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URANIUM RECOVERY FROM ALUMINUM ALLOYED FUEL
ICPP RUN NO. 25

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IDAHO NUCLEAR CORPORATION
A Jointly Owned Subsidiary of
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PHILLIPS PETROLEUM COMPANY

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ABSTRACT

About 677 kg of high-enriched uranium were recovered from aluminum alloyed fuels during Run No. 25 at the Idaho Chemical Processing Plant. Overall product recovery was greater than 99.93 percent and all product easily met required specifications. The feasibility of recovering neptunium at ICPP was again demonstrated by recovering 99 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 are actively being considered at the ICPP.

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I. SUMMARY

High-enriched uranium-aluminum alloy fuels containing 677 kg of uranium were processed at the Idaho Chemical Processing Plant (ICPP) during processing Run No. 25. A 99.93-percent recovery of uranium was achieved in the first extraction cycle using five-percent tributyl phosphate in kerosene as the extractant. In the combined second and third extraction cycles, using Hexone as the extractant, greater than 99.99-percent recovery was achieved. Overall decontamination of the recovered uranium was excellent, and all product easily met required specifications. During the run, a significant quantity of neptunium, 400 g, was also recovered as a concentrated solution from the raffinate stream of the second extraction cycle. This raffinate stream was reprocessed through the first-cycle extraction equipment in a separate operation after all of the uranium processing ended. The neptunium-recovery efficiency for this step was approximately 99 percent, with less than four grams lost to waste.

The overall performance of the process equipment was good, with the performance of some equipment being highly satisfactory. The installation of a paddle wheel feeder (Clarkson Feeder) in the second-cycle extraction system prior to startup eliminated any surges in the feed rate to the columns, and this contributed to the excellent performance of the entire Hexone extraction system.

Some equipment problems did occur during the run, but they had little effect on recovery efficiencies. Notably, the performance of the continuous fuel dissolvers was marred by persistent plugging problems with a filter on the dissolver effluent line; at times this limited overall processing rates to approximately three quarters of flowsheet values. The plug originated not from a system deficiency, but from the physical composition of the type of fuel being dissolved. The fuel, manufactured by a powder metallurgy technique, contained fuel particles that dissolved more slowly than the aluminum part of the fuel, and these dissolved particles were carried from the dissolver to the effluent filter.

Another problem involved the loss of small amounts of uranium in the first-cycle extraction system. This was caused from some periodic column flooding and a buildup of undesirable dibutyl phosphate in the system.

Experience from this run indicates that system performance can be improved on future runs by: (1) replacing the seal on the dissolver lids with a seal more resistant to acid corrosion and heat, (2) installing instrumentation to measure the pulse amplitude of the columns in the first-cycle extraction system, (3) installing a centrifuge for removal of solids from the dissolver effluent stream, (4) employing more positive methods of feed control to the first-cycle extraction system, and (5) rerouting the aqueous wash solution from the headend evaporator to the ID column, thus reducing the formation of undesirable dibutyl phosphate.

II. INTRODUCTION

During Run No. 25 at the Idaho Chemical Processing Plant (ICPP)* covering the months April to June of 1968, uranium-aluminum alloyed fuels containing about 677 kg of high-enriched uranium were dissolved and processed through three cycles of solvent extraction. This report describes the operating experience and uranium recovery and efficiency of the run, and presents an evaluation of the effect of pre-run equipment modifications on plant operation. A description of the ICPP previously was published^(1,2); modifications to ICPP equipment between Runs 24 and 25 are described in the Appendix.

The aluminum-alloyed fuels on Run No. 25 were dissolved in continuous dissolvers⁽³⁾ using mercuric-nitrate-catalyzed nitric acid, and the dissolver effluent was processed through a solvent extraction cycle using five percent tributyl phosphate (TBP). The flowsheet used is shown on Figure 1. After the inventory of fuel elements was processed, the dissolution and first-cycle process equipment was shut down and the first-cycle product solution was processed through two additional cycles of solvent extraction. The second and third extraction cycles utilized a Hexone flowsheet as shown on Figure 2.

*The ICPP is a multiple purpose nuclear fuels reprocessing plant owned by the United States Atomic Energy Commission and operated by the Idaho Nuclear Corporation, a subsidiary owned by Aerojet General Corporation, Allied Chemical Corporation, and Phillips Petroleum Company.

STREAM	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17 and 18	19	20	
DESCRIPTION	FUEL CHARGE	DISSOLVENT HNO ₃	CATALYST Hg(NO ₃) ₂	DISSOLVER PRODUCT	FEED ADJUSTMENT SOLUTION	ADJUSTED FEED SOLUTION	1 BR	1 AF	1 AX	1 AR	1 AP	1 BS	1 RC	1 CX	1 CR	1 CP	1 DX	1 DR	1 DP	FIRST CYCLE PRODUCT
Flow, l/hr		475	5	480	1	484	70	513	380	513	380	70	380	200	380	201	10	201	6.39(c)	
TBP %								5		5		5.0		5.0						
Diluent								Amsco		Amsco		Amsco		Amsco		Amsco				
Sp. Gr. at 25°C		1.20		1.30		1.30	1.16		0.78		0.79	1.16	0.79	1.01	0.78	1.01	0.76	1.01	1.30	
Al(NO ₃) ₃ , M				1.60		1.60	0.7%	1.60		1.60		0.75								
HNO ₃ , M		6.3		1.50		1.50	0.5%	1.31		1.40	0.10		0.0125	0.01		0.01		0.01	9.65	
Hg(NO ₃) ₂ , M			0.29	0.003		0.003		0.003		0.003										
U (Irr), g/l(a)				2.71		2.71	0.5%	2.63		2x10 ⁻⁴	3.22		3.04		2x10 ⁻⁴	6.39		6.39	200	
U (Unirr), g/l				3.36		3.36	0.6%	3.26		2 x 10 ⁻⁴	4.00		3.77		2x10 ⁻⁴	7.93		7.93	200	
Al, kg/day	500																			
U(Irr), kg/day	29.3																			
U (Unirr), kg/day	38.4																			
Np, g/l (b)				2.7x10 ⁻³		2.7x10 ⁻³				<10 ⁻³	3x10 ⁻³		3x10 ⁻³			6x10 ⁻³		6x10 ⁻³	0.2	
CrO ₃ , g/l					480 /hr	1.0	1.8				1.0									
Gelatin, g/l					513 g/hr	0.107	0.1		0.1											

(a) Based on 500 kg of aluminum per day with 21% burnup on ETR.

(b) Based on assumption that Np concentration is 1 gram of neptunium for each kilogram of irradiated uranium.

(c) Based on irradiated uranium.

FIGURE 1
FLOWSHEET FOR FIRST CYCLE EXTRACTION OF URANIUM-ALUMINUM ALLOYED FUEL--
FIVE PERCENT TBP

III. BRIEF PROCESS DESCRIPTION

As indicated in Figure 1, nitric acid containing mercuric nitrate catalyst was introduced near the bottom of the fuel dissolvers. From the upper part of the dissolvers, aluminum-uranyl nitrate solution continuously overflowed into one of two vessels where accountability samples were taken and solution adjustments made before the dissolver product was fed into the extraction system.

Prior to extraction, dissolver product was concentrated (when necessary) in a thermosyphon evaporator before being fed into the top of the IA or extraction column. In the IA column, the uranium along with some acid was extracted from the aluminum nitrate solution and the bulk of the fission products. The extractant, 5 percent TBP in a kerosene diluent, was fed into the bottom of the IA column. The organic stream, containing the uranium, was fed to the bottom of the IB or scrub column where it contacted a downward flowing IBS stream, an aluminum nitrate solution, to further remove fission products and nitric acid. The spent scrub stream, containing a small amount of uranium, was recycled to the feed evaporator for concentration with dissolver product. Uranium in the IBP organic stream leaving the scrub column was back-extracted into an aqueous phase in the IC or strip column with a dilute nitric acid stream, ICX. The IC column product stream, ICP, was washed with kerosene in the ID column to remove dissolved TBP and then concentrated in the product evaporator. The concentrated product was transferred for intercycle storage to critically safe vessels until all fuel elements were processed. Then, the dissolution and first-cycle extraction equipment was shut down and the intercycle product processed through the Hexone extraction systems.

Plutonium and neptunium, present in the dissolver product stream in lower valence states, were oxidized to the hexavalent states with chromic acid and extracted along with the uranium under the TBP first-cycle conditions. These materials were reduced with ferrous ion (ferrous ammonium sulfate-sulfamic acid) in the second extraction cycle and partitioned from the uranium at that time.

Aluminum nitrate waste, the IAR stream, was sent to interim storage for eventual calcination in the Waste Calcining Facility⁽⁴⁾. The spent TBP from the strip column, the ICR stream, was continuously washed in three

mixer-settlers for recycle to the process. The first and third washes used 0.04 M nitric acid; the second wash used 0.5 M sodium carbonate. The contact time in each mixer-settler was about 30 minutes. Spent TBP extractant, the IDR stream from the product wash column, was steam-stripped to remove contaminants and then burned in an incinerator.

In the second and third extraction systems, or Hexone system as shown on Figure 2, the aqueous product stream from intercycle storage was fed to the IIA column at about midheight. The aqueous stream then flowed down the column counter-current to a stream of Hexone (IIAX) which extracted the uranium. Above the midpoint, the Hexone stream was contacted by a relatively large volume of scrub solution (IIBS) introduced at the top of the column to provide a salting agent, aluminum nitrate, which also scrubbed contaminants from the uranium. Also entering with the scrub solution was sufficient ammonium hydroxide to create an acid-deficient condition which prevents nitration of the Hexone in the extraction part of the column as well as increases the fission product decontamination. The uranium in the Hexone phase, IIAP stream, leaving the IIA column flowed to a stripping or IIB column. Here the uranium was back extracted into an aqueous phase with a dilute nitric acid stream (IIBX). The aqueous or IIBP stream was then concentrated in an evaporator. The third extraction cycle was similar in most respects to the second cycle. The third-cycle product solution was concentrated to about 1.5 M uranyl nitrate for convenience in shipping.

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

Plutonium and neptunium followed the waste raffinate stream leaving the second cycle extraction column. A mixture of ferrous ammonium sulfate and sulfamic acid (0.05 M and 0.1 M, respectively) was added to the second cycle scrub stream (IIBS) to reduce the plutonium and neptunium to relatively inextractable valence states to accomplish this.

IV. DISCUSSION OF THE RUN

Fuel processing experience in Run No. 25 was generally good in all major segments of the operation. Operating difficulties with the Rare Gas Plant⁽⁵⁾ (RGP), which was operated in conjunction with fuel dissolution, did require shutdown of the fuel processing system after the first few weeks of operation, but the process was later restarted and run until the complete fuel inventory was processed. The performance of the major segments of the plant are discussed in the following sections.

1. Dissolver Performance

Continuous dissolution was generally trouble-free except for a persistent partial plugging of the dissolver filters and piping. A list of the fuels processed along with other pertinent data are shown in Table I. Accurate dissolution rates are available only for GETR fuel as shown in Table II, because only that fuel required separate accountability. Most fuel elements were comingled to facilitate loading of charging casks in the fuel storage basin. All fuels dissolved readily except those from the CP-5 reactor, which dissolved at a noticeably slower rate. A total of 676.8 kg of uranium was dissolved at an average rate of 16.9 kg per day. Dissolver product composition was satisfactory; although aluminum and acid concentrations did vary, they remained well within the process parameters desired for a five percent TBP flowsheet^(6,7). The nitric acid and the aluminum concentrations varied from 2.3 to 6.1 M and 0.15 to 0.26 M, respectively. However, the large majority of the batches of product had compositions within 20 percent of the average acid and aluminum concentrations, 1.57 M and 1.46 M, respectively, that were experienced on the run.

1.1 Dissolver Effluent Filters

The dissolution rate was generally kept between one-half and three-quarters of the flowsheet rate shown on Figure 1. This lower dissolution rate was partly a result of plugging problems which appeared early in the run. The plugging occurred mainly on the filters and/or piping through which the dissolver product flowed to the product hold tanks. The plugging at times caused dissolver product to back up into the dissolver off-gas

TABLE I
LIST OF URANIUM-ALUMINUM FUELS PROCESSED AT THE ICPP
DURING RUN NO. 25

<u>Fuel</u>	<u>Elements Dissolved</u>	<u>Shippers Estimate* of Total U, kg</u>
Omega West Reactor	56	10.08
Low Pressure Water Reactor	35	5.37
Argonne National Laboratory	60	6.54
Argonne National Laboratory cans	3	
Sandia Experimental Reactor	12	1.76
Ground Test Reactor	24	3.20
Industrial Research Reactor	28	3.20
Naval Research Reactor	30	3.37
Low Intensity Test Reactor	362	53.38
General Electric Testing Reactor	160	885.89
Materials Testing Reactor	666	110.7
Materials Testing Reactor cans	3	
Engineering Test Reactor	1143	385.84
Engineering Test Reactor cans	14	
TOTAL	2696	669.83

*Accountability measurement indicates 676.81 kg total U.

TABLE II
DISSOLUTION TIMES AND QUANTITIES FOR FUELS DISSOLVED
DURING ICPP RUN NO. 25

<u>Fuel</u>	<u>Dissolving Time (hrs)</u>	<u>Metal Dissolved*</u>		<u>Average Dissolution Rate</u>	
		<u>kg</u>		<u>kgs/day</u>	
		<u>Uranium</u>	<u>Aluminum</u>	<u>Uranium</u>	<u>Total Metal</u>
GETR	101	87.46	1,423	20.8	338.2
Other Fuels	860	589.35	11,780	16.5	334.9
Total	961	676.81	13,230	16.9	334.1

*Based on dissolver product analysis.

(DOG) condenser, requiring a reduction in acid feed rates to allow the dissolvent to drain through the partially plugged filters. Attempts to clear the plugs, ie, steaming, back-flushing with 60-percent nitric acid or water, and eventually punching holes in the filters, solved the problem for only short periods of time; in general, the difficulty persisted throughout the run.

Laboratory work after completion of the run indicated that the plugging problem probably was caused by accumulation of slow-to-dissolve uranium-aluminide particles from the fuel. Fuel elements processed during this run were produced by powder metallurgy; these particular fuel elements contained uranium-aluminide fuel particles of a larger size than those contained in fuel elements processed previously. Dissolution studies indicated that these fuel particles dissolved much slower than the aluminum matrix, and effervescent dissolution tended to float the undissolved particles out of the dissolver vessel. The particles then collected on the 100-mesh stainless-steel screen filters and in the lines to the accountability tanks. The absence of a solids buildup in the columns of the first cycle extraction system indicated that the solids dissolved after longer contact with nitric acid, and this was also substantiated by laboratory studies. Also, visual inspection of the filter screen made during and after the run revealed no gross quantities of solids.

1.2 Dissolver Recirculation Legs

Prior to startup, recirculation legs (side loops) were installed on each dissolver to permit dissolver product to recirculate and to increase the retention of the dissolvent in the dissolver. A 25-percent increase in mercury-catalyst efficiency (decreased catalyst consumption) was also expected⁽⁸⁾. To verify these expectations, three tests were conducted at different acid and catalyst rates, and the results are shown on Table III. The results of the tests were evaluated according to a relationship which was established on the basis of pilot plant development work with a dissolver having a natural-recirculation leg.

Although the tests are somewhat inconclusive, there is a fair agreement between the actual and predicted dissolution rates of Tests 1 and 2. The results of the Test 3, which used a much higher acid rate,

do not agree with the correlation. Results of Test 3 may be clouded by the dissolution problems already described; ie, the presence of slow dissolving fuel particles which were not present in material used in pilot plant work.

TABLE III
NITRIC ACID DISSOLUTION OF ETR FUEL ELEMENTS IN PLANT DISSOLVER
WITH A NATURAL-RECIRCULATION LEG

Test No.	1	2	3
Total dissolved aluminum, kg	95.2	101.2	71.8
Dissolution time, hr	9.4	9.8	6.0
Acid feed concentration, <u>M</u>	6.3	6.3	6.3
Acid feed rate, l/hr	207.5	201.5	327.7
Catalyst feed rate (0.29 <u>M</u> Hg) l/hr	5.3	3.7	8.3
Actual aluminum dissolution rate, kg/day	242.4	247.2	287.2
Predicted* aluminum dissolution rate, kg/day	277	252	427
Calculated dissolution constant*, K	0.72	0.81	.56

*Empirical relationship used to predict dissolution rate⁽⁸⁾.

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

R_a = Dissolution rate, kg Al/day

N = Acid feed rate, moles/hr

m_f = Dissolvent mercury concentration, moles/liter

K = Dissolution constant; a value of 0.82 was observed in pilot plant work for dissolvers with a natural recirculation leg.

2. Solvent Extraction Systems

The performance of the solvent extraction systems during the campaign was generally satisfactory. An overall uranium recovery of 99.93 percent was achieved in the first extraction cycle, and a combined overall recovery of greater than 99.99 percent was achieved in the second and third extraction cycles. All product easily met required specifications for shipping. Only the presence of undesirable quantities of dibutyl phosphate (DBP) and some flooding in the first-cycle extraction column marred the overall performance.

2.1 First Extraction Cycle Performance

The feed rate to the extraction (IA) column was maintained at about three-quarters of the flowsheet value because of the dissolution problems previously discussed. The pulse frequency and pulse amplitude of the IA column were approximately 55 cycles per minute and one inch, respectively, for most of the run. Feed volume velocity through the eight-inch diameter column averaged $1.14 \text{ gal/ft}^2\text{-minute}$.

Uranium losses totaled approximately 450 grams in the first cycle processing of dissolver product and were evenly split between the first-cycle waste raffinate stream and the waste solutions transferred to the process equipment waste (PEW) system. In the waste raffinate, uranium losses averaged 5.6×10^{-4} grams per liter, far below the throw-away limit of 6×10^{-3} grams of uranium per liter. This low concentration of uranium in the waste raffinate is directly attributable to the absence of any severe extraction-column upsets during the processing period.

Uranium losses to the PEW system were caused by the formation of a uranium-DBP complex in the organic extractant. A small concentration of DBP, a degradation product of TBP, seriously affects the stripping efficiency of uranium from the organic solvent and as the DBP concentration rises, a significant amount of uranium can be lost. The uranium-DBP complex leaves the stripping column in the organic raffinate stream and because it is soluble in aqueous caustic solutions, the complex is washed from the stream by the carbonate solution in the second mixer-settler of the organic-stream cleanup system.

When such uranium losses were detected through periodic sampling of the ICR stream, the carbonate wash containing the uranium was diverted to the headend evaporator instead of the PEW system in an attempt to extract and recover the uranium. However, this only returned additional DBP back into the system where another uranium-DBP-complex cycle occurred. Attempts were made to minimize the losses by (1) decreasing the stripping column pulser frequency, (2) increasing the flow of the stripping stream to the IC column while keeping the flow of the organic stream constant, and (3) increasing the flow of the carbonate wash stream. All appeared to have a beneficial effect for short periods of time; however, the

problem reappeared. No satisfactory solution to the dilemma was found during the run. The problem of DBP formation is further discussed in Section 2.4.

2.2 Second and Third Extraction Cycle Performance

Excellent performance was obtained during operation of the second and third extraction cycles. The amount of uranium in the waste raffinate stream from the combined second- and third-cycle processing steps was exceptionally small, less than 0.01 percent of the input. Approximately two-thirds of this uranium was contained in the second-cycle raffinate which was recycled to the first cycle extraction system for neptunium recovery. Overall product quality from third-cycle extraction was good.

2.3 Product Quality and Decontamination

All of the final product easily met the required specifications. The average properties of product in each of four shipments are shown in Table IV. The first shipment contained seven bottles of product from this run, along with 31 bottles from previous processing runs. The three remaining shipments consisted of product recovered only from this run, and the results accurately reflect the product quality. Values listed represent an average of several bottles, since samples from each bottle were not individually analyzed. To insure that the samples adequately represented all of the bottled product, all bottles were sampled for specific gravity to insure that a homogeneous mixture of product was used to fill each group of ten bottles.

During one period of the run, ten bottles of product failed the plutonium-concentration specification and had to be recycled. Investigation of operational procedures indicated that ferrous sulfamate solution, used in the second extraction cycle to shift the valence of plutonium and thus make it inextractable, had not been freshly made up prior to use and had deteriorated, leading to the problem.

2.4 Solvent Degradation During Processing

Previous work^(9,10) 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

TABLE IV
A COMPARISON OF SPECIFICATIONS WITH PRODUCT FROM RUN NO. 25

					Product Specifications
Shipment Date	5/2/68	6/13/68	7/11/68	8/1/68	
Bottles Shipped	38	38	38	38	
Total Uranium, kg	180.6	213.5	214.2	213.0	≥ 0.7
Alpha Ratio* Range, 10^3	100	1-242	11-154	10-184	≥ 0.7
Product Bottle Radiation, mR/hr Gamma	10	3	6	25	-
Impurities, ppm on U_3O_8 Basis					Maximum
Aluminum	1528	411	461	466	6,000
Barium	20	10	10	10	-
Calcium	25	20	20	20	200
Chromium	11	10	10	10	200
Copper	10	4	2	2	200
Iron	150	10	5	10	1,000
Magnesium	5	1	1	1	200
Manganese	6	2	2	2	-
Sodium	99	86	87	94	200
Nickel	11	10	10	10	-
Sodium	17	10	10	14	250
Tin	15	15	15	15	-
Titanium	5	5	5	5	-
Vanadium	5	5	5	5	-

*Alpha ratio = $\frac{\text{alpha, (disintegrations/min) from total tranuranics}}{\text{alpha, (disintegrations/min) from plutonium}}$

undesirable because: (1) DBP forms a 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^(11,12) 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 inter-cycle evaporator, and thus could cause pipeline and equipment plugging downstream of the product evaporator. These problems occurred to some extent, during this run.

Samples of the organic raffinate stream, ICR, from the first-cycle stripping column during this run occasionally contained a high uranium and solids content. These solids were amorphous, as shown by X-ray diffraction, and usually contained over five percent zirconium and silicon plus up to five percent phosphate. Fission product ⁹⁵Zr was the primary gamma emitter present. A DBP concentration of up to 202 milligrams per liter was found in the four samples taken of the ICR stream, as shown in Table V. Previous studies⁽¹³⁾ indicate that a DBP concentration above 21 milligrams per liter is undesirable. The high concentration of DBP in the organic stream on this run is believed to be the main cause the uranium losses from the first-cycle extraction system, as discussed in Section 2.1.

TABLE V
CONCENTRATION OF DIBUTYL PHOSPHATE IN THE ORGANIC RAFFINATE STREAM

Sample No.	Run No. 25	Run No. 21	Run No. 20
1	76*	57*	13*
2	129	41	18
3	202	55	25
4	197	--	11

*Concentration of dibutyl phosphate, milligrams per liter.

Also shown in Table V are some DBP analyses of the ICR streams encountered during Runs 20 and 21. The DBP concentrations for the run were two to four times higher than those experienced on earlier runs. The presence of this additional DBP can be partially explained by the

fact that aqueous streams from the solvent cleanup system were recycled to the headend evaporator and then in turn to the extraction column. Also contributing to the DBP buildup was the degradation of the TBP (in the recycled wash stream) occurring in the headend evaporator. Degradation of TBP is known to be accelerated by both radiation and heat, particularly at the boiling temperature.

2.5 Waste Generation

The waste generation statistics for the run are shown in Table VI. The 7.7 gallons of first cycle waste generated per kg of aluminum dissolved was larger than the flowsheet rate of 6.5 gallons per kg of aluminum dissolved. The excess was due to: (1) an inability to concentrate feed in the evaporator for parts of the run, as discussed in Section 2.8, (2) the diversion of the organic solvent wash stream to the headend evaporator, (3) dilute feed from slow dissolution of some elements, and (4) extra solution resulting from attempts to flush the dissolver filters.

TABLE VI
WASTE GENERATION STATISTICS

	<u>First Cycle</u>	<u>Second and Third Cycles</u>
Uranium, processed, kg	676.8	676.4
Aluminum processed, kg	13,202	--
Total volume of waste stored, gal	102,206	2530
gal/kg U	151.6	3.7
gal/kg Al	7.7	--

Operation of the second- and third-cycle extraction systems was excellent, and the resulting waste generation rates were very low. About 2050 gallons of the second-cycle waste were diverted to storage vessels for further processing to recover neptunium; therefore, the actual volume of waste that was generated in the Hexone systems and immediately sent to tankage was less than 500 gallons.

2.6 Neptunium Recovery

Small quantities of neptunium are present in the waste raffinate from the second-cycle extraction system because neptunium is extracted along with uranium and plutonium in the first-cycle extraction system.

Addition of ferrous sulfamate to the feed stream of the second extraction cycle reduces the plutonium and neptunium to an inextractable valence state, and these materials then remain in the second-cycle raffinate. The neptunium is then recovered⁽¹⁴⁾ as a by-product during further processing through the first-cycle extraction system. For recovery, chromic acid is added to the second-cycle raffinate to oxidize the neptunium to the extractable + 6 valence state.

Neptunium from the second-cycle aqueous raffinate (IIAR) was again successfully recovered during this run. As on previous runs^(12,15,16), approximately 400 grams of neptunium were recovered and stored with neptunium recovered from previous processing runs. Operation of the first-cycle extraction system (a flowsheet for neptunium processing is shown on Figure 3) was trouble free, and neptunium losses during this part of the processing campaign were less than four grams. The recovered neptunium will remain in storage pending further purification before it is packaged for shipment.

2.7 Effect of Pre-Run Equipment Modifications

Modifications made to the extraction systems, as listed in the Appendix, significantly improved operation of the system. The first-cycle extraction feed system was modified to simplify feeding of solutions from both the zirconium and aluminum dissolvers to the columns. The new feed system makes it possible to bypass the headend evaporator when processing zirconium fuel dissolver product and thus prevents fluoride corrosion of the titanium tube bundle in the evaporator. This dual system proved useful when a feed control valve, FCV-3-G, to the evaporator, was involved in persistent plugging problems as explained in Section 2.8. The dual system allowed bypassing of the FCV-3-G valve without shutting down the entire system for repairs.

The mixer-settler previously used for scrubbing the product stream of the first-cycle stripping column were replaced by a pulse column which performed satisfactorily during the entire run. The replacement eliminated problems encountered on previous runs of emulsion solids formation and mechanical failures of the mixer-settler.

The feed system for the second-cycle extraction (Hexone) system which was modified to include a paddle wheel feed unit (Clarkson feeder)

[illegible]

(a) Estimated composition of concentrated IIR raffinate.

FIGURE 3

FLWSHEET FOR FIRST-CYCLE EXTRACTION OF Np-237 RICH ALUMINUM NITRATE SOLUTION

also performed satisfactorily.

2.8 Other 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 quality. Problems not discussed in previous sections of this report are discussed in the following paragraphs.

The dissolver lid seals rapidly deteriorated early in the run as the neoprene seals were attacked by the high-temperature nitric-acid fumes. This lid-seal deterioration allowed significant amounts of air to enter the dissolver off-gas stream which is processed through a Rare Gas Recovery Plant⁽⁵⁾. Excessive in-leakage is undesirable because of capacity limitations on the rare-gas recovery process. When the air-leakage rates through the seals became severe, milk-can type lids were fabricated and put into the fuel charging cave to seal the dissolvers. Although air leakage still occurred, it was within tolerable limits and vacuum control on the dissolvers was good.

Concentration of dissolver product in the headend evaporator was not possible for most of the run due to a restriction in, or malfunction of, a control valve, FCV-3-G. Flow through this valve dropped off soon after processing began, and it was necessary to bypass the evaporator and use the alternate control valve, FCV-1-G. Efforts to establish flow through the valve were unsuccessful until a uranium cleanout of the extraction system was made following the first period of operation. At that time, flow through the valve was re-established and maintained. The plugging problem recurred during subsequent neptunium recovery operations, but flow was established by flushing acid and water through the piping. Flushing continued until full flow rates were consistently obtained through the valve. The valve continued to operate satisfactorily when the second period of operation was started and cold feed was put through the columns. When dissolver product was again started through the system, however, the flow through FCV-3-G dropped to zero, where it remained for the balance of the run.

Some problems were experienced with feed control for the first-cycle extraction column. The problem involved maintaining a smooth level control

in a feed pot, and the following corrections were made during the run: (1) FCV-3-G feed valve control was sensed from the headend evaporator level rather than from the feed pot level, and (2) a control valve on the air lift supply from the evaporator to the first column feed pot was switched from automatic to manual control mode.

Other problems with the above feed rate control occurred with the venturi flowmeter. Accurate measurement of the liquid flow rate by the venturi meter is possible only when all air bubbles are cleared from the venturi water purge lines. Normally, the clearing of the air occurs very slowly during initial operation of the first-cycle extraction system. However, if the feed stops completely, even momentarily, the water purge lines again accumulate air bubbles, and the feed rate can then be measured only by feed tank depletion.

Some cyclic flooding of IA column in the first-cycle extraction system occurred early in the run. Although the effect on IA column operation was minor, the effect compounded as the "bumped" organic entered first the IB column and, a little later, the IC column. This occasional column flooding and resulting erratic column operation also caused solvent losses to the solvent collection tank. Flooding in the extraction column was relieved by reducing the pulse amplitude and by dissipating any emulsion causing the flooding by adding acid to the columns through the decontamination lines.

IV. RECOMMENDATIONS FOR FUTURE PROCESSING RUNS

Recommendations to improve the overall performance of the fuel reprocessing system follow:

1. Dissolver Lid Replacement

Polyvinyl chloride (PVC) seals should be used on the fuel dissolver lids in place of the neoprene seals. PVC seals are more resistant to nitric acid attack than neoprene seals and will withstand gamma radiation exposure on the order of 10^8 R. Additional dissolver lids and seals should be provided so that lid replacement can be made during the run as required.

2. Pulse Amplitude Measurements

The re-occurring experience of periodic flooding of the IA column in the first-cycle extraction system and its detrimental effect on the other columns down-stream again points to the desirability of having some measure of the pulse amplitude in each column. A capacitance system for measuring amplitude in the pulse leg has recently been successfully demonstrated and installation of such a system is being considered.

3. Headend Centrifuge

Problems with undissolved solids in the dissolver effluent were again experienced during this run. Due to past experience with silica solids formation⁽¹²⁾, a centrifuge is being installed to remove solids from the dissolver effluent. Installation and check-out will be completed prior to the next processing campaign.

4. Feed Control

Inadequate feed control for dissolver effluent to the first-cycle extraction system has continued to be an annoying problem. Many of these problems, ie, inoperative steam jets, or airlifts, plugged lines and flow control valves, and inaccurate flowmeter measurements, may be significantly reduced with use of the centrifuge. However, further investigation must be made of better methods of flow-rate measurements and perhaps a better method for feed metering. Since the paddle-wheel feeder in the second- and third-cycle extraction system proved so successful, it should be

investigated for possible use in the first-cycle extraction system.

5. Solvent Wash Mixer-Settlers

The raffinate from the first solvent-wash mixer-settler should be rerouted so that it will combine with the strip column product rather than be sent to the headend evaporator for boildown. In effect, this will prevent additional tributyl phosphate, which is slightly soluble in the mixer settler raffinate, from degrading during the high temperature boildown in the evaporator. By combining the mixer-settler raffinate with strip column product, the TBP can be removed in the wash column. The rerouting should reduce the uranium losses caused by the buildup of dibutyl phosphate (and, in turn, the uranium losses observed) in this past run.

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APPENDIX

PRE-RUN EQUIPMENT MODIFICATIONS AND TESTS

Prior to startup of Run No. 25, processing equipment and cells were decontaminated to permit modifications to improve overall process performance. Modifications were made on the fuel dissolver, the fuel charging cave, the first- and second-cycle extraction feed systems, the ID column, and the third-cycle columns and evaporator. This work is discussed in the following paragraphs.

1. Dissolver Modifications

1.1 Recirculation Leg

In order to improve fuel dissolution rates and/or reduce the usage rates of the mercury catalyst, a recirculation leg was installed on each of the G-cell dissolvers.

Each leg consisted of a 4-inch stainless steel pipe (Cb-stabilized, Type-310) with an end-to-end length of approximately 14-feet (Figure A-1). The upper end of the loop is attached to the dissolver a few inches above the lower dissolver steam jacket, while the lower end is attached about five inches above the fuel impact plate at the base of the dissolver.

1.2 Vessel Impact Plate

A new bottom section for each dissolver was also installed. In the original installation, two separate plates as shown in Figure A-1, were used to support the fuel elements in the dissolver. The perforations and area between the perforated plates proved to be a collection spot for highly radioactive solids and prevented satisfactory decontamination of the vessels. In the modification, the separate, perforated plates were removed and replaced with a single 2-1/2 inch thick impact plate (shown in Figure A-1) which also formed the bottom of the dissolver. This arrangement allows for better dissolution of fuel particulates collecting in the dissolver bottom and for physical removal of undissolved particulate during decontamination.

2. Dissolver Charging Cave Modifications

Modifications were made on the dissolver charging cave in order to (1) handle the larger ATR fuel elements in the future and (2) to decrease

Lower Portion of Dissolver Prior to Modifications

Lower Portion of Dissolver After Modifications

Figure A-1
Dissolver Modifications

the radiation fields emitted from the charging cave. ATR fuel elements are 50-1/2 inches in length and as such are 13 inches longer than fuel elements handled to date by the slug chute into the charging cave. A longer drop length between the cask and the cave was obtained by giving the slug chute a deeper and shorter radius curve. The modification was accomplished by (1) removing the existing stainless steel floor liner, (2) chipping out enough concrete to provide the necessary depth for the longer drop length, (3) reshaping the curvature of the slug-chute slide and (4) installing a new stainless steel floor liner in the charging cave.

Increased radiation shielding on the cave was required since previous operations showed that a moderate-to-intense radioactive beam emanated from certain parts of the cave under maximum fuel loading conditions. The increased shielding consisted of stainless steel liners spaced three inches away from the cave walls with the resulting void space filled with lead shot.

3. Extraction Feed System

Modifications were made to the extraction feed system as follows:

1. The original headend evaporator was removed from the system, and the original waste evaporator was modified for use as the headend evaporator. An evaporator in the Waste Calcining Facility used to concentrate waste prior to calcination eliminates a need for a waste evaporator in the extraction system.
2. Separate feed systems were installed to permit either bypassing or using the headend evaporator to concentrate dissolved product. Zirconium fuel dissolver product cannot be concentrated due to the fluoride corrosion that would occur in the titanium tube bundle of the evaporator. These modifications, depicted in Figure A-2, include a new feed control surge pot, a new feed control valve (FCV-1-G), and associated piping between the feed tank and the column feed air lift.
3. New piping was installed to route raffinate from the scrub column (IB) and wash solution (ISW) from the first stage mixer-settler to the new headend evaporator. This allows concentration of these streams, thus reducing the required waste storage space.
4. A single bypass around the column feed flowmeter and control valve was installed to reduce the number of valves in the system.

Figure A-2
First-Cycle Extraction System Feed Modification

4. ID Column Installation

A seven stage mixer-settler used during previous runs to wash TBP and DBP from the strip column product was replaced with a pulse column. The pulse column installation was made to eliminate problems of (1) solids formation in the product evaporator due to insufficient TBP removal, (2) emulsion problems which limited flow rates, and (3) frequent mechanical failures of the motors on each stage of the mixer-settler. Based on pilot plant work, the new 4-inch diameter column has a plate section 18 feet long containing 3/32-inch perforated plates on two-inch centers. Other modifications required for the installation included a new pulser, a new syphon break and control pot downstream of the new column, plus relocation of the airlift disengaging pot to provide for proper feed control.

5. Second-Cycle Extraction Feed System

The installation of a paddle wheel feeder (or Clarkson feeder) for the second-cycle extraction system was made to improve the controllability of the feed rate. The original feed pumps were designed to meter 190 liters per hour of a dilute uranium solution. The present second cycle extraction system is designed to handle a maximum of 16 liters per hour of a highly concentrated uranium solution. This is below the normal operating range of the pulse feed pumps and resulting operating problems prompted the feed-system modification depicted in Figure A-3.

The paddle wheel feeder consists of an accumulation tank, a paddle wheel driven by a variable speed D. C. motor, and a feed tray into which feed from the paddle wheel is dumped for feeding into the second-cycle extraction column. Feed metering is accomplished by varying the feed tray position to accept the desired portion of feed from the paddle wheel. The original remote head feed pumps are used to transfer feed from storage tanks to the Clarkson Feeder.

To prevent a potential criticality hazard, the accumulation tank is provided with a constant overflow to limit the volume (the operating volume is 5 liters) of feed in the tank. An additional high-overflow line limiting the volume in the accumulation tank to six liters, and a catch pan were installed. In the unlikely event of both overflow lines

Figure A-3
Second-Cycle Extraction Feed Modification

plugging, the feed would drain from the accumulation tank to the catch pan from which it would then drain to a critically safe cell sump. Level indicators and an audible high level alarm were installed to monitor the tank level. (The feed pumps to the accumulation tank would be manually shut off at the sound of the alarm.) To eliminate the possibility of splashing of feed from the tank and to provide an added measure of safety from a criticality standpoint, a boron stainless-steel splash plate was also installed. The accumulation tank was provided with a drain to the overflow line to empty the tank after the completion of a processing run. Decontamination sprays were provided for cleaning the feeder equipment, catch pan, and all associated piping.

The new feeder and associated piping, which were installed in an accessible area above the second-cycle extraction cell, are enclosed in a cubicle surrounded with six inches of lead shielding. However, the motor, the feed trough adjustment handle, and the accumulation-tank drain handle are installed outside the cubicle for maintenance and operational purposes.

6. Third-Cycle Extraction Capacity

The original capacity of the fuel processing facilities at ICPP was limited by the capacity of the third-cycle extraction column, stripping column, and product evaporator. To increase plant capacity, a modification of the Q Cell equipment was desirable. Hence, the two-inch diameter sections of the extraction and stripping columns were replaced with five-inch diameter sections to match the five-inch diameter heads at the top and bottom of each column. The five-tube heat exchange bundle in the product evaporator also was replaced with a 14-tube heat exchange bundle. These modifications made the third-cycle extraction system identical to the second-cycle extraction system, and increased the overall capacity of the hexone system by 60 percent.