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MASTER

**FIRST ZIRCONIUM ALLOYED FUEL REPROCESSING CAMPAIGN
USING SOLUBLE NUCLEAR POISON**

G. F. Offutt and B. R. Wheeler

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The zirconium fuel processing campaign described in this report was accomplished during the period when Mr. A. L. Ayers was ICPP Operations Superintendent and Mr. J. W. Garner was Supervisor of the Process Engineering Section. Much of the credit for the successful completion of the processing campaign belong to these individuals who have since transferred to other parts of the Company.

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A B S T R A C T

Uranium was recovered at ICPP from high-enriched zirconium alloyed fuels during FY 1965-1966 using a soluble neutron poison to guarantee nuclear safety. The use of boric acid in the hydrofluoric acid dissolver made it possible to charge up to 17 kg of U-235 to a large semi-continuously operated dissolver and to achieve net processing rates up to ten times the maximum rate otherwise possible in this dissolver. Uranium recovery through the final extraction cycle averaged 99.5 percent, and product decontamination was excellent. Neptunium present in the zirconium fuels was separated and stored for future processing during the campaign instead of being discarded to the waste tank farm with second cycle raffinates as done previously.

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I. SUMMARY

High-enriched zirconium-uranium alloy fuels were processed at the Idaho Chemical Processing Plant (ICPP) in the first reprocessing campaign in the United States in which a soluble neutron poison (boron) was used for primary nuclear safety control. The processing campaign began in January 1965 and was completed, after several interruptions, in February 1966. Zirconium alloyed fuels similar to those from the Shippingport Pressurized Water Reactor were the principal fuels processed in the campaign. The overall average processing rate for the run was 535 kg of zirconium per day for the dissolution and first extraction cycle, although rates exceeding 800 kg per day were achieved for a portion of the run. A 99.50-percent uranium recovery was achieved in the first extraction cycle and a 99.96-percent recovery was achieved in the combined second, third, and fourth extraction cycles. Overall decontamination of the uranium product was excellent; decontamination factors for gross gamma and gross beta exceeded 10^6 and 10^8 , respectively.

The processing rates for this run were up to ten times as great as the average rates obtained during previous zirconium fuel processing campaigns. The increase was made possible by use of a soluble neutron poison to counter the nuclearly unsafe geometry of the dissolver and by certain pre-run equipment modifications to permit semicontinuous operation. The equipment additions and modifications included a new fuel basket for the existing batch dissolver, a new rubber-lined dissolvent makeup and feed tank for hydrofluoric acid solutions, and certain

pipng changes to permit use of an existing high-capacity first-cycle solvent extraction system. The average dissolution rate during the run was lower than expected, and the zirconium concentration in the dissolver product averaged 0.9M instead of a desired 1.0M. The more concentrated solution was desired to minimize the volume of waste solution from the process. Concentration by evaporation was not possible due to stability and corrosion considerations. Proposed modifications will allow dissolver operation at higher liquid levels and higher temperatures. This should increase the dissolution rate and permit higher zirconium concentrations to be attained in the next processing campaign.

About one kilogram of Np-237 was separated and held for future recovery during this campaign. This was done by extracting neptunium along with uranium in the first solvent extraction cycle, partitioning it from uranium in the second extraction cycle, and then re-extracting it from the second cycle raffinate. The partially pure neptunium solution is temporarily stored in tanks at ICPP; eventually it will be further purified in ion exchange equipment.

Some corrosion problems were encountered in the dissolution and first extraction cycle equipment early in the run. Equipment failures included an electromagnetic flowmeter with vitreous enamel lining, a titanium tube bundle on the feed evaporator and a Carpenter-20 (Cb) stainless steel steam jet. Corrosion to the Types 304L and 347 stainless steel, of which most of the post-dissolver equipment is made, was negligible. Corrosion of the Monel-400 dissolver was about 7.5 mils per month; 150 mils of corrosion allowance remain which should be adequate for several more processing campaigns.

II. INTRODUCTION

The zirconium fuel processing campaign completed at ICPP during FY 1966 proved the practicality of using a high-capacity aqueous process for zirconium alloyed fuels. During the campaign, up to 800 kg of zirconium per day (equivalent to 8-10 kg of uranium per day as PWR seed fuel elements) were dissolved and processed through the first extraction cycle which is approximately ten times the rate achieved in the original batch process. This increased capability for zirconium-uranium alloyed fuels was accomplished by modifying the original ICPP hydrofluoric acid process⁽¹⁾ after a detailed study indicated that development programs at other AEC sites were not sufficiently advanced to allow design of a production-scale plant based on other processing techniques. To hold the cost to a minimum and make maximum use of existing equipment, a semi-continuous dissolution process was developed. The changes in equipment are described in Appendix A, the original batch process is described in Appendix B, and a description of the alternate methods considered for expanding the zirconium fuel processing capacity at ICPP are summarized in Appendix C.

The new high-capacity process was made possible by employing a soluble neutron poison for primary criticality control in an otherwise non-geometrically safe dissolver. This approach was the first such use of a soluble poison in the United States. The nuclear safety aspects of the process were thoroughly investigated in advance and have been reported in detail elsewhere⁽²⁾. Briefly, extensive neutron calculations were performed to indicate the safety of the poisoned dissolver together with certain administrative controls under all possible normal and abnormal operating conditions. Calculations showed that a metal-volume fraction of 0.6 was the most reactive condition for PWR fuel during processing. For this condition, together with the most severe abnormal operating condition conceivable, a natural-boron concentration of 3.8 g/l was calculated to give a k_{eff} under 0.95; under normal operating conditions, the maximum k_{eff} was always less than 0.8.

Figure 1
SCHEMATIC DIAGRAM OF ZIRCONIUM-PROCESS DISSOLVER

For processing, zirconium fuel elements were charged, batchwise, to the modified dissolver, shown in Figure 1, while it was full of water to cushion the force of falling elements. The charging water contained a minimum of 5.0 g/l of natural boron as a nuclear poison. An average of about 600 kg of zirconium was charged per batch as indicated on the flow-sheet in Figure 2; the fuel charge was held in a controlled position by a 12-3/4-inch diameter slotted basket inside the 42-inch diameter dissolver. After fuel charging was complete, the cushioning solution was jetted to a storage vessel, and flow of dissolvent (6.6 - 7.3M HF) containing at least 3.8 g/l boron added as boric acid) was started to the dissolver^(a). The dissolvent then was fed continuously to the dissolver

(a) The boron content of the dissolvent was continuously monitored by a neutron attenuation instrument to guarantee the presence of the neutron poison in the dissolver. This instrument consisted of a neutron source and two neutron detectors, all enclosed in Monel sleeves, suspended in the acid feed tank. The instrument controlled a solenoid valve in the acid feed line to the dissolver and would not permit acid flow unless the boron concentration was higher than the minimum desired concentration of 3.8 g/l.

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	CHARGE WATER	DISSOLVER PRODUCT	COMPLEXING SOLUTION	COMPLEXED DISSOLVER PRODUCT	IBR	IAF	IAx	IAr	IAP	IBS	IBP	ICx	ICR	ICP	IDx	IDR	IDP	FIRST CYCLE PRODUCT
Flow, l/batch		7115	1400	7310(e)	3700	11600(e)														
Flow, l/hr		532		532(d)		600(f)	60	660	415	660	415	60	415	200	415	200	10	200	2.7	
Zr, M				0.9c		0.57		0.52		0.52										
F, M		6.60		6.42		4.05		3.68		3.68										
Al, M					1.96	0.62	0.75	0.63		0.63		0.75								
H, M (a)		6.60		2.80	1.41	2.23	0.55	2.07		2.02	0.08		0.001	0.005		0.007		0.007	0.4	
NO ₃ , M					7.29	2.31	2.80	2.35		2.29	0.09	2.25	0.01	0.005		0.02		0.02	2.1	
Sn, g/l				1.27		0.80		0.73		0.73										
Cr, g/l					2.50	0.80		0.73		0.73										
E, g/l		4.1	5.0	4.1		2.6		2.4		2.4										
U, g/l (no burnup)				1.4		0.89	0.20	0.83		4 x 10 ⁻⁵	1.32		1.29		1 x 10 ⁻⁴	2.67		2.67	200	
Sp gr at 25°C		1.05		1.18		1.20	1.15	1.20	0.78	1.20	0.79	1.14	0.79	1.00	0.79	1.00	0.76	1.00	1.29	
I, kg/batch (no B.U.)	10.3(e)																			
Zr, kg/batch	600																			
Sn, kg/batch	9.3																			
TEP, %																				
Diluent								5 Amco		5 Amco		5 Amco		5 Amco		5 Amco				

(a) Neglecting any contribution from H₃BO₃.

(b) Based on PWR Core 1, Seed 1 with no burnup.

(c) Includes 195 liters of charge water heel.

(d) Actual flowrate after dissolver fills.

(e) Includes 590 liters of jet dilution. The process is continuous from this point forward.

(f) Average rate for a 24 hour period. Dissolution time per cycle is 13.4 hours. It is assumed that downtime between dissolution cycles is 5.9 hours.

Figure 2

FLWSHEET FOR ZIRCONIUM FUEL DISSOLUTION AND FIRST EXTRACTION CYCLE USING FIVE PERCENT TBP AS SOLVENT

for about 12 hours while the dissolver temperature was controlled at approximately 65°C by adjustment of the flow of the coolant through the dissolver jacket and control of the dissolvent flowrate.

Dissolver product overflowed continuously from the dissolver and was transferred by a nitrogen gas lift to a feed adjustment tank for continuous complexing with aluminum nitrate solution. Complexing established proper conditions for low corrosion, long stability, and good uranium extraction. Complexed dissolver product overflowed continuously from the feed adjustment vessel to tanks in the first-cycle-extraction system. The first extraction cycle used 5- or 10-percent tributyl phosphate (TBP) in Amsco as a solvent. To assure solution stability, the feed and waste streams in the first extraction cycle were never heated or evaporated.

Two flowsheets employing 5- and 10-percent TBP in Amsco as a solvent were used during the run. However, a 5-percent TBP flowsheet, as shown in Figure 2, was used for about 80 percent of the processing campaign. The other flowsheet used during the run is discussed in Appendix D. Use of a 5-percent TBP, rather than a 10-percent TBP, flowsheet theoretically results in about 15 percent more waste. However, in order to achieve the theoretical benefits of the 10-percent TBP flowsheet discussed in Appendix D, it is necessary to generate a more concentrated dissolver product than was practical on this run with irradiated fuel. The low concentration is believed to have been caused from a lower dissolution rate for irradiated fuel in the plant dissolver than was achieved with unirradiated fuel in development studies⁽³⁾.

The second and third solvent extraction cycles used for the zirconium fuel campaign were identical to those routinely used for other fuels at ICPP. A fourth cycle was employed during the run only to establish the net effect on decontamination factors, not because it was required to meet product specifications. Flowsheets for the second and third extraction cycles are shown on Figure 3; the fourth extraction cycle is not shown, but it is identical to the third extraction cycle.

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, thus minimizing manpower requirements. With segmented operation, only the dissolution and first-cycle-extraction facilities were operated while all other facilities were in standby; first cycle product was placed in inter-cycle storage. Later, the second, third, and fourth cycle facilities were operated and the final product was packaged while the dissolution and first cycle facilities were in standby.

III. DISCUSSION OF RUN

1. Fuel Information

1.1 Fuel Description

Several types of fuel were processed during the run. The fuels processed during the run are typified by the fuel subassemblies from the Pressurized Water Reactor, PWR, Core 1 (Shippingport); a typical description of a subassembly from this core is shown in Table I.

Table I

DESCRIPTION OF A TYPICAL PWR SUBASSEMBLY AS PROCESSED

Length, in.	72
Cross Section, in.	2.5 x 2.5
Zircaloy-2, kg	36
Tin, kg	0.56
Uranium (before burnup), kg	0.62
Enrichment (before burnup), percent	93
Average burnup, percent	45
Burnup range, percent	36-50

1.2 Fuel Charging

The fuel charging operation required 7-8 hours per dissolution cycle because several casks of fuel had to be moved from the fuel storage basin (about 1/3 mile away) to the processing plant to fill the dissolver. Prior to fuel charging, about 1400 liters of borated water were transferred from a charge water tank into the dissolver to cushion the fall of fuel elements. Enough fuel elements were then dropped into the dissolver--about 600 to 800 kg of zirconium--to completely fill the

Figure 4
ZIRCONIUM FUEL DISSOLVER

charging chute (shown on Figure 4) after which all but 200 liters of the charge water were jetted back to the storage tank for use on the next charging cycle; the remaining 200 liters of charge water were transferred to the complexing tank and thence to the extraction system to recover any uranium in the water picked up in the dissolver. By employing this procedure, which required charge water makeup, the equilibrium concentration of uranium in the charge water was maintained during the campaign at about 0.3 g/l.

2. Dissolution

After the charge water was jetted from the dissolver, dissolvent, containing about 6.6 to 7.3M HF and 4 g/l boron, was continuously introduced to the dissolver at a rate of about 530 liters per hour. The acid-zircaloy reaction was often spontaneous but sometimes it was necessary to heat the dissolver contents to initiate the reaction. During operation, the temperature of the dissolver contents was controlled at 65°C by the HF addition rate, and by use of a closed loop employing borated cooling water circulating between the cooling jacket on the dissolver and a heat exchanger.

Acid flow to the dissolver was controlled to yield a dissolver product solution having a desired zirconium concentration which was monitored by the specific gravity of the solution. The relationship between specific gravity and dissolver solution composition for this process is given by the following empirical equation:

$$\text{Sp gr @ } 25^{\circ}\text{C} = 0.9971 + 0.149 \text{ Zr} + 0.31 \text{ U} + 0.17 \text{ Sn} + 0.0362 \text{ B} \quad (1)$$

(concentrations are in gram-moles per liter)

Equation 1 is based on laboratory and plant data and is accurate within two percent for the dissolver product solutions generated in this process. The temperature effect on specific gravity of the dissolver product solution is shown on Figure 5.

Under normal operating conditions, dissolution was rapid and the average specific gravity and zirconium concentration of the dissolver product were 1.16 and 0.93M, respectively. Near the end of each dissolution cycle, or when the fuel bridged in the charging chute, the rate of dissolution decreased--as evidenced by the lower specific gravity of the dissolver solution and a decrease in the hydrogen concentration in the off-gas--which made it necessary to reduce the acid

Figure 5

/TEMPERATURE EFFECT ON DENSITY OF ZIRCONIUM FUEL DISSOLVER PRODUCT

input rate from normal flowsheet conditions in order to maintain the desired zirconium concentration in solution. Each dissolution cycle was terminated when hydrogen evolution ceased and dissolvent consumption indicated the dissolution of a batch of fuel was essentially complete. The contents of the dissolver were then cooled to about 35°C and jetted to the complexing tank.

During dissolution, dissolver product continuously flowed from the dissolver through one of two overflow loops shown on Figure 4. These two loops, installed at different elevations (for reasons discussed in Appendix E), permitted some flexibility in controlling the average solution residence time in the dissolver. The average holdup in the dissolver was 700 liters when operating with the low loop and 1150 liters with the upper loop. Dissolver product overflow from either of the loops was continuously transferred by a nitrogen lift to the complexing vessel. Nitrogen (rather than air) was always used to sparge the dissolver and to motivate the gas lift because hydrogen, formed from the zirconium-HF reaction, could form an explosive mixture and because air will cause excessive corrosion of Monel in HF solutions.

2.1 Dissolver Production Rate and Product Composition

The average zirconium concentration in the dissolver product for the campaign was 0.9M--somewhat lower than the desired concentration of 1.0M; this was due in part to the high burnup of the fuel processed. Burnup appeared to have a significant effect on the average dissolution rate of the PWR fuel as shown by the comparisons on Figures 6 and 7. Figure 6 shows a log-log correlation of dissolver production rates (per unit volume of dissolver basket) as a function of reagent flowrate (per unit volume of dissolver) for (a) unirradiated fuel dissolved in the laboratory⁽³⁾, (b) unirradiated fuel dissolved in the plant, and (c) highly burned up PWR-type fuel dissolved in the plant. The effect of burnup is more obvious when the pertinent portion of the correlation is plotted on a linear scale as shown in Figure 7. The volume used for the plant dissolver for the correlation was that portion of the fuel basket containing liquid. For simplicity, the reagent flowrate used in the correlation is moles of "free" fluoride (F-4B) which assumes that each mole of boron entering the dissolver complexes four moles of

Figure 6

A LOG-LOG COMPARISON OF IRRADIATED FUEL DISSOLUTION RATES
WITH UNIRRADIATED FUEL DISSOLUTION RATES

Figure 7

A LINEAR COMPARISON OF IRRADIATED FUEL DISSOLUTION RATES
WITH UNIRRADIATED FUEL DISSOLUTION RATES

fluorine as HBF_4 making this fluorine essentially unavailable for dissolving zirconium.

The fluoride and boron concentrations in the dissolver product solution averaged 6.6M and 4 g/l , respectively. The uranium and tin concentrations in the solution averaged about 1.3 g/l .

For much of the run it is believed uranium may have been leaving the dissolver as finely divided solids of uranium tetrafluoride which rapidly dissolved upon reaching the complexer tank later in the process. Figure 8 shows solubility data obtained in the laboratory⁽³⁾ for solutions containing various concentrations of uranium, zirconium, and fluoride. In brief, the laboratory results show that the solubility of uranium tetrafluoride increases with either decreasing fluoride-to-zirconium mole ratios or with increasing fluoride concentrations. As shown on Figure 8, the solubility for UF_4 under plant operating conditions^(a) was expected to be significantly lower than the average concentration-- 1.3 g/l --in the solution leaving the dissolver. No uranium-containing solids were ever found in any of the plant samples of complexed dissolver product taken during the run.

2.2 Effect of Nitric Acid

At the start of the campaign, 0.03M nitric acid was included in the dissolvent to dissolve tin in the fuel elements that amounted to about 1.5 percent of the total fuel weight. However, about midway through the run, the nitric acid was omitted from the dissolvent because of indications of excessive corrosion on a Monel cooling coil in the dissolvent makeup tank and on the Monel dissolver. Omission of the nitric acid did result in the formation of black solids (identified as a tin compound) in the dissolver, and some carryover of the solids in recycled charge water was observed. However, these solids caused no operating problems because they were dissolved later in the process--in the complexing tank.

(a) Plant-data relationships were based on true fluoride in solution (F-4B) for this correlation.

Figure 8
URANIUM TETRAFLUORIDE SOLUBILITY IN THE
ZIRCONIUM-FUEL DISSOLVER PRODUCT

2.3 Effect of Increasing HF Concentration

Also, about midway through the run, the concentration of HF in the dissolvent was increased from 6.6M to 7.1M in an attempt to increase the dissolution rate and the zirconium concentration of the dissolver product. This resulted in a concentration increase of about 0.05M zirconium in the dissolver product with no apparent adverse effects.

2.4 Material Balance

2.41 Boron: A boron material balance was made around the dissolver early in the campaign to determine whether any of the neutron poison was precipitating in the dissolver. Over 94 percent of the measured boron input was accounted for in the complexed dissolver product. This indicated that the boron was remaining in the aqueous solution during dissolution to effectively guarantee nuclear safety in the dissolver.

2.42 Uranium: A continuous uranium material balance was made around the dissolver to insure that the specified mass limit on U-235 was not exceeded. The limit of uranium charged to the dissolver per batch was set at 17 kg while the uranium heel was limited to 50 kg. These limits were established after extensive criticality calculations⁽²⁾ were made assuming that various quantities of $UF_4 \cdot 3/4H_2O$ plated out on the dissolver walls. The calculations showed that the dissolver with a plate-out containing 50 kg of uranium and 22 kg of uranium as PWR fuel in the basket would have a k_{eff} of 0.91. The uranium charge to the dissolver was based, conservatively, on before burnup figures, and the heel plot was based on the after burnup figures. Figure 9 shows a typical heel plot for PWR fuel. The practical heel size was limited to about 30 kg of uranium because of the lag time between charging one batch of fuel and receiving analytical results from the previous dissolution cycle.

The slow buildup rate of the uranium heel proved that even though most of the uranium left the dissolver as a uranium fluoride slurry very little adhered to the walls of the dissolver.

Figure 9
TOTAL URANIUM HEEL PLOT FOR THE DISSOLVER (PWR FUEL)

2.43 Acid: An acid balance was made around the dissolver to determine the quantity of acid actually used in the dissolution process. The results indicated that 3.92 moles of HF were consumed per mole of zirconium dissolved.

2.5 Special Dissolutions

2.51 EBR-I Fuel Co-Dissolution: To save processing time and minimize waste volume, an attempt was made to co-dissolve EBR-I, Core 3 fuel with some of the zirconium fuel. The EBR-I fuel was about 98-percent uranium and 2-percent zirconium, while the PWR-type zirconium fuel being processed was about 97 percent zirconium, 1.5 percent uranium, and 1.5 percent tin. After charging two kilograms of the EBR fuel to each of eight successive fuel batches, the material balance indicated an excessive heel buildup. It was impossible to determine whether fuel was dissolving inadequately, or whether the fuel was dissolving and the uranium precipitating as UF_4 . Consequently, co-dissolution of the EBR-I fuel was terminated, and it was thereafter dissolved in a separate five-inch diameter dissolver. However, the dissolver products from the two fuels were blended for co-extraction in the first-cycle extraction system and this mode of processing had almost the same advantage as the co-dissolution scheme.

For the separate dissolution of the EBR fuel, a $6M\ HNO_3$ - $0.75M\ HF$ dissolvent was used as briefly described in the following procedure:

- (1) For each batch, eight fuel pins containing about 2.1 kg of uranium were charged to a small stainless steel dissolver.
- (2) About 12.8 liters of dissolvent ($6M\ HNO_3$ - $0.75M\ HF$) were then added. The minimum amount of dissolvent was established such that the F/Zr mole ratio exceeded 3.1 to prevent any epsilon phase formation, with its resulting explosion hazard⁽⁴⁾.
- (3) During a 5-6 hour dissolution, the dissolver was controlled at a temperature less than $50^\circ C$ and sparged with nitrogen to minimize corrosion of the Carpenter-20(Cb) type stainless steel dissolver vessel.
- (4) After each batch dissolution, the dissolver contents were diluted, sampled for uranium, and transferred to the complexing tank to be mixed with zirconium-fuel dissolver product.

With this procedure, the EBR fuel was processed without added processing time--saving several days that would have been required had it been totally processed separately from other fuel. The desired minimization of waste was achieved, and the dissolution rate of EBR fuel was adequate. About 53 kg of fully enriched uranium were recovered from the EBR-I Core 3 fuel in this manner.

2.52 Dissolution of SNAPTRAN 2/10A-3 Core: Fuel debris from the SNAPTRAN 2/10A-3 test also was dissolved⁽⁵⁾ during the zirconium fuel campaign in a dissolver temporarily installed in the Hot Pilot Plant. The SNAPTRAN fuel, 10 percent uranium and 90 percent zirconium hydride, was dissolved in 5M HF. Because of uranium solubility considerations, additional zirconium metal was dissolved along with the fuel so that the weight of uranium in the dissolver at all times was less than 2.2 percent of the total weight of zirconium metal being dissolved. Despite the addition of the extra zirconium metal, considerable amounts of uranium-containing precipitates (predominantly $UF_4 \cdot 3/4 H_2O$) were formed. The precipitation of $UF_4 \cdot 3/4 H_2O$ is believed to have been caused by a high operating temperature (about 90°C) and localized uranium concentrations in the dissolver exceeding the 2.2-percent value. The precipitates adhered to the interior surfaces of the vessel during the HF dissolution but were subsequently removed with heel-out dissolutions using 0.1M chromic acid at room temperature.

About 42 kilograms of total metal containing 3.9 kg of uranium from the SNAPTRAN debris were dissolved in five batches in this manner. Three heel cleanout dissolutions were required. The dissolver solution, after adequate adjustment, was combined with solution being generated in the plant dissolver and then processed through the plant solvent extraction system.

2.53 Heel-Out Dissolutions: Special heel-out dissolutions were made to clean out the dissolver when the unaccountable uranium (heel) approached specified nuclear safeguard limits. Also, heel-outs were made at the end of the campaign and at other times to satisfy special uranium accountability requirements. The usual procedure for a dissolver heel-out was: (1) to dissolve all the metal possible batch-wise with the standard HF dissolvent, (2) to rinse the dissolver with

water, and then (3) to introduce 0.1M chromic acid solution into the dissolver to dissolve any UF_4 plated out on the vessel walls. The dissolver was always rinsed before and after any chromic acid dissolutions because mixtures of HF and chromic acid are excessively corrosive to Monel, the construction material of the dissolver. The reaction⁽⁶⁾ of uranium tetrafluoride with chromic acid is:

The chromic acid dissolution was repeated batchwise until the uranium removal from the dissolver became negligible. Table II shows the amount of uranium and zirconium dissolved in a typical fuel heel-out.

Table II

<u>TYPICAL HEEL-OUT DISSOLUTION INFORMATION</u>					
<u>Heel-Out Solution</u>			<u>Final Concentration of Complexed Heel-Out Solution</u>		
<u>Batch</u>	<u>Dissolvent</u>	<u>Volume, l</u>	<u>U, g/l</u>	<u>Zr, M</u>	<u>U, g/batch</u>
1	6.9M HF	1681	0.41	0.15	689
2	0.1M CrO_3	2085	0.34	----	709
3	0.1M CrO_3	1094	0.04	0.006	44
4	0.1M CrO_3	2020	0.04	--	81

2.6 Dissolution Problems

2.61 Pressurization of the Dissolver: During the shakedown portion of the campaign, when unirradiated scrap fuel was dissolved (as discussed in Appendix E), the dissolver pressurized each time the dissolution reaction became vigorous. Various tests performed in the plant led to the conclusion that the off-gas condenser was plugging with foam.

Thereupon, one of the two overflow loops on the dissolver, which maintain the liquid level in the vessel, was lowered to provide more room for the foam to break (see Figure 4). This modification was very successful and eliminated pressurization problems for the remainder of the run.

2.62 Fuel Bridging: Fuel bridging in the dissolver charging chute was a serious problem during the campaign and contributed significantly to a low fuel processing rate. A fuel bridge occurred when fuel lodged in the top of the dissolver basket and would not fall into the dissolvent. This occurrence, of course, caused the dissolution to stop after all of the fuel in the lower portion of the vessel was dissolved, even though considerable fuel was hung up in the charging chute.

Fuel bridges became more frequent as the run progressed. This situation partially resulted because shorter elements, which are more likely to bridge, were processed primarily during the latter part of the run. Also, the dissolver charging chute walls became rougher as the run progressed, thereby making it easier for an element to lodge. Many fuel bridges broke without any operational action being taken. In these cases only a temporary slowing of the dissolution occurred. Sometimes raising the liquid level in the dissolver would break a bridge, because it had occurred low in the basket. However, the liquid level could not be raised higher than the off-gas outlet (see Figure 4) because the dissolver would pressurize. Therefore, when a severe bridge occurred, it was necessary to stop the dissolvent flow, empty the dissolver, and try to break the bridge mechanically by prying some of the elements. This method was hazardous because of radiation and the possibility of a hydrogen explosion.

Toward the end of the run, a fuel bridge occurred that could not be broken by mechanical means and processing of fuel was delayed for about two days. A temporary method of introducing dissolvent into the top of the dissolver was devised using tygon tubing and a spray nozzle. This proved quite effective and broke the bridge within 45 minutes after the dissolvent flow was started. Thereafter, this dissolvent-addition method was routinely used for breaking fuel bridges. Modifications which will provide a more convenient way to add dissolvent to the top of the dissolver will be made before the next campaign.

2.63: Hydrogen Explosion: A minor explosion occurred in the dissolver while fuel was being charged toward the end of the campaign. No equipment damage occurred and no personnel were injured, but dissolver operation after the incident was terminated while an investigation was made. About 16 hours after the incident, a gas sample taken from the top of the dissolver was found to contain 11.4 percent hydrogen. Tests showed that residual HF in the charge water was reacting with zirconium metal and releasing hydrogen. The original charging procedure employed a sufficiently large volume of charge water in the dissolver that it covered the bottom off-gas line preventing hydrogen release from the dissolver except through an upper off-gas line. Gas generated in the dissolver was then forced to go through a small one-inch line near the top of the dissolver and with this condition, a high concentration of hydrogen existed in the charging chute. A spark caused from fuel striking the charging chute walls during the charging operation apparently ignited the explosive mixture of hydrogen and air.

Processing was continued by slightly changing the charging procedure. A smaller volume of charge water was used so that the bottom off-gas line (a four-inch line) remained open during charging, thereby allowing hydrogen to be swept out of the dissolver at all times.

3. Complexing the Dissolver Product

The dissolver product solution resulting from the dissolution of zirconium fuel elements in a hydrofluoric acid dissolvent cannot be extracted directly without the addition of an aluminum nitrate complexing solution. Aluminum nitrate is required: (a) to complex the excess fluoride ions and thereby make it possible to process the solution in stainless steel equipment without corrosion, and (b) to provide nitrate ions for the subsequent TBP extraction for salting the uranium into the organic phase. The aluminum nitrate complexing solution must also contain a small amount of chromic acid, about 0.05M, to dissolve UF_4 , oxidize the uranium to an extractable plus-six valence state, and dissolve tin compounds.

The composition of the uranium-bearing aqueous stream after complexing is highly important and must be held within narrow concentration limits because of the limited solubility of zirconium and aluminum fluoride as shown by the relationships⁽⁷⁾ on Figure 10. It was highly desirable to minimize the total amount of aluminum nitrate used for complexing purposes in order to minimize the final volume of waste solution generated in the process. Consequently, every effort was made to minimize the amount of aluminum used for complexing.

The flowsheets used during the plant processing campaign were partially based on the information in Figure 10 as well as on considerable other data⁽⁸⁻¹³⁾ that have been published over the years relative to the precipitation of the hydrolysis products of zirconium and aluminum fluorides. One rule-of-thumb relationship⁽⁶⁾ to determine whether or not a solution is stable suggests that the mole ratio $(F-4Zr)/Al$ be in the range 0.5 to 1.6 and the acid concentration above about 0.8M. Ratios below 0.5 result in zirconium precipitation while ratios above 1.6 result in aluminum precipitation. For the existing process this relationship is an over-simplification; high acid concentrations and boron concentrations must also be taken into account, for these also play a role in solution stability.

A modification of the simplified relationship (to take into consideration both the high acid concentration and boron concentrations) was useful to predict the short term stability of plant solutions. An appropriate relationship for doing this is shown on Figure 11. Short-term stability was deemed especially important to avoid the formation of gross quantities of solids before the uranium was extracted from the aqueous solution. Long-term stability was desired but was not as critical as short-term stability. Instability of raffinate solutions leaving the plant results in sludge formation in the interim waste storage tanks, whereas the short-term instability could cause equipment plugging and column upsets.

Figure 10

EFFECT OF ZIRCONIUM CONCENTRATION ON THE STABILITY OF
ZIRCONIUM-ALUMINIUM-TiN-FLUORIDE SOLUTIONS

Figure 11

STABILITY RELATIONSHIP FOR COMPLEXED SOLUTIONS FROM THE ZIRCONIUM ALLOYED FUEL PROCESS

In general the composition of the complexed dissolver product was adjusted such that a stability ratio $[F-4 (Zr + B)]/Al$ was about 1.6 where F, Zr, B, and Al refer to the molar concentrations of fluoride, zirconium, boron and aluminum, respectively. This type of solution, after being combined with an aluminum nitrate recycle stream from the scrub column prior to extraction, was well within the long-term stability region.

3.1 Complexing Operations

For the most part, complexing operations were trouble-free during the run. A complexing stream containing aluminum nitrate and chromic acid was combined with the dissolver product in the complexing tank. A continuous flow of aluminum nitrate into the tank was proportioned according to the input flow of dissolver product solution.

Control of the complexer-to-dissolvent flow was excellent; however, about ten percent of the complexed dissolver product was insufficiently complexed because the zirconium concentration in the dissolver product was too low--which in turn caused a high fluoride content. When this happened it was necessary to adjust the solution by adding more aluminum nitrate in other batch tanks before processing it through the extraction system.

On one occasion too much aluminum nitrate was added to a batch of solution yielding a final concentration of 1.13M Al with unknown concentrations of Zr and F. A precipitate of $\text{ZrOHF}_3 \cdot \text{H}_2\text{O}$ formed which could not be redissolved by HNO_3 or water. The precipitate caused the venturi flowmeter on the feed line to the extraction column to plug and resulted in some relatively high uranium losses for a short time.

Many samples of complexed dissolver product during the run contained white solids which were an amorphous species of material containing zirconium and aluminum. These solids appeared to dissolve in water forming a gelatinous solution when observed under the microscope. In the laboratory similar solutions were prepared and similar precipitates identified as $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$ were formed. Nearly all of the dissolver product solutions from the plant contained black flakes of material which were identified as ZrO_2 and which originated as a scale film that forms on the surface of the fuel elements during irradiation. This ZrO_2 scale would not dissolve in the dissolvent used during the campaign. It is believed the ZrO_2 flakes did not affect uranium losses in the extraction process; however, they did plug probes, valves, and flowmeters on several occasions.

3.2 Complexing Relationships

To minimize the number of analyses required on each batch of solution before extraction to insure that the dissolver product was properly complexed, a relationship was developed between zirconium concentration in the complexed dissolver product, HF concentration in the dissolvent, and complexer-to-dissolvent volume ratio. This relationship is shown on Figure 12. The basis for this relationship was that the complexer-to-dissolvent volume ratio was a known value and the dissolvent

Figure 12

COMPLEXING RELATIONSHIPS FOR FIVE PERCENT TBP ZIRCONIUM FUEL FLOWSHEET

and complexing solutions had exact compositions corresponding to specifications. The aluminum, fluoride, and boron concentrations in the complexed dissolver product could then be calculated and only a zirconium analysis was required to fix the composition of the solution.

For the purpose of developing the complexing relationship on Figure 12, the following bases were used:

1. The aluminum concentration in the complexing solution was 1.96M.
2. The boron concentration in the dissolvent was 4.1 g/l.
3. For simplicity, a charge water heel and jet dilution of 295 liters was evenly distributed over the total quantity of complexed dissolver product produced from a charge of fuel.
4. One mole of zirconium complexes four moles of fluoride as ZrF_4 .
5. One mole of boron complexes four moles of fluoride as HBF_4 .
6. One mole of aluminum complexes two moles of fluoride as AlF_3 .

The relationship on Figure 12 actually is somewhat conservative because some species of aluminum fluoride are formed that contain three or more moles of fluoride per mole of aluminum.

The acid and fluoride concentrations in the dissolvent corresponded closely with each other. Therefore, acid analyses of the dissolvent were used to determine fluoride concentrations during most of this run because an acid analysis is simpler and faster than a fluoride analysis.

The use of Figure 12 was simply a convenient means to determine whether or not complexed dissolver product leaving the complexing tank had been properly adjusted. When it had not, it was necessary to use routine material balance calculations to determine the additional quantity of aluminum nitrate solution required to adjust the batch to suitable extraction column feed specifications.

3.3 Specific Gravity

A linear equation was developed by computer methods to calculate the specific gravity of complexed dissolver product, feed, or raffinate solutions of a known composition. One-hundred data points were used to develop the equation. Each data point represented a known composition (Zr, B, U, Sn, Al) in moles per liter and specific gravity at 25°C of a sample of the complexed dissolver product. The resulting equation is:

$$\text{Sp gr at } 25^{\circ}\text{C} = 0.9971 + 0.1367 \text{ Zr} + 0.1774 \text{ Al} + 0.04975 \text{ B}$$

All of the chemical symbols represent concentrations in gram moles per liter. Uranium, nitric acid, and tin were left out of the equation because they made insignificant contributions to the specific gravity of the solutions. The accuracy of the equation over the range of values for the one hundred data points was plus or minus two percent.

4. Extraction

4.1 First Cycle Extraction

Uranium was recovered from the complexed dissolver product in the same equipment used for extracting uranium from aluminum fuels. A detailed description of the first cycle extraction equipment has been previously published⁽¹⁴⁾. Uranium was extracted from the bulk of the

metal and fission products in the extraction column by an organic stream of Amsco 125-90W containing five to ten percent TBP. Small amounts of acid and fission products which were extracted along with the uranium by the solvent were scrubbed out in the scrub column. Uranium was then stripped from the solvent in the strip column. A seven-stage mixer-settler removed residual TBP from the stripping column product by contacting it with solvent-free Amsco. The clean aqueous product stream was then concentrated to 200 g/l uranium and stored in N cell for later processing through three additional cycles of hexone extraction.

Total uranium losses from the first cycle extraction and stripping columns were on the order of 0.50 percent of the total amount of uranium charged into the process. Most of these losses occurred during short periods of poor operation and were due primarily to emulsion problems.

4.11 Rates Achieved: Flowsheet processing rates were easily achieved in the extraction system. Feed rates in excess of those shown in the flowsheet (Figure 2) were often used. The highest feed rate maintained for a significant period of time was about 700 l/hr.

The overall average processing rate for dissolution and first cycle extraction during the campaign was about 535 kg of zirconium per day. However, for one trouble-free portion of the campaign, the average processing rate exceeded 800 kg of zirconium per day.

4.12 Raffinate: The average amount of first cycle waste generated was about 7.6 gallons per kilogram of zirconium processed. Its average composition is shown in Table III. The flowsheet raffinate rate shown in Figure 2 of 6.0 gallons per kilogram excludes heel-out solutions, recycled raffinate, solvent-wash liquid, and jet dilution during transfer to the waste tank farm. In general, all waste solutions transferred to the tank farm were in the stable regions shown on Figure 11.

4.13 Extraction Efficiency: Uranium recovery in the first cycle extraction column was normally about 99.9 percent as shown in Table IV. This table also contains other information typical of the campaign. The number of theoretical stages in the column, as determined by McCabe-Thiele methods, varied from 3.3 to 5.1 with the arithmetic average being 4.1. The active length of the column is 23 feet;

Table III
AVERAGE FIRST CYCLE WASTE COMPOSITION
FROM ZIRCONIUM FUELS PROCESSING

Al	0.61 <u>M</u>
Zr	0.38 <u>M</u>
F	2.88 <u>M</u>
B	0.17 <u>M</u>
NO ₃	1.72 <u>M</u>
Cr	0.01 <u>M</u>
H	1.61 <u>M</u>
<u>F-4 (B + Zr)</u> Al	1.30

Table IV
TYPICAL DATA FROM FIRST CYCLE EXTRACTION
OF ZIRCONIUM PROCESS SOLUTIONS

Feed Composition		Uranium in Raffinate, g/l		Aqueous to Organic Flow Ratio	E ⁰ A	Number of Theoretical Stages
<u>Al, M</u>	<u>U, g/l</u>	<u>Actual</u>	<u>Predicted</u>			
0.80	0.61	4.6 x 10 ⁻⁴	5 x 10 ⁻⁴	1.6	7.0	4.9
0.79	0.39	5.1 x 10 ⁻⁴	5 x 10 ⁻⁴	1.5	7.0	4.3
0.86	0.36	1.0 x 10 ⁻³	5 x 10 ⁻⁴	1.3	8.0	3.3
0.83	0.32	3.1 x 10 ⁻⁴	5 x 10 ⁻⁴	1.2	7.5	3.8
0.75	0.43	3.6 x 10 ⁻³	5 x 10 ⁻⁴	1.4	6.2	3.3
0.75	0.62	2.6 x 10 ⁻⁴	5 x 10 ⁻⁴	1.4	6.2	<u>5.1</u>
Average						4.1

therefore the height equivalent to a theoretical stage averaged 5.6 feet. Distribution coefficients used to determine the number of theoretical stages were estimated from Figure D-9 in the Appendix.

4.14 Scrubbing Efficiency: The function of the scrub column is to remove acid and fission products from the organic stream before the uranium is stripped back into the aqueous phase in the next column. During most of the campaign the composition of the scrub stream was 0.75M $\text{Al}(\text{NO}_3)_3$. It was impossible to obtain samples and in turn data to make a full evaluation of the efficiency of the scrubbing operation. However, acid concentrations in the first extraction cycle product indicated that the performance of the scrub column was satisfactory.

4.15 Stripping Efficiency: In general, stripping of uranium was less efficient than expected. Published data⁽¹⁵⁾ indicate that the height equivalent to a theoretical stage (HETS) in the strip column is about seven feet. There should be, therefore, two theoretical stages in the fourteen-foot stripping column used in this campaign. Average distribution coefficients (E_o^A) shown in Table V for the stripping operation were calculated for several sets of samples using two theoretical

Table V

<u>CALCULATED DISTRIBUTION COEFFICIENTS FOR STRIPPING COLUMN</u>	
<u>Uranium in Stripping Column Raffinate Stream g/l</u>	<u>Calculated Distribution Coefficient, E_o^A</u>
3.2×10^{-3}	29.4
6.9×10^{-3}	23.8
1.6×10^{-3}	37.0
9.8×10^{-4}	58.8
9.4×10^{-4}	77.0
4.1×10^{-4}	77.0
4.1×10^{-4}	77.0
1.0×10^{-3}	58.8
1.8×10^{-3}	83.4
4.0×10^{-4}	95.2
8.0×10^{-4}	<u>71.4</u>
Average 1.7×10^{-3}	62.6

stages in the column as a basis. The distribution coefficients for stripping were in a range from 24 to 95 with an average of 62, somewhat lower than the expected coefficients shown on Figure D-10 in the Appendix. It is believed, as later discussed in this report, that degradation products of tri-butyl phosphate adversely affected the stripping operation.

4.16 Solvent Wash System Efficiency: The organic raffinate from the stripping column was passed through three consecutive mixer-settlers before being recycled to the extraction column. The first and third mixer-settlers contacted the organic stream with 0.04M HNO_3 while the second one used 0.5M Na_2CO_3 . The purpose of these mixer-settler treatments was to wash degradation products of TBP--mostly dibutyl phosphate--and residual fission products from the organic stream. Samples were taken from the five-percent TBP solvent upstream (ICR) and downstream (IAX) of the wash system and analyzed for dibutyl phosphate (DBP) to determine the efficiency of the system. Table VI shows some concentrations of DBP in the IAX and ICR streams and the corresponding decontamination factors (DF's) for the mixer-settlers for an aqueous-to-organic ratio of 1/10.

The decontamination factors for DBP observed in the plant agree reasonably well with data from a laboratory study performed during the run. The laboratory study showed that a DF of 2.5 could be expected from one stage of washing using 0.5M Na_2CO_3 and an aqueous-to-organic ratio of 1/10; the average DF observed in the plant was 3.1.

Table VI

DIBUTYL PHOSPHATE DECONTAMINATION IN THE SOLVENT WASH SYSTEM

<u>DBP in ICR, M</u>	<u>DBP in IAX, M</u>	<u>Decontamination Factor</u>
6.9×10^{-5}	1.5×10^{-5}	4.6
1.8×10^{-3}	7.1×10^{-4}	2.5
2.8×10^{-3}	8.9×10^{-4}	3.2
2.0×10^{-3}	9.9×10^{-4}	2.0
	Average	<u>3.1</u>

Figure 13
 EFFECT OF DBP ON URANIUM DISTRIBUTION
 COEFFICIENT FOR STRIPPING COLUMN CONDITIONS

It is important to remove as much DBP from the solvent stream as possible because it reduces the uranium distribution coefficient for stripping. Figure 13 presents a laboratory-established relationship (16) that shows the effect of the DBP concentration on the uranium distribution between a five percent TBP and 0.04M HNO_3 system. The higher concentrations of DBP in the strip column raffinate (ICR) as tabulated in Table VI were high enough to reduce the uranium distribution coefficient for stripping by a factor of ten over that which would be expected if no DBP were present. This then is the basis for a belief that DBP was responsible for relatively poor performance of the stripping column.

The data in Table VI also shows that significant amounts of DBP would be present in the solvent by the time it reached the strip column even if the mixer-settlers removed all of the DBP. Hence, improving the performance of the solvent wash system will not solve the TBP degradation-product problem.

4.2 Second, Third, and Fourth Extraction Cycles

The flowsheet (Figure 3) for the second and third extraction cycles, using packed columns and methyl isobutyl ketone (hexone) as a solvent, are typical of those used for previous fuel processing campaigns at ICPP. A fourth cycle was used on the run to establish the net effect on decontamination factors. The flowsheet was similar to that used for third cycle. In general, the hexone extraction system performed well during this run. Uranium losses were about 0.035 percent and decontamination of the uranium product was excellent.

The only serious problem that occurred during the hexone part of the processing campaign was the appearance of solids in the extraction column of the third extraction cycle. These solids partially plugged the organic outlet line (IIIAP) of the extraction column on several occasions and forced solution out of the top of the column through a vent line. These same solids were also found in the IIBP stream. Analysis showed the solids were mostly iron and aluminum. It is believed the iron was in the form of iron hydroxide and that the aluminum was physically trapped by the flocculant precipitate. Iron as ferrous sulfamate was introduced to the extraction columns in both second and third cycles to reduce plutonium to Pu(III) which is inextractable in hexone.

Laboratory studies showed that when an oxidizing agent was added to the acid-deficient ($0.3 N_b$) scrub stream (see Figure 3 for composition) containing ferrous sulfamate, a precipitate was formed identical in appearance to the one observed in the plant. The precipitate was also formed by bubbling air through combined samples from plant IIIAS, IIIAF, IIIAX streams; a piece of stainless steel was also put into the solution during the test. An oxidizing condition may have existed in the extraction columns during the campaign which caused the iron precipitate to form. However, this problem has not yet been resolved satisfactorily.

The waste generation rate for the second extraction cycle was about 9 gallons per kg of uranium; for combined third and fourth cycles, the waste generation rate was about 5.5 gallons per kg of uranium. The corresponding flowsheet waste generation rates each are about 3.2 gallons

per kg of uranium. The large waste volume was due primarily to the fact that the uranium concentration of first cycle product was more dilute than that on which the flowsheet was based. A more dilute product than otherwise desired was deliberately produced, however, because of a corrosion problem in the product evaporator; this is discussed further in Section IV.

4.3 Decontamination Efficiency

Decontamination of uranium through one cycle of TBP and three cycles of hexone extraction was excellent. Table VII shows average log decontamination factors for various radioactive isotopes. The decontamination factor is the concentration of a contaminant in the feed stream per gram of uranium divided by the concentration in the product stream per gram of uranium.

Table VII
AVERAGE LOG (BASE 10) DECONTAMINATION FACTORS FOR EXTRACTION
OF ZIRCONIUM ALLOYED FUEL SOLUTIONS

	<u>Gross β</u>	<u>Gross γ</u>	<u>Zr-Nb⁹⁵</u>	<u>Ru¹⁰⁶ 103</u>	<u>Pu</u>
First Extraction Cycle	4.0	3.9	4.8	2.8	1.9
Second Extraction Cycle	3.0	2.4	2.2	3.3	3.6
Third Extraction Cycle	0.6	0.3	1.2	0.8	1.9
Fourth Extraction Cycle	0.4	0	0.5	0	0
Overall for Four Cycles	8.0	6.6	8.7	6.9	7.4

4.4 Neptunium Recovery

Neptunium-237, an isotope needed for research and for the production of Pu-238 which has become an important heat source in space units,⁽¹⁷⁾ is now routinely recovered from all fuels processed at ICPP. About one kilogram of Np recovered from the zirconium fuels processed during this campaign is stored at ICPP awaiting further purification.

Neptunium was oxidized to the plus VI valence state in the complexing tank with chromic acid. It was then extracted along with

uranium in the first extraction cycle, and partitioned from the uranium in the hexone second cycle--neptunium is essentially inextractable in an acid-deficient hexone system. The second cycle raffinate containing the neptunium was concentrated and stored for a later extraction step using TBP. After this extraction, the relatively pure neptunium product was concentrated and stored. Eventually it will be further decontaminated after the planned installation of new ion exchange facilities.

IV. CORROSION

Possible corrosion of process equipment by fluoride solutions was a major concern with the zirconium fuel process. Materials of construction used in various parts of the process include Monel-400, Carpenter-20 (Cb) stainless steel, vitreous enamel, rubber, titanium, and stainless steel Types 304L and 347. Some equipment failures did occur during the run because of corrosion.

1. Normal Corrosion on Process Equipment

1.1 Monel Cooling Coil in Dissolvent Makeup Tank

Corrosion measurements were made on the Monel cooling coil in the dissolvent makeup tank. The corrosion rate was found to be about seven mils per month when in contact with the dissolvent containing 6.6M HF, 0.4M H_3BO_3 , 0.03M HNO_3 at 30°C and only about one mil per month without the HNO_3 .

1.2 Monel Dissolver

Estimates of corrosion rates in the dissolver were made based on test specimens. One specimen was a Monel pipe which extended the length of the vessel. Another set of specimens (small pieces of Monel pipe) was used to measure the corrosion rate during special heelout dissolutions with HF, CrO_3 , and H_2SO_4 . The corrosion rate during normal operation was estimated to be 7.5 mils per month⁽¹⁸⁾. The corrosion rate during the special heelout dissolutions was 2 mils per month. Based on these figures and other corrosion measurements taken in the past, the dissolver should have an additional operating life-time of about 20 months before the remaining 150 mils of corrosion allowance is expended.

1.3 Stainless Steel Equipment

No physical measurements of corrosion were made for plant equipment constructed of stainless steel. However, one visual observation made on a section of pipe from the feed line to the first cycle

extraction column revealed no evidence of excessive corrosion.

A laboratory corrosion test of Type 347 stainless steel was run at 35°C in a series of nine different solutions simulating process solutions produced in the plant during the campaign. The corrosion rate was less than 0.3 mil per month when the value of the ratio $F-4 (Zr + B)/Al$ was below 3.9. The absence of boron in these solutions without a compensating reduction in fluoride or increase in either Al or Zr resulted in a marked increase in the corrosion rate.

1.4 Rubber Lining in Dissolvent Feed Tank

After about one year of service with solutions comprised of 7M HF and sometimes 7M HF and 0.03M HNO_3 some of the rubber lining on the bottom and lower one-third of the walls of the dissolvent feed tank deteriorated⁽¹⁸⁾. Nevertheless, the lining generally was still flexible. Based upon the inspection, this vessel is believed suited for continued prolonged service, however, the lining should be reinspected after each six months of service.

2. Special Problems in this Run

2.1 Electromagnetic Flowmeter

An electromagnetic flowmeter used to measure the feed rate to the first-cycle extraction column failed due to corrosion during the early part of the run. The flowmeter was lined with vitreous enamel which was unsatisfactory for service with fluoride-containing solutions even though the fluoride was adequately complexed with aluminum. The EM flowmeter was replaced with a stainless steel venturi flowmeter.

2.2 Feed and Raffinate Evaporators

First cycle feed and raffinate solutions were never heated nor evaporated during this campaign because of stability and corrosion considerations; to avoid piping changes it was necessary to route the complexed dissolver product solution through both the feed and raffinate evaporators in the first extraction cycle. Early in the campaign, a titanium elbow on the feed evaporator tube bundle failed due to corrosion. After decontamination, the titanium tube bundles of both evaporators were removed. Inspection of the titanium tube bundle from the

raffinate evaporator showed that it had corroded considerably less than that from the feed evaporator. The average composition of solution which passes through the two evaporators was similar except for uranium concentration. However, the feed evaporator was used during the campaign as a mix pot to blend the complexed dissolver product with scrub column raffinate (from the B column). This stream contained additional aluminum nitrate for salting uranium into the aqueous phase and perhaps complexed some free-fluoride ions. It is possible that the solution normally in contact with the titanium part of the feed evaporator may not have been thoroughly mixed with the scrub column raffinate stream for parts of the run. This would account for the difference in corrosion rates.

Laboratory tests have shown that titanium is a poor material for use with inadequately-complexed fluoride solutions and steps have been taken to avoid bringing such solutions in contact with any titanium vessels. Stream blending will be accomplished elsewhere in the process on future campaigns.

2.3 Carpenter-20(Cb) Stainless Steel Steam Jets

One of a pair of steam jets made of Carpenter-20(Cb) stainless steel, which are used to empty the dissolver, failed and the other one was badly corroded during the campaign. The corrosion occurred in the vicinity of welds and was believed a result of improper heat treatment. Carpenter-20(Cb) is a recommended material for fluoride service and therefore jets made of this material properly annealed will continue to be used in this process.

2.4 Product Evaporator

During a startup period in the campaign, product solution in the first cycle product evaporator contained as much as 0.1M fluoride along with some aluminum nitrate. This evaporator has a Type 347 stainless steel tube bundle, and the head contains a large number of borated Type 304L stainless steel plates for nuclear safety. When the fluoride was first discovered, analyses of the evaporator effluent for stainless steel indicated that a corrosion rate of 1.4 mils per month (MPM) based on the total surface of the boron stainless steel plates

was occurring. This rate decreased steadily; two days after startup the calculated corrosion rate was 0.7MPM and the effluent contained 0.02M fluoride. Initially it was believed some fluoride may have been extracted from the LAF stream by the TBP and then stripped into the aqueous stream along with the uranium; therefore, operation of the plant was switched from a ten to a five percent TBP flowsheet. Laboratory tests indicated that five percent TBP would extract less fluoride than ten percent TBP. After the new flowsheet was put into use, the fluoride concentration in the evaporator effluent continued to decrease to about 0.002M and the calculated corrosion rate leveled off at about 0.2 MPM.

The 0.1M fluoride concentration in the first cycle product was probably due to a carry-over of aqueous solution or an emulsion from the extraction column during startup. For a ten percent TBP flowsheet the steady state fluoride concentrations in the evaporator product, assuming no entrainment from the A column, should have been less than 0.02M; for five percent TBP it was about 0.002M.

Laboratory tests⁽¹⁸⁾ showed that vapor phase corrosion on boron stainless steel should be 0.1 to 0.3 MPM above a boiling, nitric-acid solution similar to the first-cycle product solution resulting from this campaign. This rate agrees well with the steady-state corrosion rate observed for the evaporator.

Test coupons from the disengaging section of the evaporator that were in the same environment as the boron stainless-steel plates were examined after the campaign and found to have lost 0.05 mils per month during about 14,600 hours of operation. From this information, it was estimated that the plates (141 mils thick) have lost one mil on each face since the original installation. Only a portion of the 14,600 hours were spent processing zirconium fuels so the exact corrosion rate experienced while processing zirconium fuels is unknown. It is believed, however, that the corrosion rate on the boron stainless steel plates while processing zirconium fuels is not unusual.

V. RECOMMENDATIONS

As a result of this processing campaign two objectives for the next processing campaign are apparent. One is to increase the processing rate and the other is to reduce the amount of waste generated. To achieve these goals, some equipment modifications are planned, and a ten percent TBP flowsheet is recommended.

1. Planned Equipment Modifications

1.1. Dissolver Off-Gas

The dissolver off-gas outlet will be raised about two feet above its present location and the present one-inch condenser bypass line near the top of the dissolver will be replaced with a two-inch line.

These changes should minimize dissolver pressurization problems and allow for operations at a higher liquid level. The higher liquid level will increase the surface area of fuel exposed to dissolvent and increase the residence time of dissolvent in the dissolver-- both of which should increase the zirconium concentration in the dissolver product. It is estimated that the concentration of zirconium in the dissolver product will be increased by about 0.1 moles per liter which will reduce the waste generated by about 4,400 gallons per 100 kg of uranium processed. This represents an out-of-pocket savings of about \$7,600 per 100 kg of uranium in calcination costs. In addition, plant processing time could be reduced by about ten percent which could save an additional \$5,200 per 100 kg of uranium.

1.2 Dissolvent Addition System

The dissolvent addition system will be revised so that dissolvent either can be added to the bottom or top of the dissolver as desired. This involves installing another line from the process make-up area to the top of the dissolver. The modification will provide

an easy way to break slug jams. Also, it is believed that continuous acid addition into the top of the vessel may increase the dissolver production rate.

1.3 Feed Evaporator

The equipment in G Cell will be modified so that the raffinates from the scrub column (0.75M aluminum nitrate) and the first-stage solvent wash mixer-settler (0.04M HNO_3) can be routed to the feed evaporator and concentrated to about 1.8M aluminum nitrate. This concentrated stream will be blended with the complexed dissolver product (which will bypass the evaporator) to form the feed to the extraction column. By concentrating these streams separately, which could not be done during this past campaign, a waste volume reduction of about 4,000 gallons per 100 kg of uranium may be realized. The estimated out-of-pocket savings will be about \$7,000 per 100 kg of uranium in waste calcining costs. Also, uranium lost due to incomplete stripping will be returned to the feed stream for extraction rather than be combined with the raffinate for discharge to the waste tank farm.

1.4 Solids Removal from Dissolver Product Stream

Solids in the zirconium fuel dissolver product are troublesome. The usual problems with solids include plugging of flowmeters and valves. Also, decontamination of equipment following the campaign proved to be difficult because of solids. Although uranium losses appear to be independent of solids in the zirconium-fuel dissolver product, there is a real need for reliable equipment to remove solids from process streams. A centrifuge is being installed which will remove solids from the feed to the TBP extraction system.

2. Flowsheet Changes

If possible, future processing should be done with a ten-percent TBP flowsheet. A suitable flowsheet is shown on Figure 14; if adopted, use of this flowsheet could reduce the volume of waste solutions by almost 6,000 gallons per 100 kg of uranium. This represents an out-of-pocket savings of about \$10,400 per 100 kg of uranium in waste calcination costs.

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	CHARGE WATER	DISSOLVER PRODUCT	COMPLEXING SOLUTION	COMPLEXED DISSOLVER PRODUCT	I BR	I AF	I AX	I AR	I AP	I AS	I BP	I CX	I CR	I CP	IDX	IDR	IDP	FIRST CYCLE PRODUCT
Flow, l/batch		6335	1400	6580(c)	2240	9370+e														
Flow, l/hr	5.42		532(d)		500(f)	21(g)	521	500	521	500	50	500	275	500	275	10	275		2.8	
Zr, M			1.00		0.70		0.68		0.68											
F, M	6.44		6.35		4.45		4.29		4.29											
Al, M				2.0	0.45	1.8	0.53		0.53		0.75									
H, M (a)	6.44		2.32		1.61	2.1	1.66		1.51	0.15	-0.5(h)	0.01	0.005		0.02		0.02		1.8	
NO ₃ , M				6.0	1.45	8.7	1.72		1.57	0.16	2.25	0.01	0.005					0.02		3.5
Sn, g/l			1.42		1.0		0.9		0.9											
Cr, g/l				3.7	0.9		0.8		0.8											
B, g/l	4.11	5.0	4.1		2.9		2.7		2.7											
U, g/l (No Burnup)			1.57		1.10	0.60	1.08		8 x 10 ⁻⁴	1.12		1.10		8 x 10 ⁻⁴	2.00			2.00		200
Sp gr at 25°C	1.05	1.00	1.18	1.31	1.20	1.35	1.20	0.79	1.20	0.79	1.14	0.79	1.00	0.79	1.00	0.76	1.00		1.29	
U, kg/batch (no B.U.)	10.3(b)																			
Zr, kg/batch	600																			
Sn, kg/batch	9.3																			
NH ₄ , M						1.2	0.05		0.05		0.5									
TBP, % Diluent								10-Amsco		10-Amsco		10-Amsco		10-Amsco		Amsco				

(a) Total acid analytical procedure.

(b) Based on PWR Core 1, Seed 1 with no burnup.

(c) Includes 195 liters of charge water heel.

(d) Actual flowrate after dissolver fills.

(e) Includes 550 liters of jet dilution. The process is continuous from this point on.

(f) Average rate for a 24 hour period. Dissolution time is 12 hours. It is assumed that down time between dissolution cycles is 5.7 hours.

(g) After concentration in the CPM evaporator.

(h) Acid efficient.

Figure 14

MODIFIED TEN-PERCENT TEP FLOWSHEET FOR ZIRCONIUM FUELS

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APPENDIX A

MODIFICATIONS MADE TO INCREASE THE ZIRCONIUM FUEL PROCESS CAPACITY

1. Non-Radioactive Solution Make-Up Area

Modifications of some of the existing equipment and installation of some new equipment were necessary to handle process solutions for the zirconium fuel process.

1.1 Hydrofluoric Acid Handling

A carbon steel tank with a capacity of 1200 gallons was installed outside the process makeup building to store 70 percent HF. This vessel is equipped with a pressure indicator, level indicator, and a pump to transfer HF to the dissolvent makeup tank. During operation, the tank was blanketed with a nitrogen atmosphere to prevent corrosion.

The transfer pump leaked all during the run and the tank was too small to hold tank-truck loads of HF. Therefore, the system will be replaced by a larger tank and a pressure system for transfer of HF.

A dissolvent makeup tank with a 2500-gallon capacity was installed in the process makeup building. It is rubber lined for HF resistance and contains a Monel cooling coil. This vessel is equipped with a level recorder, a temperature indicator, a density recorder, a mixer, and a boron detector. A nitrogen atmosphere blanket was maintained in the vessel to help prevent corrosion.

Monel piping, a flowmeter and control valve, block valves, and a rotameter were installed to handle solution flowing from the dissolvent makeup tank into the dissolver. Also, a solenoid valve was installed in the dissolvent outlet line. This valve is connected to a boron detector and automatically closes when the detector indicates a boron concentration in the dissolvent less than 3.8 g/l. A heat exchanger to cool the dissolvent makeup tank, the dissolver vessel, and the dissolver off-gas condenser was also installed. Borated

water was used in the tube side of the heat exchanger so that any leak into any of the vessels being cooled would not dilute the neutron poison. A radiation monitor also was installed on the cooling water system to detect any process leaks to the coolant.

1.2 Boron Monitor

A boron monitor was developed to insure that a minimum of 3.8 g/l of boron was present at all times in any dissolvent added to the dissolver. The monitor consisted of a neutron source and two BF_3 neutron detector tubes immersed in the dissolvent makeup tank. The neutron source is Pu-Be and has a strength of one curie. The neutron detector tubes are located 4.5 inches from the source, center to center. The source and detector tubes are located inside capped Monel pipes to protect them from the dissolvent solution. Current produced by ionization in the detector tubes was measured by a micro-microammeter (one for each tube) and recorded on a recorder chart. The current produced was proportional to the boron concentration in solution. The voltage used in the detector tubes was 3200 volts D.C.

Figure A-1 shows a calibration curve for one of the two detector tubes. The region of interest is in the 4 g/l-boron region where the curve is quite flat. Because of the flatness of the curve precise measurements of the boron concentration by this method were very difficult. The instrument is capable of a precision of about plus or minus 0.3 g/l in the 4 g/l-boron range and the dissolver was operated to compensate for this amount of variance. In addition, two other checks were routinely made to guarantee the boron concentration: (1) during makeup, a weighed amount of boric acid was used to prepare the dissolvent, and (2) after makeup, the boron concentration was always measured by analytical methods. In the event either of the neutron detectors ever indicated boron concentrations less than 4.1 g/l, an alarm sounded and a valve in the dissolvent feed line automatically shut off the flow of dissolvent to the dissolver. During the run the monitor did alarm occasionally; however, all such alarms were caused by instrument malfunctions or surges in the

Figure A-1

CALIBRATION CURVE FOR BORON DETECTOR AT 3200 VOLTS

electrical power supply. Spare equipment was always on hand and was substituted for malfunctioning equipment in a few minutes to avoid any prolonged shut down periods.

1.3 Complexing Solution Handling

A new flowmeter was installed and some piping changes were made to enable complexing solution to be made up and fed to the complexing tank continuously.

2. In-Cell Modifications

2.1 Zirconium Fuel Dissolver Modifications

The primary modifications made to the dissolver was the installation of a new 12-3/4 inch ID fuel basket inside the original basket and charging chute. This modification is shown schematically in Figure 1. The reason for installing the new basket was to contain fuel in a small space for nuclear safety. The old basket contained openings too large to hold partially dissolved fuel; the new basket has

1/4 x 6-inch slots at various levels to permit adequate circulation of dissolvent.

Piping connections were made from the dissolver and off-gas condenser cooling jackets to a closed-loop borated cooling water system. Borated water was circulated through the tube side of a heat exchanger from which it split into three streams. One stream cooled the dissolvent makeup tank, one cooled the off-gas condenser and the other one cooled or heated the dissolver. Borated cooling water was used so that any leaks into the system would not dilute the neutron poison in the dissolver. With this system the condenser could not be cooled while the dissolver was being heated. Therefore, changes will be made to make this possible.

A pair of nitrogen gas lifts were installed on the dissolver to transfer dissolver product to the complexing tank. Nitrogen was used because air accelerates the corrosion rate of Monel in a fluoride media. A pressure recorder and temperature recorder-controller were also installed on the dissolver.

2.2 In-Cell Piping Changes

Several piping changes were made in Cells E, G, and J so that complexed dissolver product could be processed in the aluminum-process extraction equipment which has a much larger capacity than the old zirconium fuel extraction equipment in F Cell.

3. Equipment Modifications Made During the Processing Campaign

3.1 Lowering the Dissolver Overflow Loop

During the shakedown run (Appendix E) both overflow loops from the dissolver were at the same elevation. However, it was quickly established that the operating liquid level in the dissolver was too high because at times the reaction in the dissolver was so vigorous that foam from the reaction partially obstructed the off-gas condenser causing the vessel to pressurize. (The dissolver was normally operated under a vacuum of about 14 inches of water.) Consequently,

one of the two product overflow loops from the dissolver was lowered 18 inches (see Figure 5). This enabled the liquid level to be varied as desired over a distance of about two feet during operation by changing the flow of nitrogen to the nitrogen lifts. Thereafter dissolver pressurization problems were negligible.

3.2 Installation of Venturi Flowmeter

A venturi flowmeter was installed to replace an electromagnetic flowmeter that failed due to corrosion (see Section IV). This flowmeter was used to measure the flowrate of feed to the A column in first extraction cycle. The venturi meter performed well at times but it often gave erroneous flow indications because of partial plugs in the pressure probes or throat.

3.3 Air Lift Disengaging Pot Elevation

An air lift disengaging pot in the feed line to the A column in the first extraction cycle was elevated several feet to provide more head to the column. This change was necessary to achieve feed rates up to 700 liters/hour.

3.4 Product Evaporator Feed Flowmeter

A vitreous-enamel-lined electromagnetic flowmeter in the feed line to the product evaporator was removed because there was a possibility that it would fail due to fluoride corrosion. This flowmeter was used as part of the cascade control system on the evaporator. It was not replaced and the evaporator was controlled by solution density. This simpler method of controlling the evaporator has been satisfactory.

APPENDIX B

BRIEF DESCRIPTION OF THE ORIGINAL ICPP ZIRCONIUM PROCESS

1. Process Description

The zirconium fuel process at ICPP was first installed to process available zirconium fuels⁽¹⁾. It consisted of a batch dissolver and feed adjustment tanks (which are still in use), and a set of small capacity first-extraction cycle columns and associated equipment (still occasionally used). The dissolver was made of Monel-400, the coarse feed adjustment tank was made of Carpenter-20 (Cb) stainless steel and all other equipment was Type 347 or 304L stainless steel.

The present process is similar to the old process except that a larger capacity is possible because the innovation of boron as a soluble neutron poison in the dissolver allows greater fuel charges and semi-continuous operation. Also, the high capacity extraction equipment--used for aluminum fuels--can now be employed.

2. Criticality Control

The dissolver for the old zirconium fuel process was the limiting factor governing capacity because of nuclear safety consideration. The established guidelines limited the dissolver contents at 1700 grams of total uranium before burnup assuming this was the minimum amount of U-235 that could go critical when a homogeneous solution was in the dissolver⁽¹⁹⁾. A control chart was used to insure that the limit was not exceeded.

Once the 1700 gram limit was established, nuclear safety control in downstream equipment was simple as the columns were small and presented no nuclear safety problem. Extraction equipment sizes are shown in Table B-I.

Table B-I

PHYSICAL SIZE OF SMALL-SCALE FIRST EXTRACTION
CYCLE EQUIPMENT IN F-CELL

<u>Column</u>	<u>Function</u>	<u>Height, ft</u>	<u>Diameter, inches</u>
A	Extraction	21	2.9
B	Dual:		
	Scrub	6.6	1.9
	Extract	12.2	1.25
C	Strip	13	1.9
D	Wash	10	1.25

APPENDIX C

A REVIEW OF THE STUDY MADE FOR A NEW PROCESS WITH INCREASED CAPACITY

A study of available processes for expanding the capacity of the zirconium fuel process was made in 1962⁽¹⁾. Six processes were selected for preliminary evaluation: the expanded existing process, the barium fluozirconate process, the sodium formate process, the Zirflex process, the ARCO process, and the fused salt fluoride volatility process. The first four processes were aqueous, and the last two were non-aqueous.

The two non-aqueous processes were eliminated because of inherent weaknesses requiring considerable development work that could not be accomplished in the limited time before hot processing was to commence.

Economic evaluations of the four aqueous processes were made for processing capacities of five and ten kilograms of uranium per day from 40-percent burned-up PWR seed fuel elements. The existing process with increased capacity was adopted because it required the least capital expenditure. The adopted process is described in the Introduction. The other processes are described briefly below.

1. The Barium Fluozirconate Process

Dissolution with the barium fluozirconate process is done with hydrofluoric acid and may be either batch or continuous. A mixture of barium nitrate and barium fluoride is added to the dissolver effluent solution. After digestion for one hour at 90°C, over 90 percent of the zirconium and fluoride precipitate as BaZrF_6 and BaZrF_5 . Essentially no uranium is precipitated. The precipitate is washed and sent to waste storage as a slurry or dried powder. The supernate and wash solutions are concentrated by evaporation to form feed for the first extraction cycle.

2. Sodium Formate Precipitation Process

The sodium formate process is similar to the barium fluozirconate process. The feature of the sodium formate process that distinguishes

it from the barium fluozirconate process is the use of a sodium formate solution instead of barium salts. A standard HF dissolution is used followed by chromic acid addition to the dissolver product to oxidize the uranium to the hexavalent state. A 26-weight percent sodium formate solution is mixed with the dissolver product in a ratio of four moles of sodium per mole of zirconium. Formation of finely divided sodium fluozirconate is almost instantaneous at 60°C, however, the solids precipitate slowly and a flocculating agent is required for satisfactory filtration rates.

The precipitate is washed with dilute sodium nitrate or nitric acid and the combined supernate and wash solution is concentrated to two molar sodium nitrate. This solution is treated with chromic acid to destroy residual sodium formate and formic acid and fed to the extraction cycle.

3. Zirflex Process

With the Zirflex process, the fuel is dissolved in boiling 6M NH_4HF - 1M NH_4NO_3 solution. Then zirconium and uranium are precipitated with NH_3 , washed, and centrifuged out. The precipitate is then dissolved in nitric acid and fed to the extraction system.

APPENDIX D

FLWSHEETS AND DATA USED FOR ZIRCONIUM FUEL PROCESSING

Two different flowsheets were used for the dissolution of zirconium alloyed fuels and recovery of uranium from the complexed dissolver product in the first extraction cycle. The ten-percent TBP flowsheet used for twenty percent of the run is discussed and shown below as Figure D-1. The five-percent TBP flowsheet used for eighty percent of the run is shown and discussed in the Introduction of this report. However, data pertaining to the five-percent TBP flowsheet are presented below. The dissolution was semi-continuous, while the extraction was continuous for both flowsheets. The dissolution portions of the flowsheets were nearly identical, but the extraction portions were different.

1. Flowsheet Using Ten Percent TBP as Solvent

The ten-percent TBP flowsheet shown on Figure D-1, was designed to produce minimum waste by using a minimum amount of aluminum nitrate (ANN) to complex all the fluoride and yet insure good extraction of uranium. Part of the ANN in the feed stream (IAF) was provided by the recycled scrub stream (IBR); the feed stream was made as concentrated in aluminum as practical to minimize the total volume of waste produced. Dibasic aluminum nitrate (DiBan) was used to make the IBS 1.1M acid deficient because a concentrated stream of aluminum nitrate alone is ineffective in scrubbing acid from TBP. The DiBan neutralized the acid in the IAP stream and allowed the use of a IBS stream containing 1.5M aluminum nitrate.

Distribution coefficients for extraction of uranium were estimated from Figure D-2 which shows pilot plant data⁽²⁰⁾ for the distribution of uranium for ten percent TBP as a function of the aqueous phase composition. The symbol E_A^O represents the uranium concentration in the organic phase divided by the uranium concentration in the aqueous phase at equilibrium. McCabe-Thiele methods of determining the proper aqueous to organic flowrate ratios were used. It was conservatively assumed that the extraction column had three theoretical stages based on previous work.

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	CHARGE WATER	DISSOLVER PRODUCT	COMPLEXING SOLUTION	COMPLEXED DISSOLVER PRODUCT	1BR	1AF	1AX	1AR	1AP	1BS	1BP	1CX	1CR	1CP	1DX	1DR	1DP	FIRST CYCLE PRODUCT
Flow, l/batch	7115	1400	7310 ^(c)	1862	9670 ^(e)	472 ^(f)	65	537	500	537	500	65	500	225	500	225	10	225	2.5	
Flow, l/hr	532		532 ^(d)																	
Zr, M			0.30		0.68			0.60		0.60										
F, M	6.60		6.42		4.85			4.26		4.26										
Al, M				2.0	0.38	1.50		0.52		0.52		1.50								
H, N(a)	6.63		2.33		2.14	0.0	1.88		1.74	0.15	-1.13 ^(g)		0.005		0.005		0.005	0.7		
NO ₃ , M	0.03		0.03	6.0	1.17	4.50	1.57		1.43	0.16	3.36	0.01	0.005		0.02		0.02	2.4		
Sn, g/l			1.27		0.96		0.84		0.84		0.84									
Cr, g/l				4.92	0.95		0.84		0.84		0.84									
B, g/l	4.1	5.0	4.1		3.1		2.7		2.7		2.7									
U, g/l (No burnup)			1.41		1.07	0.0	0.94		4x10 ⁻³	0.87		0.67		8x10 ⁻⁴	2.24		2.24	200		
Sp gr at 25°C	1.05		1.18		1.13	1.23	1.19	0.79	1.19	0.80	1.19	0.80	1.30	0.79	1.00	0.76	1.00	1.29		
U, kg/batch (No B.U.)	10.3 ^(b)																			
Zr, kg/batch	600																			
Sn, kg/batch	9.3																			
TBP, %								10		10		10		10						
Diluent								Amsco		Amsco		Amsco		Amsco		Amsco				

(a) Neglecting any contribution from H₂BO₃.

(c) Includes 195 liters of charge water heel.

(e) Includes 500 liters of jet dilution. The process is continuous from this point forward.

(b) Based on PWR Core 1, Seed 1 with no burnup.

(d) Actual flowrate after dissolver fills.

(f) Average rate for a 24 hour period. Dissolution time per cycle is 13.4 hours. It is assumed that down time between dissolution cycles is 7.1 hours.

(g) Made acid deficient by using di-basic aluminum nitrate.

Figure D-1

FLWSHEET FOR ZIRCONIUM FUEL DISSOLUTION AND FIRST EXTRACTION CYCLE USING TEN PERCENT TBP AS SOLVENT

Figure D-2

URANIUM DISTRIBUTION DATA FOR TEN PERCENT TBP AND
Zr-Al(NO₃)₃-HF SYSTEM

Plant data taken during this run showed that the column had an average of 4.1 theoretical stages.

Figure D-3 was used to determine nitric acid distribution coefficients for estimating the amount of acid extracted by the organic stream. The figure shows pilot plant data⁽⁷⁾ for the distribution of nitric acid into ten percent TBP as a function of the Al(NO₃)₃ concentration in the aqueous phase. The concentrations of other constituents in the aqueous phase for the curve shown were 0.75M zirconium, 4.0M fluoride and 0.88M acid as H⁺ ion.

Nitric acid distribution data for the scrub column was not needed in the ten-percent TBP flowsheet because the acid in the organic stream was theoretically neutralized by DiBan instead of being scrubbed out.

Uranium distribution coefficients for stripping were estimated from Figure D-4. The relationships shown in Figure D-4 are from pilot plant data⁽²²⁾. Uranium distribution coefficients for ten percent TBP are shown as a function of the uranium and nitric acid concentrations in

Figure D-3

NITRIC ACID DISTRIBUTION DATA FOR TEN PERCENT TBP AND
 $\text{Zr-Al}(\text{NO}_3)_3\text{-HF}$ SYSTEM

Figure D-4

URANIUM DISTRIBUTION DATA FOR TEN PERCENT TBP AND HNO_3 SYSTEM

the aqueous phase. The strip column was assumed to have two theoretical stages based on previous work and McCabe-Thiele methods were used to determine the necessary aqueous to organic phase flowrate ratios for good stripping.

Figures D-5 to D-7 present flooding data believed applicable to the extraction, scrub and strip columns respectively. The data were taken from pilot plant development work on the zirconium fuel process⁽²²⁾. These figures were helpful to estimate the pulse frequency needed for good extraction (the best extraction efficiency in solvent extraction equipment occurs near the flooding point). The zirconium fuel flowsheets were designed for column operation near 80 percent of flooding.

2. Flowsheet Using Five Percent TBP as Solvent

A change to the five-percent TBP flowsheet shown on Figure 2 was made after 19 batches of fuel had been processed during the campaign because a carryover of fluoride from the extraction column to the product evaporator was believed related to the use of higher concentrations of TBP.

Uranium distribution coefficients for five percent TBP and the feed solution being processed were estimated from Figure D-8. The figure shows relationships between uranium distribution coefficients and aluminum nitrate concentrations in the aqueous phase for two compositions of zirconium feed solution and five percent TBP. An extrapolation (of the data shown in Figure D-2 for ten percent TBP) was used to determine the relationships in Figure D-8. Data taken during the run proved that the extrapolation was valid and that the relationships in Figure D-8 are sufficiently accurate for predicting pulsed column performance.

Distribution coefficients for nitric acid in the scrub column were taken from Figure D-9. The figure shows nitric acid distribution coefficients that were determined in the laboratory for a five percent TBP - $\text{Al}(\text{NO}_3)_3$ system.

Figure D-10 shows uranium distribution coefficients for the strip column for five percent TBP. The relationships in this figure are based on pilot plant development work⁽²³⁾ using 4-1/2 percent TBP. The scrub and strip columns were assumed to have two theoretical stages each based on previous work⁽²²⁾.

Figure D-5
EXTRACTION COLUMN FLOODING DATA

Figure D-6
SCRUB COLUMN FLOODING DATA

Figure D-7
 STRIP COLUMN FLOODING DATA

Figure D-8
 URANIUM DISTRIBUTION DATA FOR FIVE PERCENT TBP AND
 $\text{Zr-Al}(\text{NO}_3)_3\text{-HF}$ SYSTEM