found and is now being processed for neptunium in the ORNL Metal Recovery Plant. An examination of streams in the Paducah Metal Recovery Plant reveals a corresponding neptunium content of about 300 grams of neptunium per year contained in all the feed material. In the existing flow sheet this neptunium is largely discarded to waste.

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Table IV

Neptunium in Mixer-Settler and Pulse Column Solutions

5-15-57

Set #1

Sample Code	Description of Sample	Np^{237} (αc/m/ml)	Flow Rate (gal/hr)	Np^{237} (mg/hr)	Np^{237} (mg/da)	Total Np^{237} (%)	Np^{237} (g/yr)
N-3132	Raffinate From Mixer-Settler	100	120	57.5	460	84.4	168
N-2118	Uranyl Nitrate From Mixer-Settler	32	70	10.7	85.6	15.6	31.4
N-1639	Raffinate From Pulse-Columns	85	70	28.4	682	74.1	249
N-1653	Uranyl Nitrate From Pulse-Columns	52	40	9.9	238	25.9	94.5
			Set #2				
N-2123	Raffinate From Mixer-Settler	109	120	62.5	500	81.3	182.5
N-2125	Uranyl Nitrate From Mixer-Settler	43	70	14.4	115.2	18.7	42.0
N-2103	Raffinate From Pulse-Columns	65	70	21.7	521	68.1	190
928	Uranyl Nitrate From Pulse-Columns	54	40	10.2	244	31.9	89

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[redacted]

REFERENCES

1. G. W. Parker, et al., Chemistry Division Semiannual Progress Report, ORNL-2046, p. 65, March 19, 1956.

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