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URANIUM RECOVERY FROM ALUMINUM ALLOYED FUEL
ICPP RUN NO. 21

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

B. R. Wheeler, G. F. Offutt, and R. E. Commander

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ATOMIC ENERGY DIVISION

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ICPP RUN NO. 21

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A B S T R A C T

About 505 kg of high-enriched uranium were recovered from aluminum alloyed fuels during Run No. 21 at the Idaho Chemical Processing Plant. Overall product recovery exceeded 99.85 percent, and product log decontamination factors exceeded 7.0. This processing campaign was unique in that 66 of the 505 kg of uranium were recovered on a part-time basis with spare manpower not needed for operation of the Waste Calcining Facility. The feasibility of recovering neptunium at ICPP was demonstrated during the run by recovering over 90 percent of the neptunium in the second cycle raffinate generated during the campaign. Pre-run modifications to the extraction systems simplified the processing campaign and as a result of the experience gained on the run other modifications and processing schemes are actively being considered at ICPP.

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URANIUM RECOVERY FROM ALUMINUM ALLOYED FUEL
ICPP RUN NO. 21

I. SUMMARY

High-enriched uranium-aluminum alloy fuels containing 505 kg of uranium were processed at the Idaho Chemical Processing Plant (ICPP) during processing Run No. 21. A 99.90 percent recovery was achieved in the first extraction cycle; a 99.95 percent recovery was achieved in the combined second and third extraction cycles. Overall decontamination of the recovered uranium was excellent; all product easily met required specifications. The average log decontamination factors (DF's) for uranium in the first and second extraction cycles were similar to those experienced during previous campaigns; however, the DF's for the third extraction cycle were much higher. Consequently, overall DF's for the three extraction cycles--ranging from 8 to 63×10^6 --were about a factor of ten higher than during previous campaigns.

This processing campaign was unique for the ICPP in that 66 of the 505 kg of uranium were recovered on a part-time basis covering a span of four months. Manpower not needed for operation of the Waste Calcining Facility was used to process fuels, usually on the day shift only. Highly burned up fuels having very slow dissolution rates and small batches of fuel which required separate accountability were dissolved and processed through the first extraction cycle during this period. No adverse effects were noticed from starting up and shutting down the system once each day. Uranium recovery in the first extraction cycle during the part-time processing period averaged 99.88 percent.

The feasibility of recovering neptunium at the ICPP was partially demonstrated by recovering over 90 percent of the neptunium in the second cycle raffinate generated during the processing campaign. Analytical determinations indicated that less than three percent of the neptunium in the second cycle raffinate was actually lost to waste. For this demonstration, the oxidation state of neptunium was shifted to the VI state by adding chromic acid to the raffinate. The raffinate was then processed through the first cycle extraction system using a ten-percent TBP flowsheet. About 28 grams of neptunium were recovered (as a concentrated solution) during the demonstration.

Modifications made to the extraction systems prior to the processing campaign significantly improved processing operations. These modifications included the elevation of an airlift disengaging pot on the organic stream between the extraction and scrub columns in the first extraction cycle, lowering the jacklegs on the aqueous outlet streams of the stripping columns in the second and third extraction cycles, and enlarging the vent lines to the samplers on the stripping columns in the second and third extraction cycles.

From the beginning of the continuous operating portion of the run, a seven-stage mixer-settler--used to scrub TBP and its degradation products from the strip column product stream with Amsco--did not function properly due to a partial obstruction in the raffinate stream pipeline. Fortunately, the poor performance of the mixer-settler did not seriously affect the throughput or efficiency of the extraction system. A combination of pulser trouble and suspected solids in the dissolver product from SPERT fuel caused excessive uranium losses from the first cycle extraction column during the last part of the run. The pulser malfunction was caused by a worn push rod on an air pulser poppet valve. The solids are believed to have contributed to the trouble by accumulating on the sieve plates in the column. Second cycle product containing considerable uranium was inadvertently transferred to a hot salvage cell because of a leaking RVC valve on a transfer pump between the second and third extraction cycles. All of the uranium was recovered; most was recovered by recycling to the second extraction cycle system; the remaining amount was recovered later along with neptunium from second cycle raffinate.

II. INTRODUCTION

During Idaho Chemical Processing Plant (ICPP) Run No. 21, covering the period June 3 through December 11, 1964, high-enriched aluminum alloyed fuels containing about 505 kg of uranium were dissolved and processed through three cycles of solvent extraction. A description of equipment used for processing uranium at ICPP has been previously published^(1,2). Modifications made to ICPP equipment between Runs 20 and 21 are described in Appendix A; also included in Appendix A is a brief description of work involving decontamination and pre-run testing of equipment.

The aluminum-alloyed fuels on Run No. 21 were dissolved in continuous dissolvers in G Cell, processed through a solvent extraction cycle using 3-1/4 percent tributyl phosphate (TBP) in G and H Cells, and then processed through two extraction cycles using hexone in P and Q Cells. The flowsheet used for the dissolution and first cycle extraction steps is shown on Figure 1; the flowsheet used for the other two extraction cycles is shown on Figure 2. A brief description of the solvent extraction process used with the aluminum-alloyed fuels during this run is given in Appendix B.

As during other ICPP processing campaigns, a segmented type of operation was used. During segmented operation only part of the processing equipment is operated at any one time to minimize manpower requirements. Usually fuel elements are processed through dissolution and first cycle extraction equipment with the first cycle product being collected in intermediate storage vessels. This segmented operation is employed in alternation with operation of the Waste Calcining Facility (WCF).

After the inventory of fuel elements is processed or all intermediate storage vessels are full, the dissolution and first cycle process equipment is shut down; then the intercycle product solution is processed through the other necessary cycles of solvent extraction. When there is no fuel to be processed at ICPP, the WCF is operated to convert stored waste solutions into solids for permanent storage. Potential plant capacity during segmented-type operation is reduced by about 50 percent; the size of the operating crew is reduced about 30 percent. Since the plant capacity significantly exceeds the present ICPP fuel load, segmented operation results in lowest unit fuel processing costs.

Run No. 21 was unique for the ICPP in that 66 of the 505 kg of uranium processed were dissolved and processed through the first extraction cycle on a part-time basis covering a span of four months during WCF operation. Manpower not needed for operation of the WCF was used to process fuel, usually on the day shift only. Highly-burned-up fuels which are very slow in dissolving and small batches of fuel which required separate accountability were processed during this part-time operation. Round-the-clock operation began with a full crew on November 2 and ended December 11, 1964.

STREAM	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
DESCRIPTION	FUEL CHARGE	DISSOLVENT	DISSOLVER PRODUCT	LAF	IBR	LAX	LAR	LAP	LBS	IBP	ICX	ICR	ICP	IDS	IDR	IDP	FIRST CYCLE PRODUCT
Flow, l/hr	500	482	516	58	380	514	380	58	380	200	300	201	10	10	201	4.06 ^(b)	
IBP, %					3.25		3.25		3.25		3.25						
Diluent					Amsco		Amsco		Amsco		Amsco			Amsco	Amsco		
Sp gr at 25°C	1.20	1.29	1.29	1.16	0.77	1.29	0.78	1.16	0.78	1.00	1.77	1.01	0.76	0.76	1.01	1.30	
Al(NO ₃) ₃ , M		1.60	1.60	1.00		1.60		1.00									
HNO ₃ , M	6.3	1.00	0.95	0.16		0.91	0.06		0.002	0.01		0.01			0.01	0.65	
NH ₄ Cl, M									0.30								
NH ₄ NO ₃ , M			0.03	0.30		0.03											
H ₂ (NO ₃) ₂ , M	0.007	0.007	0.007			0.007											
H (Irr), g/l		1.69(a)	1.62	0.40		2x10 ⁻⁴	2.20		2.14		2x10 ⁻⁴	4.04			4.04	200	
U (Unirr), g/l		2.21	2.12	0.40		2x10 ⁻⁴	2.87		2.80		2x10 ⁻⁴	5.31			5.31	200	
Al, kg/day	500																
J (Irr), kg/day	12.55																
U (Unirr), kg/day	22.55																
			</														

(a) Based on 500 kg of aluminum per day from 50 percent burnup MTR elements.

(b) Volume for irradiated fuel.

Fig. 1 Flowsheet for the dissolution and first extraction cycle of high-enriched aluminum alloyed fuels

[illegible]

Fig. 2 Flowsheet for the second and third extraction cycles of high-enriched uranium.

III. DISCUSSION OF RUN

1. DISSOLUTION

A list of the fuels processed during Run No. 21 along with other data pertinent to the dissolution part of the campaign is shown in Tables I and II. Table I contains data covering the continuous processing period of the campaign--November 2 through December 11--while Table II contains data for the part-time processing period.

Dissolution of all fuels was essentially trouble-free and, for the most part, the composition of the dissolver product met flowsheet specifications. During continuous processing, each of the dissolvers, G-101 and G-151, were operated at less than half rate to dissolve the fuels shown in Table I. The actual dissolution rate of these fuels, as shown by Figure 3, agrees extremely well with the rates predicted from the

Fig. 3 A comparison of actual with predicted aluminum dissolution rates, ICPP Run 21.

TABLE I

FUEL AND DISSOLUTION DATA
(Continuous Operation)

	Reactor Element						Total
	<u>MTR</u>	<u>LPTR</u>	<u>LITR</u>	<u>ETR</u>	<u>SPERT</u>	<u>NASA</u>	
Elements dissolved, no.	310 ⁽¹⁾	21 ⁽²⁾	226	879 ⁽³⁾	243	193	1872
Total aluminum, kg	1032	93	917	5040	763	800	8645
Total uranium, kg	40.9	3.8	35.5	304.1	26.1	28.7	439.1
Total dissolving time, hours	56	4	46	261	29	57	453
Average product composition:							
U, g/l	1.73	1.83	1.66	2.46	1.56	1.50	
Al, <u>M</u>	1.62	1.65	1.59	1.54	1.73	1.59	
H ⁺ , <u>M</u>	0.76	0.87	0.95	1.08	0.38	0.85	
Sp Gr	1.282	1.290	1.283	1.279	1.288	1.280	

(1) Includes 20 OWR elements

(2) Includes 1 UF element

(3) Includes 18 CP-5 and 2 STR elements

TABLE II

FUEL AND DISSOLUTION DATA
(Part-Time Operation)

	Reactor Element									Total
	BGRR	NRX	McMasters	NRU	NRL	SWE	IRL	FNR	GTR	
Elements dissolved, no.	1221	279	9	68	36	216	28	28	24	1909
Total aluminum, kg	727	191	31	208	155	904	98	114	101	2529
Total uranium, kg	13.28	6.82	1.48	3.52	4.82	25.17	3.96	3.50	3.31	65.86
Total dissolving time, hours	55	259	31	183	44	61	13	13	11	670
Average product composition:										
U, g/l	0.86	1.47	1.62	0.71	1.53	1.27	1.59	1.36	1.51	
Al, <u>M</u>	1.75	1.53	1.27	1.57	1.32	1.69	1.45	1.63	1.71	
H ⁺ , <u>M</u>	0.34	1.25	1.60	1.12	0.01	0.41	1.48	0.29	0.45	
Sp Gr	1.288	1.276	1.247	1.280	1.284	1.276	1.272	1.263	1.280	

following empirical relationship established by extensive pilot plant work^(3,4).

$$R_a = K(N)^{0.95} (m_f)^{0.2}$$

Where R_a = dissolution rate, kg Al/day

K = empirical constant

N = acid feed rate, moles/hr

m_f = dissolvent mercury concentration, moles/l

In recent pilot plant work⁽⁵⁾ the value of the empirical constant, K , for once-through operation was found to be 0.65; for natural recirculation this value was found to be 0.82. For correlation of the actual plant data on Figure 3, once-through operation, a value of 0.64 was used to yield the best relationship.

The averaged daily data from all of the fuels processed during the continuous processing period of the campaign were used in preparing Figure 3. These fuels had a burnup of less than 30 percent. The concentration of Hg catalyst used in the dissolution ranged from 0.0044 to 0.025M; the dissolvent acid concentration was 6.3M; and the acid concentration of the dissolver product ranged from slightly acid deficient to 1.4M. The aluminum concentration of the dissolver product ranged from 1.31 to 1.89M.

During the continuous operating period of the run, plant throughput for the dissolution system averaged 18 to 19 kg of aluminum per hour. During the part-time operating period of the run, the dissolution throughput rate for those fuels shown in Table II varied from 0.7 (for NRX fuel) to 9.2 kg of aluminum per hour. These lower throughput rates occurred because these fuels required separate uranium accountability (thus necessitating complete dissolver clean-outs) and in some cases because the fuels had a high uranium burnup. Fuel burnups of greater than 40 to 50 percent (among other factors) have a marked effect on dissolution rate, the extent of which has yet to be accurately determined. The empirical constants for the aluminum dissolution equation need to be adjusted to account for a burnup factor, and this is a goal to be achieved during future processing campaigns; thus the equation must not be used indiscriminately.

In view of the low dissolution throughput realized for the fuels listed in Table II, operating the plant on a part-time basis for these fuels was a notable success. A low dissolution throughput rate in this case did not limit the solvent extraction throughput as it would have done had the fuels in Table II been processed on a continuous basis with a full operating crew. In terms of man-hour savings, it is estimated that the work accomplished by employing part-time operation required one-third the man hours that would have been used had these same fuels been processed with a complete operating crew. These savings realized during part-time operation were only possible by careful manpower scheduling at a time when less than a full crew was needed to operate the WCF.

2. SOLVENT EXTRACTION SYSTEMS

The performance of the solvent extraction systems during the campaign was entirely satisfactory. An overall uranium recovery of 99.90 percent was achieved in the first extraction cycle and a combined overall recovery of 99.95 percent was achieved in the second and third extraction cycles. Overall uranium decontamination was excellent; all product easily met required specifications. A variety of problems were encountered during the run, of course, and some of these problems did cause uranium losses in excess of flowsheet values; otherwise, uranium recovery factors would have been higher. The causes of the uranium losses as well as other pertinent facets related to the solvent extraction part of the run are discussed in this section of the report.

2.1 Uranium Losses, First Extraction Cycle

Essentially all of the uranium losses during first cycle processing were incurred in the extraction or A column. For much of the run, up until November 15, losses were modest and averaged less than 0.05 percent. During the period November 2 through November 15, the uranium concentration in the raffinate from the A column varied from 2×10^{-4} up to 4×10^{-3} grams per liter, well below the raffinate throwaway limit of 6×10^{-3} grams of uranium per liter. An evaluation of operating conditions, ie, stream compositions and flowrates and column pulsing conditions, shows that the A column uranium losses were about equal to those calculated using simple extraction theory. Specifically, the variation in uranium losses were, for the most part, related to variations in the uranium distribution coefficients and the flow rates of the organic and aqueous streams to the A column. The uranium distribution coefficient, of course, was directly related to the composition of the aqueous feed stream in accordance with the relationships shown on Figure 4. Using the plant data, the Height Equivalent to a Theoretical Stage, HETS, for the A column under normal operating conditions was calculated to range from 7.5 to 8.5 feet. These values for HETS are consistent with previously reported values⁽⁶⁾.

Uranium losses from the A column between November 15 and the end of the first cycle processing were appreciably higher, averaging 0.29 percent of the input material during this period. These excessive losses, not entirely predictable by extraction theory, were caused by a combination of factors. Some of the dissolver product fed to the A column was off-specification with respect to the aluminum nitrate and acid components. But, of even greater consequence, much of the dissolver product contained excessive amounts of silica solids which partially obstructed the sieve plates in the A column. Also contributing to poor extraction column performance to some extent during this period were troubles with the air pulser on the A column.

The solids in the dissolver product originated from the SPERT fuel; some of these solids evidentially were held up during passage through the 1/8-inch holes in the column sieve plates. For several days during this period, feed streams to the A column had to be reduced by more than 50 percent to avoid column flooding, and several batches of raffinate had to be recycled because of a high uranium content. An attempt was

Fig. 4 Uranium distribution data for the 3 1/4-percent TBP, $\text{Al}(\text{NO}_3)_3$ - HNO_3 system.

made to stop the column flooding problem by adding gelatin at a concentration of 0.1 g/l; this attempt failed to produce the desired effect obtained with gelatin addition during past runs when silica solids were encountered. On November 19, the first cycle extraction system was shut down while the A column was washed with 13M, hot nitric acid.

During this same period, the A column had inadequate pulsing due to air leakage in an automatic shutoff valve in the pulse leg of the column and due to a worn push rod on an air-pulser poppet valve. After the pulsing problems were corrected and after the nitric acid flush, the A column could be operated up to 3/4-rate without flooding during the last four days of the run. About two weeks later when the solvent extraction system was started up to recover neptunium, the extraction column performed properly at full flowsheet rates. It is believed that some silica solids, remaining after the nitric acid flush, were gradually washed from the extraction column during the last four days of the fuel processing campaign.

This experience with the silica solids, believed to be a major cause of the column flooding and high uranium losses, again indicates the desirability of minimizing the introduction of such solids to a solvent extraction system. Consideration is being given to the installation of a solids removal system on the dissolver product stream.

2.2 Uranium Losses, Second and Third Extraction Cycles

The amount of uranium in the raffinate from the combined second and third cycle processing steps was small, about 0.05 percent of the total uranium input. However, less than 0.01 percent of total uranium input was lost to waste storage. Most of the uranium in the second cycle raffinate did not end up in waste storage because the second cycle raffinate at the end of the campaign was processed through a TBP extraction cycle to recover neptunium. During this processing essentially all uranium in the second cycle raffinate was recovered.

Most of the uranium losses to the second cycle raffinate was caused by an off-specification aqueous composition in the IIA column and by an improper control of aqueous-to-organic flow rates to the column. Part of the composition problem was caused by a steam leak into the IIA column; the other part of the problem was caused by a low scrub rate to this column. Both of these factors tended to cause a low aluminum nitrate concentration in the aqueous phase in the column and resulted in an inadequate nitrate concentration for salting uranium into the organic phase. After the steam leak was eliminated and the scrub rate adjusted, the uranium concentration in the second cycle raffinate decreased to normal flowsheet values.

2.3 Product Quality and Decontamination

Overall decontamination of the recovered uranium product was excellent; all product easily met the required specifications. Decontamination factors (DF's) for uranium based on three sets of samples taken from each extraction cycle are shown in Table III. The average

DF's for uranium in the first and second extraction cycles are similar to those reported for the previous aluminum processing campaign, Run 20⁽⁹⁾; however, the average DF's for the third extraction cycle were much higher than those reported for the previous run. Consequently, overall average DF's for the three extraction cycles were about a factor of ten higher than those reported for Run 20. The reason for the unusually high DF's observed in the third extraction cycle during this run as compared to those observed for Run 20 is not known. Also, the cause of variation of the decontamination factors during the run is unknown.

TABLE III

LOG DECONTAMINATION FACTORS FOR URANIUM PRODUCT

<u>Date of Sample</u>	<u>Gross Beta</u>	<u>Gross Gamma</u>	<u>Pu</u>	<u>Zr - Nb</u>
<u>FIRST EXTRACTION CYCLE</u>				
November 7	2.7	1.7	1.6	1.8
November 12 - 13	2.9	2.1	1.1	2.0
November 23 - 24	<u>2.3</u>	<u>1.7</u>	---	<u>0.8</u>
Average	2.7	1.9	1.4	1.7
<u>SECOND EXTRACTION CYCLE</u>				
November 30	3.2	3.5	1.7	3.3
December 4	1.8	2.7	1.9	2.5
December 8	<u>1.6</u>	<u>2.4</u>	<u>1.8</u>	<u>1.9</u>
Average	2.7	3.1	1.8	2.9
<u>THIRD EXTRACTION CYCLE</u>				
November 30	1.0	1.1	0.1	2.8
December 4	2.7	1.8	0.0	2.6
December 8	<u>2.2</u>	<u>2.1</u>	<u>0.0</u>	<u>3.5</u>
Average	<u>2.4</u>	<u>1.9</u>	<u>0.0</u>	<u>3.1</u>
OVERALL AVERAGE	7.8	6.9	3.2	7.7

2.4 Solvent Degradation During Processing

Previous work^(10,11) has shown that the TBP used in the solvent extraction system goes through successive stages of degradation (from radiation and chemical attack) to form dibutyl phosphate (DBP), monobutyl phosphate, and ultimately phosphoric acid. This degradation is undesirable because: (1) DBP forms an extractable complex with fission product zirconium and thus adversely affects uranium decontamination; (2) DBP forms an organic-soluble complex with uranium that is difficult to back-extract

into the aqueous phase in the stripping column and thus causes excessive uranium losses to the organic raffinate stream; and (3) DBP forms slightly soluble salts with uranium, fission products, and corrosion products in the intercycle evaporator and thus could cause pipeline and equipment plugging downstream of the evaporator. None of these undesirable effects were observed during this campaign, however.

As during previous processing campaigns⁽¹²⁾, the organic streams entering and leaving the C column were sampled and analyzed to gain further insight into the formation of DBP and to measure the efficiency of the organic-raffinate clean-up system. The results are shown in Table IV.

The data for the IAX stream indicate that the concentration of DBP remaining with the organic stream after passing through the raffinate clean-up system increased as the run progressed. Data⁽¹²⁾ gathered during Run 20 showed the same general trend. Hahn⁽¹²⁾ reported log decontamination factors for DBP in the organic clean-up system for Run 20 ranging from 0.6 to 0.8; these factors compare favorably to the values 0.6 to 1.2 observed during this run. The decontamination factors for Zr-Nb and gross gamma during this run are somewhat higher than the similar factors, up to 3.3, observed during the previous run.

One unexplainable fact relative to the formation of DBP is that during this run the ICR stream had a DBP level varying from 40 to 57 mg/l; during Run 20 this same stream had a DBP level varying from 13 to 25 mg/l. Fuels of the same level of burnup were being processed for the comparative periods.

2.5 Waste Generation

The waste generation statistics for the run are shown in Table V. The volume of first cycle waste generated on each part of the run was very close to the flowsheet value of 5.3 gallons per kg of aluminum processed; the waste volume was slightly larger during part-time operation because of the greater number of heel cleanouts required for accountability purposes during that part of the run. With respect to the amount of uranium processed, the first cycle waste generation rate for the part-time operation was about twice that for the continuous operation. The major reason for this is that fuels of different uranium concentration were being processed during the two periods.

2.6 Neptunium Recovery

The feasibility of recovering Np-237 from reactor fuels at ICPP was demonstrated during Run 21 by recovering over 90 percent of the neptunium in the second cycle raffinate generated during this campaign. Neptunium-237 is an isotope needed for research and for the production of Pu-238 which has become an important heat source in space power units⁽¹³⁾. Neptunium is formed from radioactive capture of neutrons by uranium as shown by the following reactions:

TABLE IV
EFFICIENCY OF ORGANIC-RAFFINATE CLEANUP SYSTEM

Days of Operation Prior to Taking Sample	Approximate Fuel Burnup (percent)	Organic Raffinate (ICR)			Organic Feed Stream (IAX)			Log Decontamination Factors in Cleanup System		
		DBP (mg/l)	Zr-Nb (d/m/ml)	Gross γ (d/m/ml)	DBP (mg/l)	Zr-Nb (d/m/ml)	Gross γ (d/m/ml)	DBP	Zr-Nb	Gross γ
5	24	57.1	2.5×10^9	1.1×10^9	3.8	2.0×10^5	2.4×10^5	1.2	4.1	3.7
12	24	40.9	4.2×10^{12}	8.7×10^{11}	6.8	5.3×10^6	1.3×10^6	0.8	5.9	5.8
22	24	54.9	1.0×10^{10}	2.7×10^9	13.4	2.8×10^7	5.5×10^6	0.6	2.5	2.7

TABLE V
WASTE GENERATION STATISTICS

	First Cycle		Second and Third Cycle
	Continuous Operation	Part-Time Operation	
Uranium processed, kg	439.1	65.8	504.9
Aluminum processed, kg	8,645	2,529	
Total volume of waste stored, gal	45,060	14,610	3,800
Actual waste generation rate,			
gal/kg U	103	222	7.6
gal/kg Al	5.2	5.8	
Flowsheet waste generation rate,			
gal/kg Al	5.3	5.3	
gal/kg U			6.5

Most of the neptunium available for recovery at ICPP originates by the first reaction because the principal fuels processed are those which are highly enriched. Future plans call for recovering and purifying Np-237--perhaps 400-600 grams yearly--during normal fuel processing at the ICPP.

Neptunium can be extracted with TBP from aqueous process solutions only if the neptunium is in the IV or VI valence state. Ordinarily, unless a reductant or oxidizer is added to aqueous solutions containing neptunium, a significant portion of the neptunium will be in the inextractable V valence state. This behavior along with the fact that neptunium, regardless of its valence state, is essentially inextractable in an acid-deficient hexone system makes it rather simple to recover neptunium at ICPP. During fuel processing campaigns, an extractable species of neptunium can be picked up by the TBP organic stream along with uranium in the extraction column in the first cycle of processing. Later, the neptunium can be partitioned from the uranium into the raffinate phase in the second cycle of processing.

In order to prove the feasibility of recovering neptunium, the second cycle raffinate generated during Run 21 was collected and jetted to the first solvent extraction system in G and H Cells. (Normally second cycle raffinate during fuel processing flows to U Cell for concentration and analysis prior to discharge to the waste tank farm.) For this run, the second cycle raffinate was processed instead through the first cycle solvent extraction system using a ten percent TBP flowsheet as shown in Figure 5. Of the ~ 32 grams of neptunium in the second cycle raffinate from this run, over 28.8 grams were recovered.

STREAM	1	A	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
DESCRIPTION	SECOND CYCLE RAFFINATE	ADDITIVE	RAW FEED	AF	BR	AX	AR	AP	BS	BP	CP	CX	CR	DR	DX	DP	PRODUCT	EVAPORATOR OVERHEAD
FLOW, l/batch																		
FLOW, l/hr		475	500	25	500	500	500	25	500	200	200	500	10	10	200	2.5	197.5	
TBP, %					10		10		10			10						
DILUENT					Amsco		Amsco		Amsco			Amsco	Amsco	Amsco				
Sp Gr	1.274	1.281		1.159	0.78	1.280	0.78		0.78			0.78	0.76	0.76	1.001	1.02		
Al(NO ₃) ₃ , M	1.73	1.57	1.54	1.00		1.54		1.00										
HNO ₃ , M		131.05	1.00							0.01	0.01				0.01	0.8		
NH ₄ Cl, M	0.23																	
NH ₄ NO ₃ , M	0.21	0.40	0.38			0.38												
CrO ₃ , M		0.01	0.01	0.01		0.01		0.01										
Np, g/l	0.03	0.027	0.026			1.3x10 ⁻³	0.024		0.024	0.06		2.4x10 ⁻⁴			0.06	4.8		
U, g/l	5.8x10 ⁻³	5.3x10 ⁻³	5.0x10 ⁻³			2.0x10 ⁻⁴	4.8x10 ⁻³		4.8x10 ⁻³	0.01		4.8x10 ⁻³			0.01	0.8		

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Fig. 5 Flowsheet for neptunium recovery from second cycle raffinate.

Most of the neptunium in the reactor fuels processed during the run was lost to first cycle raffinate because the neptunium was in the inextractable V valence state. During one part of the run, an attempt was made while processing fuel to shift the valence of neptunium to the extractable IV species by use of ferrous sulfamate. During this attempt, only about 20 percent of the available neptunium was recovered. The ferrous sulfamate was added directly to the extraction column, rather than to the feed tanks, because the ferrous ion would have been destroyed in passing through a headend evaporator, and the neptunium valence would then have shifted to the inextractable V state. It is believed the low neptunium recovery was caused by insufficient time for ferrous sulfamate in the column to shift the valence from Np(V) to the extractable state, Np(IV) ; a contact time of at least 30 minutes⁽¹⁴⁾ at 50°C or one hour at room temperature^(15,16) is required for this reduction.

During future fuel reprocessing campaigns, as indicated on the schematic diagram, Figure 6, neptunium will be oxidized with chromic acid to the highly extractable VI valence state for the first solvent extraction cycle and extracted with the uranium; these two elements then will be partitioned in an acid-deficient hexone second cycle. In this step, neptunium will be reduced to a non-extractable valence state and will remain with the second cycle raffinate. Following reoxidation with chromic acid, the neptunium will be decontaminated from most fission products and concentrated in another TBP extraction cycle. A final TBP cycle will be used to separate neptunium from the plutonium whose extraction behavior has been similar to that of neptunium up to this point. In this final cycle, ferrous sulfamate will be used to reduce the valences to extractable Np(IV) and non-extractable Pu(III) . The only significant contaminants in the neptunium solution at this point should be zirconium and niobium; these will be separated by an anion exchange process.

2.7 Effect of Pre-Run Equipment Modifications

Modifications made to the extraction systems, as listed in Appendix A, significantly improved the operation of the systems. One such modification was the elevation of the airlift disengaging pot on the organic stream between the extraction and scrub columns in the first extraction cycle into a shielded portion of the process makeup area. This change improved the hydraulics of the scrub column and allowed the extraction system to "line out" in a much shorter time than during previous campaigns. Another major modification involved lowering the jacklegs on the aqueous streams of the stripping columns in the second and third extraction cycles. This change improved the hydraulics of these columns and significantly improved interface level control. Also, the vent lines to the samplers on the stripping columns in the second and third extraction cycles were enlarged to minimize column upsets when samples are taken.

2.8 Processing Problems

For the most part, this processing campaign was relatively trouble-free; however, a few operating problems did occur. These were mostly of an annoying nature that did not significantly affect product throughput

Fig. 6 Flow diagram for the proposed recovery of neptunium from reactor fuels.

rates or product quality. Problems that did affect product throughput or quality have been discussed in previous sections of this report; all other problems are discussed in the following paragraphs.

Almost from the start of the run, a seven stage mixer-settler (H-125) failed to function properly due to a partial obstruction (that got worse as the run progressed) in an outlet line. The purpose of the mixer-settler--to scrub residual TBP from the uranium-bearing aqueous before concentration in the product evaporator, H-130--was hindered by this obstruction; there were no other adverse effects. The obstruction (caused by Versene used as a decontamination solution before the processing run) was in a solvent line connecting the mixer-settler to a solvent run tank, H-108. Early in the run it was necessary to reduce the flow of Amsco to the mixer-settler and to shut off one mixer motor to prevent flooding of the unit and erratic flow rates. Midway through the run, the Amsco stream was shut off because most of it was being carried into the evaporator along with the aqueous stream. After the run, the obstruction was flushed from the line.

For a time, some difficulty was experienced in maintaining an adequate boil-up rate in the product evaporator, H-130, due to condensate in the steam supply header. The problem was corrected by cleaning a condensate strainer.

Several problems were encountered with leaky valves while operating the hexone solvent extraction systems. In one case, valves 7-PA and 8-PA in lines between the intercycle pumps, PA-203, PA-204, and J-Cell vessels leaked a considerable amount of uranium product into vessel J-135. To correct the problem, it was necessary to enter the service corridor and cap a line--1/2-inch TPA-20363Y. Another leaky valve on pump PA-208 allowed the undesirable recycle of strip solution (intended for column Q-106) through a relief line into a feed tank. The relief line was disconnected and capped to eliminate the problem.

Another problem during the uranium processing portion of the run involved the feed pumps, PA-201 and PA-202, in the hexone solvent extraction system. It was necessary occasionally to bleed air from the hydraulic line between the primary and secondary heads on the pumps and to adjust the stroke of the pumps.

Just prior to the neptunium recovery portion of the run, while the columns in G and H Cells were being operated on dummy solutions, a line between the feed evaporator, G-110, and the extraction column plugged. The sequence of events leading to the problem is as follows: Aluminum nitrate scrub solution was being circulated from the scrub column through the feed evaporator (for concentration) and then into the extraction column. A leaky steam control valve leaked excessive steam to the evaporator and over-concentrated the aluminum nitrate. The aluminum nitrate then precipitated and plugged the evaporator outlet line. In order to free this line, the evaporator was filled with nitric acid and steam was introduced to the evaporator through a liquid level instrument line. Simultaneously, the temperature in the cell housing the evaporator was raised about 15°C by introducing steam through a spray header and taping shut the louvers on the cell door.

A normal number of minor instrumentation problems were encountered during the run, but these were all readily corrected without requiring access to radioactive areas.

IV. RECOMMENDATIONS FOR FUTURE PROCESSING RUNS

1. SPECIAL FUEL PROCESSING

The trouble-free operation experienced during part-time operation of the dissolution and first-cycle extraction systems during this run clearly points out the desirability of continuing special fuel processing at ICPP. There are many fuels that are troublesome and expensive to process in a normal campaign due to high burnup, unusual fuel composition, necessary separate accountability requirements, low fuel quantity, or unusual geometric configuration. By processing these fuels on a part-time basis with manpower not needed for other tasks, processing costs can be pared considerably.

During the part-time portion of Run 21, it was demonstrated that the extraction system could be brought to satisfactory state of operation in less than one-half hour. During previous runs, similar type operations usually required a complete day. The improved operation of the solvent extraction system was undoubtedly due, in large measure, to improvement in column hydraulics as a result of pre-run equipment modifications.

2. EQUIPMENT MODIFICATIONS

The mixer-settler, H-125, used to scrub TBP from the aqueous stream leaving the strip column was troublesome again during this run. The cause of the problem during this run was unrelated to any problem encountered during Run 20; however, the mixer-settler, even when operating satisfactorily, limits the amount of stripping solution that can be used to back-extract uranium into the aqueous phase during processing. It is believed, therefore, that this mixer-settler should be replaced with a pulsed column when convenient.

3. SOLIDS REMOVAL FROM DISSOLVER PRODUCT STREAM

Again during this run as during other runs, silica solids in dissolver product caused excessive uranium losses from the first cycle solvent extraction system. A simple, trouble-free means to remove solids from process streams continues to be a desirable goal for improving plant processing.

4. DATA

The effects of fuel composition and burnup on fuel reprocessing should be better defined. Some attempt should be made during future runs to classify fuel according to composition and burnup level for processing under closely controlled conditions. A thorough evaluation of the resulting data may add considerable knowledge concerning fuel reprocessing.

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APPENDIX A

PRE-RUN EQUIPMENT MODIFICATIONS AND TESTS

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PRE-RUN EQUIPMENT MODIFICATIONS AND TESTS

During the time between the end of Run No. 20 (September 13, 1963) and the start of Run No. 21 (June 3, 1964) processing equipment and cells were decontaminated to permit various equipment modifications and equipment tests. This work is discussed in the following paragraphs.

1. DECONTAMINATION WORK

Decontamination of various cells and equipment was conducted between September 1963 and February 1964. For decontamination, solutions containing 20 percent HNO_3 followed by solutions containing 10 percent NaOH -2.5 percent tartaric³ acid were used alternately with water rinses and equipment steaming. Repetitive use of these decontamination solutions and procedures gradually reduced radiation levels sufficiently to permit entrance to the cells. In some cases various hot spots in the cells were cleansed with solutions of Versene, oxalic acid, and Turco-4324.

2. PRE-RUN EQUIPMENT MODIFICATIONS

The major work performed prior to Run 21 involved the modification of the zirconium headend process in E Cell to permit an increased zirconium fuel processing capability⁽¹⁷⁾. A detailed description of this modification is beyond the scope of this report; this information will be published in the near future in a topical report covering the first large scale zirconium fuel processing campaign at ICPP. Very briefly, this modification included the installation of a 13-inch perforated basket in an existing dissolver, a dissolvent makeup tank, a concentrated HF storage tank, a neutron-poisoned, closed-loop cooling system, miscellaneous piping, neutron detection instrumentation, and other control instrumentation.

A description of equipment modifications made on equipment used in this aluminum fuel campaign follows.

2.1 Relocation of Disengaging Pot H-132

The air disengaging pot (H-132) in the feed line to the first cycle scrub column (H-100) was elevated from near the ceiling in H Cell into a shielded portion of the PM area to provide additional head for the organic stream to the column. The additional head was needed to eliminate hydraulic problems that had occurred with this column whenever the aluminum molarity of the scrub solution was 1.0 or greater. Relocation of this pot increased the head level on the organic stream by over five feet to a total of about eleven feet.

2.2 Replacement of Motors on Mixer-Settlers

During the previous run, one of the motors on mixer-settler H-125 failed due to a defective starting brush. To prevent a similar occurrence on any subsequent run, all motors on mixer-settlers H-115, H-116, H-117,

and H-125 were replaced with brushless motors having centrifugal switches on the starting windings.

2.3 Column Jackleg and Sample Pot Modifications

All jacklegs on the stripping columns in P, Q, and S Cells were lowered from 1-1/2 to 3 feet prior to the run to eliminate a reoccurring hydraulics problem with the hexone solvent extraction systems. During all previous runs, it was impossible to maintain the flowsheet rate of the aqueous product stream when the density of that stream increased slightly above flowsheet values. A study of the problem showed that adequate flowrates could be maintained by careful control of the density of product streams during processing or by lowering the jacklegs in the cells. The latter approach was adopted and on Run 21 operation of the columns was significantly improved over past operation.

In one other modification, the 3/4-inch vent lines to the sample pots on the stripping columns in P, Q, and S Cells were replaced with one-inch pipe lines. During past runs, columns upsets, due to a back pressure originating in the sample vent lines, were frequently experienced while samples were taken. This modification proved beneficial during Run 21.

2.4 Process Equipment Waste Evaporator

During the period that the plant was shut down, the tube bundle on the process equipment waste evaporator was removed and replaced as a matter of routine preventative maintenance. This tube bundle was in operating service for about 3 1/2 of the 12 years that it was installed in the waste evaporator.

3. PRE-RUN TESTS

3.1 Feed Metering System

An extensive test was conducted to determine the capacity of the feed metering system to the extraction column in G Cell.

A maximum flow rate of 550 l/hr of water was obtained through the control valve, and a maximum of 760 l/hr of water was obtained through an RVC bypass valve with the control valve closed. With both the control and bypass valves open, a maximum flow rate of 930 l/hr was achieved. With a synthetic feed solution having viscosity and specific gravity characteristics similar to zirconium dissolver product solution, a flow rate as high as 750 l/hr was achieved.

3.2 Flow Characteristics of RVC Valves

Flow characteristics were determined for a 3/4-inch RVC valve similar to the one tested and described in the preceding section. This type of valve is designed only for on-off service, therefore, this information was desired to determine the feasibility of using the bypass valve previously discussed for flow control. Full travel of the valve

was accomplished with a three psi change in air signal pressure (one-fifth of the normal range for a control valve). When the valve was tested with reverse flow--the type of use possible in its present plant location--20 percent hysteresis during calibration tests and up to 30 percent hysteresis during smooth changes in air signal pressure were observed. With flow in the normal direction, the hysteresis was 6 percent during calibration tests and 1 percent during smooth changes in air pressure. These results indicate that RVC valves should not be used for flow control, especially when the flow is in the reverse direction.

3.3 Flooding Rates for Steam Stripper

Flooding tests were completed on the steam stripper (in K Cell) used in the plant for decontamination of organic streams. The column, which has a cross-sectional area of 0.317 ft², flooded at a feed rate of 160-180 liters per hour of Amsco when using 0.5 pounds of steam per pound of organic material. The flooding point for 30 percent TBP in Amsco, although it was not accurately established, is well above the maximum expected feed rate of 80 liters per hour that may be employed at ICPP.

APPENDIX B

BRIEF DESCRIPTION OF PROCESS USED AT ICPP FOR ALUMINUM-URANIUM ALLOYED FUELS

APPENDIX B

BRIEF DESCRIPTION OF PROCESS USED AT ICP FOR ALUMINUM-URANIUM ALLOYED FUELS

As indicated on Figure 1, nitric acid containing mercuric nitrate catalyst is introduced near the bottom of the dissolvers, G-101 and -151. From the upper part of the dissolvers, aluminum-uranyl-nitrate solution continuously overflows into one of two vessels, G-105 or -155, where accountability samples are taken before the dissolver product is fed into the extraction system.

In the extraction system, dissolver product is first concentrated in a thermo-syphon evaporator (when necessary) before it is fed into the top of the IA or extraction column. In the IA column, the uranium and some acid are extracted from the aluminum and the bulk of the fission products. The extractant is usually 3-1/4 percent TBP in a kerosene diluent (Amsco). The organic stream, containing the uranium, flows to the IB or scrub column where it is contacted with the IBS stream, aluminum nitrate, to remove fission products and nitric acid. The spent scrub stream, containing a small amount of uranium, is recycled to the feed evaporator to be concentrated with dissolver product. Uranium in the IBP organic stream leaving the scrub column is back-extracted into an aqueous phase in the IC or strip column with a dilute nitric acid stream, ICX. Prior to concentration, the IC column product stream, ICP, is washed in a mixer-settler with Amsco to remove dissolved TBP. The concentrated product from the evaporator is placed in intercycle storage in N Cell until all fuel elements are processed. Then, the dissolution and first cycle extraction equipment are shut down and the intercycle product is processed through the hexone extraction systems.

Plutonium and neptunium present in the dissolver product stream in the tetravalent state are extractable under the TBP first cycle conditions. These materials are reduced with ferrous sulfamate or ferrous ammonium sulfate-sulfamic acid in later extraction cycles and are partitioned from the uranium at that time.

Aluminum nitrate waste, the IAR stream, is concentrated in an evaporator for interim storage and eventual calcination. The spent TBP in Amsco from the strip column, the ICR stream, is continuously washed in three mixer-settlers for recycle to the process. The first and third washes use 0.04M nitric acid; the second wash uses 0.5M sodium carbonate. The contact time in each mixer-settler is about 30 minutes. Spent Amsco, the IDR stream, from mixer-settler H-125 is steam-stripped and then burned in an incinerator.

In the hexone extraction systems as shown on Figure 2, the aqueous product stream from intercycle storage in N Cell is fed to the IIA column at about midheight. The aqueous stream then flows down the column countercurrent to a stream of hexone, IIX, flowing up the column and extracting the uranium. The hexone stream entering the bottom of this compound A column passes first through an extraction section and then a scrubbing section. A relatively large volume of scrub solution, IIBS;

introduced at the top of the A column provides a salting agent, aluminum nitrate, to force the uranium in the extraction section of the column into the organic phase. Also entering with the scrub solution is sufficient ammonium hydroxide to create an acid-deficient condition in the extraction part of the column needed to obtain adequate fission product decontamination of uranium. The uranium in the hexone phase, IIAP, leaving the IIA column flows to a stripping or IIB column. Here the uranium is back-extracted into an aqueous phase with a dilute nitric acid stream, IIBX. Feed is prepared for the third extraction cycle by concentrating the aqueous or IIBP stream in an evaporator. The third and last extraction cycle is similar in most respects to the second cycle. The third cycle product solution is concentrated to about 1.5M uranyl nitrate for convenience in shipping.

Plutonium and neptunium follow a path similar to that of the fission products in the second and third extraction cycles. Ferrous ammonium sulfate and sulfamic acid, 0.05M and 0.1M, respectively, are added to the second cycle scrub stream, IIBS, to reduce the plutonium and neptunium to relatively inextractable valence states. Similar reducing agents may also be used in the third extraction cycle for the same purpose if additional alpha decontamination is required to meet uranium product specifications.

Spent hexone, the IIBR and IIIBR streams from the stripping columns, is treated with a small volume of 3.0M sodium hydroxide and then steam-distilled to remove decomposition products and fission product contamination. The solvent is then recycled to the process.

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