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SEMIANNUAL PROGRESS REPORT

FOR PERIOD ENDING JUNE 20, 1956

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CHEMISTRY DIVISION

SEMIANNUAL PROGRESS REPORT

for Period Ending June 20, 1956

E. H. Taylor, Director
M. A. Bredig, Associate Director

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CHEMISTRY DIVISION SEMIANNUAL PROGRESS REPORT

ABSTRACT

The processing of a special lot of Chalk River uranium solution by a modified Purex method led to the recovery of approximately 28 g of Np^{237}. Evidence was obtained for the occurrence of a valence shift of Np(V) to extractable Np(IV) in contact with TBP. The limits of acid strength both for extraction and partitioning were determined.

The rate of production of neptunium by the $n,2n$ reaction on U^{238} was found to be 0.3% of the plutonium production rate.

EXTRACTION AND RECOVERY OF NEPTUNIUM FROM CANADIAN TANK-CAR URANIUM SOLUTION

G. W. Parker P. M. Lantz
W. J. Martin G. E. Creek

The initial recovery of gram quantities of the 2.2×10^6 year alpha emitter, Np^{237}, as a by-product of the ORNL metal-recovery and plutonium-production process has been discussed in previous reports.[1,2] In the uranium strip solutions from the plutonium ion-exchange concentration cycle, a fairly reliable source of neptunium was found,[1,2] which appears at this time to be without duplicate in similar Purex process plants. The yield of neptunium in this concentration-column effluent had previously been observed to vary with the amount of recycled waste acid but was generally found to be less than 50%.

The present work describes the results obtained in the processing of a special 20-ton lot of Chalk River uranium solution incompletely stripped of plutonium by means of one extraction cycle. The presence of large quantities of neptunium in this solution was discovered by routine analysis of plant fuel materials.

Neptunium Extraction in ORNL Metal-Recovery Program

Metal-Recovery Process. – The metal-recovery Purex process from which neptunium has been obtained is essentially a nitric acid–salted extraction system comprising a parallel series of pulse columns for extracting, partitioning, and decontaminating uranium and plutonium. Feed material in the form of uranyl nitrate is adjusted with excess nitric acid in the range 1.8 to 2.0 *M* and is contacted with 30% TBP in a kerosene type of diluent. Partitioning of plutonium and uranium is accomplished by means of a stripping column (IB) to which a reductant (ferrous sulfamate) is added to convert Pu(IV) to Pu(III). The separate streams are then subjected to a second extraction cycle (ID) and (IIB) for further decontamination. The ORNL Purex process appears to be unique in that the neptunium is partitioned with the plutonium and is largely re-extracted along with plutonium in the second cycle. This mixture is stripped in dilute acid and continuously fed to a short Dowex 50 resin column where both elements, as well as traces of uranium, are adsorbed. Eluting the uranium with hydroxylamine sulfate prior to stripping the plutonium results in neptunium being complexed and collected relatively free of plutonium.

Modification of the Process to Obtain Neptunium. – The processing of the 20 tons of metal solution was adapted to a Purex flowsheet with a modification providing for a nearly quantitative recovery of neptunium at the expense of a small residual content of plutonium. This provision required only the omission of $NaNO_2$ [oxidant for Pu(III)] from the second-cycle plutonium feed. Sufficient nitrite would also oxidize Np(IV) to inextractable Np(V). By this adjustment, the plutonium, in the presence of ferrous sulfamate from

[1] G. W. Parker *et al.*, *Chem. Semiann. Prog. Rep. Dec. 20, 1955*, ORNL-2046, p 62.

[2] G. W. Parker *et al.*, *Chem. Semiann. Prog. Rep. June 20, 1955*, ORNL-1940, p 57.

[redacted]

the TBP solution, was left inextractable as Pu(III), while the neptunium as Np(IV) was extracted as product in its place.

The success of this procedure became immediately evident when the neptunium rapidly replaced plutonium in the TBP product stream. A continuous record of the neptunium analysis of the waste and product streams with other data is given in Fig. 1.

Effect of Acidity and Ferrous Ion on the Extraction of Neptunium in the First Stage. – In view of the success mentioned above, some freedom was exercised in improvising a flowsheet to provide sufficient alpha decontamination of the uranium in a single cycle. It was proposed that ferrous sulfamate be added to the IA column, accompanied by a reduction of plutonium to Pu(III) and of neptunium to Np(IV), so that the neptunium would continue to extract and the Pu(III) would remain with residual fission products. A similar conclusion had been reported by Dawson, Elliott, and McKay,[3] who proposed this valency difference as the most attractive means of separating the two elements.

Unfortunately, the addition of the reductant to the flowsheet (Fig. 1) was accompanied by a simultaneous drop in the acid strength from 2.0 *M* to 1.25 *M*

[3] J. K. Dawson, R. Elliott, and H. A. C. McKay, *The Extraction of Neptunium by Tri-Butyl Phosphate*, AERE-C/R-1117, p 6 (Feb. 1953).

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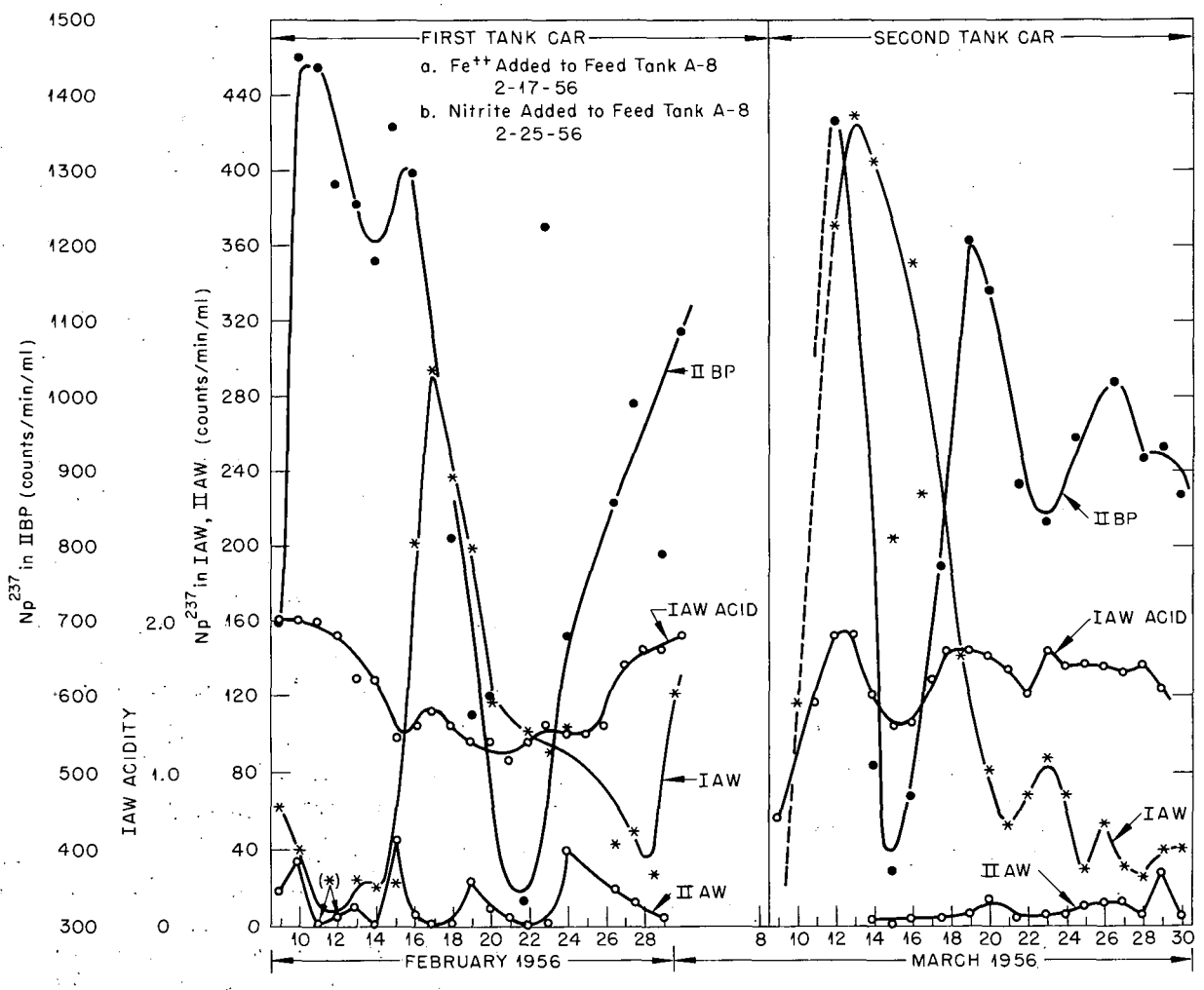

Fig. 1. Np^{237} Distribution in Chalk River Tank Car Uranium Extraction Process.

in the IA column. During this period both plutonium and neptunium losses to the IAW (raffinate) stream were high and remained high (almost quantitative) even after the addition of ferrous sulfamate was discontinued. The only effective means of resuming the extraction was to increase the acid in the IA column. Since the same effect of low acidity was observed, later (as indicated in the figure) it appeared that the ferrous ion in the IA column was not necessarily deleterious to the extraction of neptunium; therefore it was concluded that neptunium was probably being extracted as Np(IV) and not as NpO_2^{++}, as has been considered plausible both by the authors and by others.[4]

In Fig. 1 the recurring rise and fall in acid strength are associated with each new feed-tank makeup, which had to be partly consumed before space was available for acid butting. The material balance across the process is apparent from the figure and Table 1.

TABLE 1. Np^{237} DISTRIBUTION IN TANK-CAR URANIUM-EXTRACTION PROCESS

Stream	Distribution of Np^{237} (counts/min/ml) At Low Acidity (1.3 *N*) in IAW Column*	At High Acidity (1.8 *N*) in IAW Column**
IAW	203	22
IIAW	0	5
IBP	426	733
IIBP	372	1280

*See curve for March 15, 1956, in Fig. 1.
**See curve for February 12, 1956, in Fig. 1.

Ion Exchange Behavior of Neptunium

In order to evaluate the feasibility of other ion exchange type of separations of neptunium and associated heavy elements, the susceptibility of these ions to sulfate complexing was measured, and can be inferred from Figs. 2 and 3. Figure 4 is a comparative study of the nitrate complex formed by Np(IV), which is similar to that known for Pu(IV);

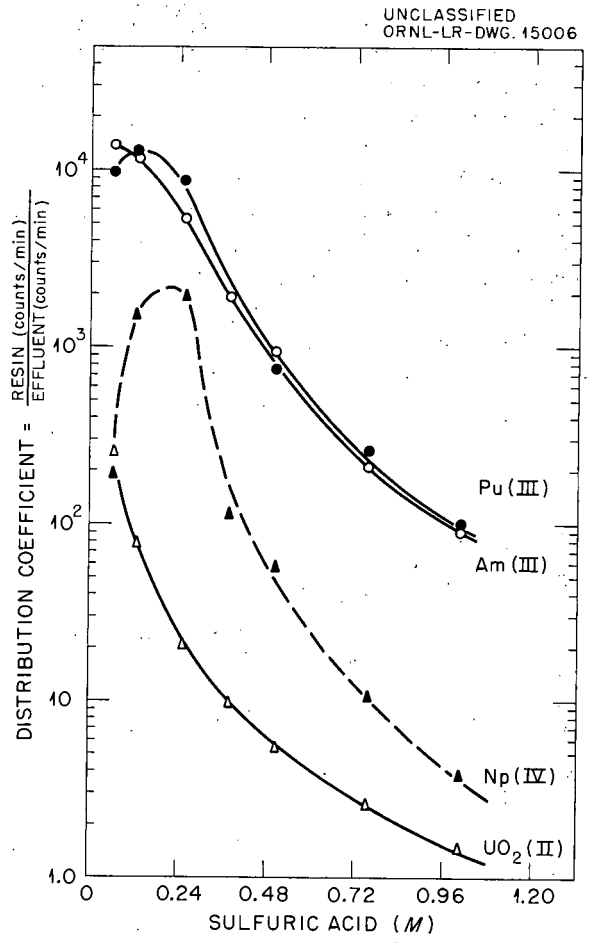

Fig. 2. Distribution Coefficients of Pu(III), Am(III), Np(IV), and UO_2(II) on Dowex 50 × 12 in H_2SO_4.

Am(III) and U(VI) show very little evidence of complexing. Figure 5 is a reproduction of an actual plant-scale elution curve of 12 g of neptunium by the sulfate process. The effective separation of uranium from neptunium is clearly seen.

Further Valence Studies of Neptunium in TBP Extraction

The extraction coefficients for neptunium in 20% TBP have been reported by the Canadian[5] and

[4] R. W. Durham and L. I. Baird, *Tributyl Phosphate Process XXIV. Recovery of Neptunium*, CRCE-589, p 6 (March 1955).

[5] J. P. Butler, M. H. Menzies, and J. S. Adam, *The Production of Np^{237} in NRX Reactor Irradiated Uranium and the Extraction of Np^{237} from Waste Solutions from the Plutonium Extraction Plant*, CRC-485 (April 1952).

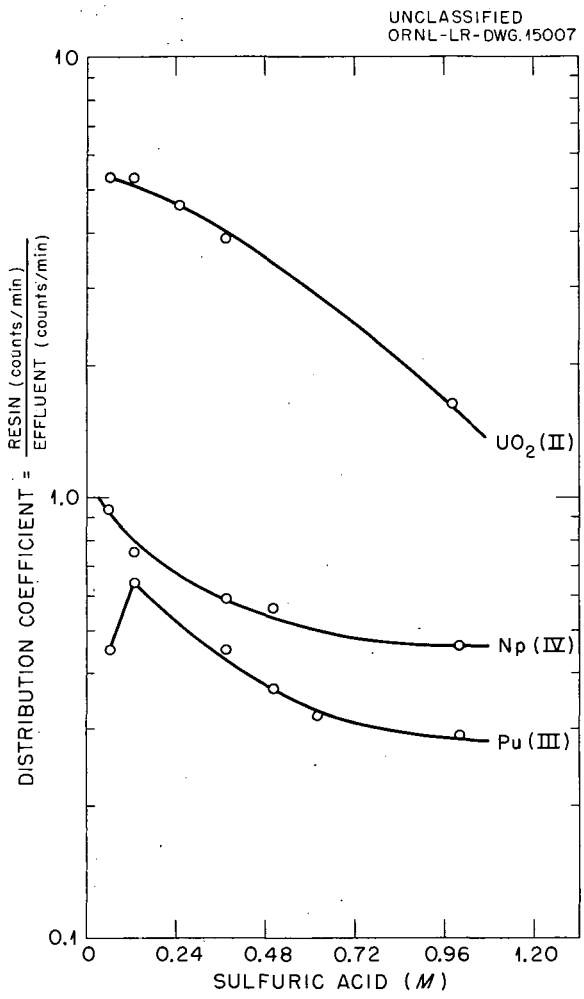

Fig. 3. Distribution Coefficients of UO_2(II), Np(IV), and Pu(III) on Dowex 1 × 10 in H_2SO_4.

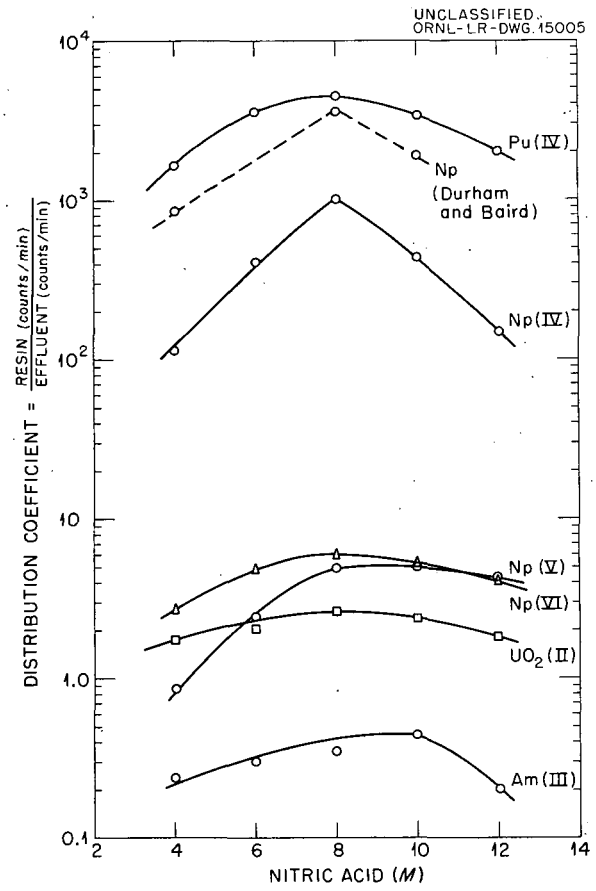

Fig. 4. Distribution Coefficients of Pu(IV), Np(IV), Np(V), Np(VI), UO_2(II), and Am(III) on Dowex 1 × 10 in HNO_3.

British[3] workers. However, in a more recent study by Durham and Baird[4] the effect of uranium saturation is also considered.

In order to measure directly the effect of uranium saturation and to gain a clue to the valence of the neptunium under process conditions, partition coefficients for Np(IV), Np(VI), and an Np(IV, V, and VI) equilibrium mixture (believed to be the true condition in the process-plant first stage) have been compared over a series of acid strengths covering the range experienced in plant solutions. The results of some of these comparisons are summarized in Fig. 6. The most apparent conclusion to be drawn from this figure is that Np(VI) is far more extractable than Np(IV) or the Np(IV, V, VI) mixture. A second observation is that the plant mixture, which was shown by analysis to be essentially Np(V) (Table 2), shows about the same extraction behavior as pure Np(IV). This could only be explained by a rapid reduction of Np(V) and (VI) to Np(IV) by TBP. This effect was tested by using Np(VI), which gave a contact half-time for reduction of 10 min. In the plant, a reasonable residence time is 40 to 60 min, which would allow sufficient time for almost complete reduction.

The very low value of the partition coefficient (0.2) at 65% uranium concentration (2 *N* HNO_3) suggests that a slightly higher acid reflux condition actually prevails in the extraction column (estimated 3.0 *N*) corresponding to a value of 0.45, which in a fivefold organic volume and in five or

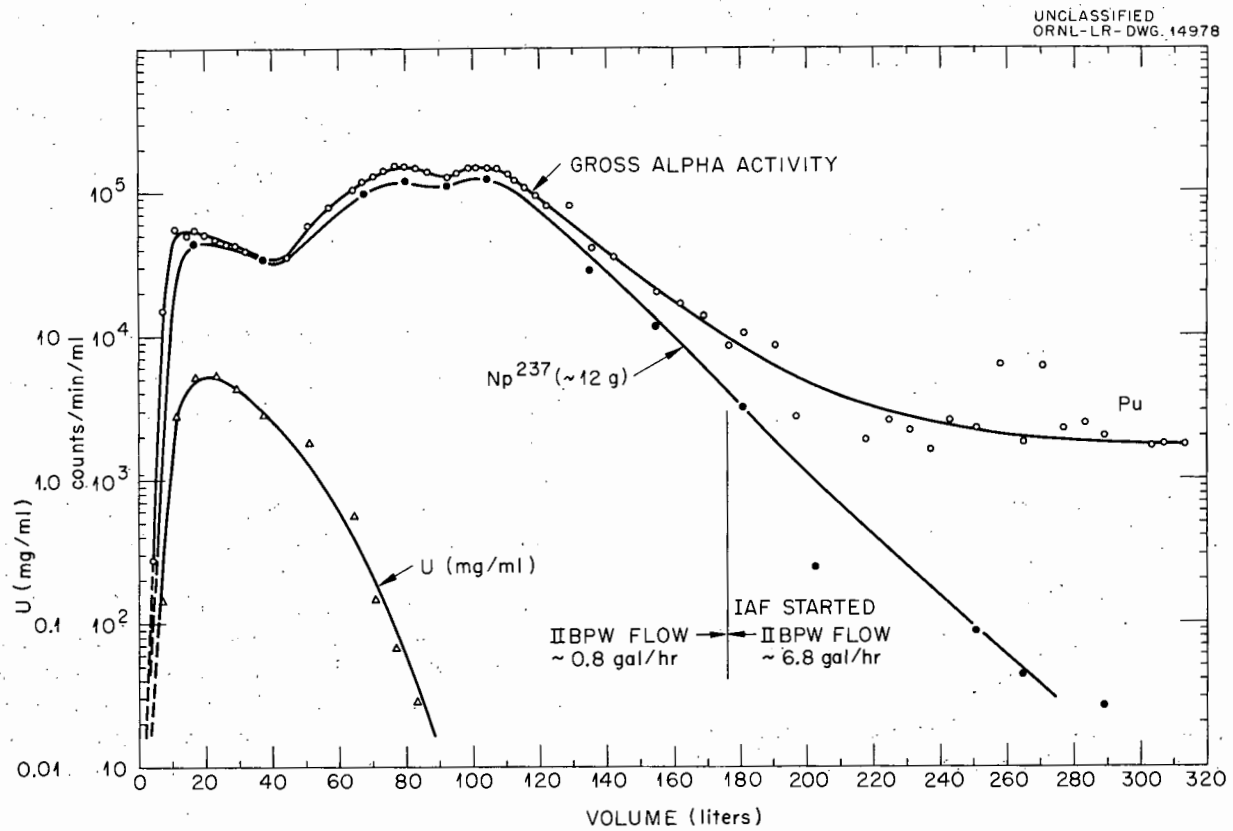

Fig. 5. Elution of 12 g of Np^{237} from Resin Column No. 1 by Metal Recovery.

TABLE 2. NEPTUNIUM DISTRIBUTION AND VALENCE STATES IN ORNL METAL-RECOVERY PROCESS

	Total Np^{237} (counts/min/ml)	Distribution (%)		
		Np(IV)	Np(V)	Np(VI)
IAF* (feed)	375	10	80	10
IAW (fission-product waste)	50	10	80	10
IBP (Pu, first aqueous)	327	100	0	0
IIAW (Pu, waste)	96.5	22	78	0
IIBP (Pu, second cycle)	284	100	0	0

*Pu concentration, 9.73×10^6 counts/min/ml.

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more stage heights should account for 95% extraction.

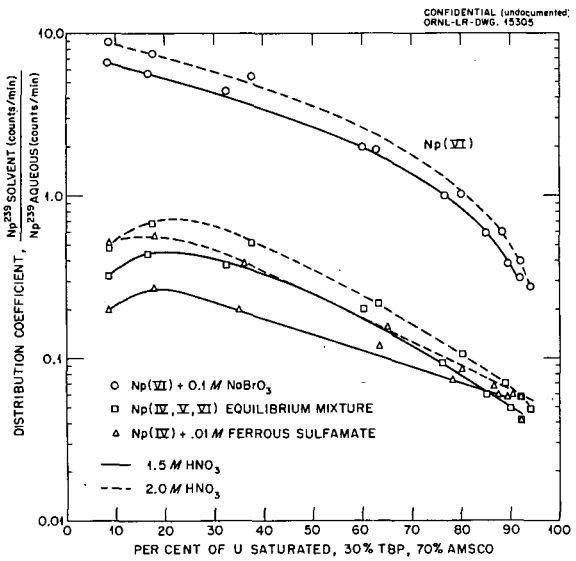

Fig. 6. Variation of Neptunium Distribution Coefficients in TBP with Per Cent Uranium Saturation.

Partitioning with the plutonium in the IB column, which is unique at present to ORNL, can be explained by the significant differences which occur in the acid strength of this stream, as was revealed by an examination of the flowsheets. It is believed that a study of these coefficients will show a borderline condition existing here which can be varied to favor either stream.

Yields of Np^{237} by the $n,2n$ Reaction on U^{238}

In the papers mentioned previously,[4,5] it was calculated that the yield of neptunium by the $n,2n$ process would result in a neptunium ratio of 0.6% to plutonium produced. As shown in Table 3, the weight ratio of neptunium to plutonium found in the two feed solutions is 0.0031 and 0.0032. The yield on the basis of 0.013 barn at low nvt values is 0.0032. The contribution from U^{235}-U^{236} (n,γ) is only 10%. This yield has been observed consistently through the NRX program, from which the recovery of neptunium was 28 g of a possible 40 g. As shown in Fig. 1, the losses occurring during the low acid periods account for most of the difference.

TABLE 3. YIELDS OF Np^{237} BY THE $n,2n$ REACTION ON U^{238}

Source Material	Analysis Made		Weight Ratio Np^{237}/Pu^{239} Observed
	U^{235} Content (%)	Pu Content (g per kg of U)	
NRX uranium solution (low burnup)	0.645	0.6 (calc)	3.2×10^{-3}
NRX high burnup rods		2.26	3.1×10^{-3}

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