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ICPP PROCESSING OF VBWR STAINLESS STEEL FUEL
(April 14 to June 2, 1965)

R. N. Legan, N. Kormanik, and B. R. Wheeler

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IN NUCLEAR SCIENCE ABSTRACTS

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ATOMIC ENERGY DIVISION

NATIONAL REACTOR TESTING STATION
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by

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Atomic Energy Division

Contract AT(10-1)-205

Idaho Operations Office

U. S. ATOMIC ENERGY COMMISSION

A B S T R A C T

This report documents a campaign made at ICPP to process high-enriched stainless steel-uranium alloy fuel elements from the Vallecitos Boiling Water Reactor. Some of the capabilities of the plant and the process chemistry are discussed.

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ICPP PROCESSING OF VBWR STAINLESS STEEL FUEL
(April 14 to June 2, 1965)

I. SUMMARY

The Idaho Chemical Processing Plant (ICPP) inventory of stainless steel fuel elements from the Vallecitos Boiling Water Reactor (VBWR) was processed in E and F Cells. The dissolution was begun April 14, 1965, and the solvent extraction portion of the processing was completed by June 2, 1965.

A two-step batch dissolution process combined with a continuous solvent extraction process was employed for the VBWR fuel elements. Sulfuric acid was used to dissolve the stainless steel, and nitric acid was used to dissolve the uranium dioxide. Steel wool was charged with the fuel elements to trigger the stainless steel-sulfuric acid reaction. The dissolver effluent was adjusted to 3.0M nitrate ion to obtain a favorable distribution coefficient and then processed through a solvent extraction system using ten volume percent tributyl phosphate (TBP) in Amsco diluent as the extractant. Concentrated product was stored for future processing through two hexone extraction cycles.

A total of 153 fuel elements containing 37.0 kg of uranium (32.8 kg of U-235) and approximately 514 kg of stainless steel was processed during the run. In addition, 8 kg of uranium in a uranyl sulfate solution from another source were processed through the solvent extraction system. The throughput rates achieved in the dissolution part of the process, after the first few days of operation, ranged from about 15 to 18 kg of stainless steel per day with an overall uranium throughput of 1.05 kg per day.

Overall uranium recovery from the solvent extraction cycle was 99.69 percent; overall logarithmic decontamination factors for the first-cycle product exceeded 4.6. The overall throughput rate for the solvent extraction system averaged 0.97 kg of uranium or 11.1 kg of stainless steel daily, and the waste produced during the run averaged 267 gallons per kg of uranium dissolved.

About two-thirds of the total uranium loss occurred in the raffinate stream from the extraction column. Analysis of the plant data indicates that much of the loss to this raffinate stream was caused by erratic feed and solvent flow rates; restriction in the feed metering system due to a high concentration of silicon solids in the dissolver product was a principal cause of erratic feed rate.

McCabe-Thiele diagrams for the extraction and strip columns based on their performance during this campaign indicated that they averaged 6.2 and 2.1 theoretical stages, respectively. Thus, the average heights equivalent to a theoretical stage in the extraction and strip columns were 3.4 and 6.2 feet, respectively.

The greatest potential for flowsheet improvement is in reducing waste generation. It is believed that the waste generation rate for fuel similar to VBWR fuel could be reduced by a factor of 2.8 in the future by adopting the following changes in the flowsheet:

- (1) Use 200 percent instead of 300 percent of the stoichiometric amount of sulfuric acid required to dissolve the stainless steel.
- (2) Dissolve two, instead of one, heavy fuel elements per batch dissolution.
- (3) Use 13M instead of 6M nitric acid dissolvent for the second step of the dissolution.
- (4) Send the second and subsequent dissolver water rinses to the process equipment waste tanks for concentration.

One other benefit with the recommended flowsheet would be an increase in uranium throughput rate to at least 1.5 kg of uranium daily.

The plant capacity may be further increased by assuming a realistic value for the combined error in volume and analytical measurements; during this run, a value of six percent of the total uranium processed was used. In any future operation, it may be possible to choose a smaller value for the error and thereby decrease the number of required cleanouts, thus obtaining a higher overall throughput rate.

II. INTRODUCTION

An existing inventory of stainless steel alloyed fuel elements from the Vallecitos Boiling Water Reactor (VBWR) was processed in E and F Cells at the Idaho Chemical Processing Plant (ICPP) between April 14 and June 2, 1965, using a two-step, sulfuric-nitric acid dissolution flowsheet. In the batch mixed-acid process, the stainless steel first was dissolved in sulfuric acid; afterwards, the uranium was dissolved in nitric acid. The resulting mixed acid dissolver product, after adjustment, was processed through small-scale solvent extraction equipment using a ten volume percent tributyl phosphate (TBP) flowsheet. This report summarizes the pertinent details of the VBWR fuel processing campaign. This sulfuric-nitric acid process probably was used at ICPP for the last time for this type of fuel, as all future stainless steel alloyed fuels are scheduled to be processed at the Savannah River Plant where an electrolytic dissolver is being installed.

Ten different types of VBWR elements were processed. Each of these elements contained from four to nine fuel plates and two side plates. The meat of the fuel plates was 23 weight percent uranium dioxide, with a before-burnup enrichment of 93.4 percent, and 77 weight percent Type 304L stainless steel. The meat also was clad in Type 304L stainless steel. The fuel elements as received at ICPP were about 3 x 3 x 37 inches. Other data pertinent to these VBWR fuel elements are summarized in Table I. In the table, the type of element is identified by the two numbers shown in the first column. The first number indicates the number of fuel plates per element while the second number indicates the approximate weight of U-235 in grams per plate.

Because no stainless steel fuel elements had been processed at ICPP since early 1960, some equipment modifications and checkouts were necessary prior to starting the campaign. Operating curves for the F Cell air pulsers--amplitude as a function of pressure and frequency based on flowsheet conditions--were determined experimentally and fitted to a mathematical model⁽¹⁾. Based on this work, it was necessary to replace the 1/2-inch diameter pulse leg on the extraction column with a 3/4-inch

TABLE I
PERTINENT DATA FOR VBWR FUEL ELEMENTS PROCESSED AT ICPP^(a)

Fuel Element Type	Number of Elements	Uranium Content per Element, grams				Stainless Steel Content per Element, grams
		Before Burnup		After Burnup		
		U-235	Total U	U-235	Total U	
9-30	40	275	294	221	254	3,780
9-25	20	236	253	190	218	3,850
9-40	24	362	389	342	382	3,700
9-70	6	672	---	455	---	3,700
8-35	4	278	298	207	237	3,350
8-30	2	244	262	180	209	3,400
4-30	1	122	131	118	131	2,105
5-30	3	153	164	139	156	3,405
6-30	50	183	196	147	170	2,750
6-40	<u>3</u>	242	259	<u>216</u>	242	<u>2,650</u>
Total	153			33,299		514,170

(a) Information furnished by personnel at the Vallecitos Reactor.

diameter pulse leg. All solvent extraction instrumentation in F Cell then was checked, and water tests were performed to determine the operability of the various pumps, airlifts, jets, and samplers.

Actual dissolution of the VBWR elements in E Cell began on April 14 and lasted through May 19, 1965. On April 9, the solvent extraction equipment in F Cell was started on simulated feed. On April 12, residual feed solution from a zirconium fuel campaign was processed through the solvent extraction system, and on April 17 solvent extraction of the stainless steel feed solution was started. The solvent extraction portion of processing continued past termination of the dissolution part of the run until June 2.

III. PROCESS DESCRIPTION

A brief description of the major pieces of equipment used during processing of the VBWR fuel elements is given in Appendix A. However, a detailed description of the process theory and the small-scale equipment used is beyond the scope of this report; this information has been reported previously⁽²⁾.

The principal factors that determined the flowsheets used during this campaign were the physical size of the process equipment and the fuel composition. The amount of fuel along with the necessary acid that could be charged to the dissolver per batch was limited to about 6 kg of stainless steel by the physical size of the dissolver. To stay within this weight limit, no more than two elements were charged to the dissolver per batch dissolution, and for much of the campaign only one element was charged per batch.

The element weight and composition--and thus the stoichiometric acid requirements--for each of the ten types of VBWR elements differed slightly. However, by grouping all elements for processing according to weight, it was possible to complete the campaign with only two flowsheets. These flowsheets are shown on Figure 1 for heavy elements (eight- and nine-plate) and on Figure 2 for light elements (four-, five-, and six-plate).

In the dissolver, the stainless steel portion of the fuel elements dissolved in sulfuric acid. The uranium dioxide, however, formed a slurry in sulfuric acid; hence, after all of the stainless steel was in solution, it was necessary to add nitric acid to dissolve the uranium. The chemical reactions that describe the dissolution of stainless steel in sulfuric acid are:

FIGURE I
SCHEMATIC FLOWSHEET FOR PROCESSING HEAVY VBWR FUEL ELEMENTS

STREAM	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
DESCRIPTION	FUEL CHARGE	FIRST STEP DISSOLVENT	SECOND STEP DISSOLVENT	DISSOLVER PRODUCT	WATER RINSE	ADJUSTING SOLUTION	I AF	I AX	I AR	I AP	I BS	I BX	I BR	I BP	I CX	I CR	I CP	IDS	IDR	IDP	FIRST CYCLE PRODUCT
Volume, liters	37	15	52	90(2)	44	203(3)															
Flow, liter/hr						31.5(4)	32	31.5	32	8	6	8	38	9.5	38	9.5	0.2	0.2	9.5	0.23	
TBP, %							10		10		10		10		10						
Diluent							Amsco		Amsco		Amsco		Amsco		Amsco		Amsco	Amsco			
U, gram/batch	295																				
U, gram/liter			5.67			1.45		1.2x10 ⁻⁸	1.43			5x10 ⁻⁵	1.20		7x10 ⁻⁴	4.81			4.81	200	
ss, gram/batch	3770(1)																				
ss, gram/liter			72.4			18.5		18.5													
H ⁺ , M	12.0	6.0	5.55		13.0	4.23		3.91	0.32			0.66	0.004	0.01		0.02				0.8	
SO ₄ ²⁻ , M	6.0		4.27			1.09		1.09													
NO ₃ ⁻ , M		6.0	0.80		13.0	3.01		2.69	0.32				0.01	0.01		0.06		0.06	2.5		
Al(NO ₃) ₃ , M										0.70		0.70									
NH ₄ OH, M										0.60											
NH ₄ NO ₃ , M												0.60									
Sp gr	1.335	1.187	1.3	1.0	1.367	1.18	0.78	1.17													

- (1) About 50 grams of steel wool was charged to the dissolver to initiate the dissolution of the stainless steel.
- (2) Consists of two consecutive water rinses.
- (3) Includes jet dilution.
- (4) The actual dissolver performance was 4.6 batch-dissolutions per day; however only the solution from 3.7 batch dissolutions per day was processed through the solvent extraction system.

FIGURE 2
SCHEMATIC FLOWSHEET FOR PROCESSING LIGHT VBWR FUEL ELEMENTS

STREAM	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
DESCRIPTION	FUEL CHARGE	FIRST STEP DISSOLVENT	SECOND STEP DISSOLVENT	DISSOLVER PRODUCT	WATER RINSE	ADJUSTING SOLUTION	IAF	IAx	IAR	IAP	IBS	IBx	IBR	IBP	ICx	ICR	ICP	IDs	IDR	IDP	FIRST CYCLE PRODUCT
Volume, liters	45	18	63	80 ⁽²⁾	48	221 ⁽³⁾															
Flow, liters/hr						26.5 ⁽⁴⁾	32	26.5	32	8	6	8	38	9.5	38	9.5	0.2	0.2	9.5	0.21	
TBP, %							10		10		10		10		10						
Diluent							Amsco		Amsco		Amsco		Amsco		Amsco		Amsco	Amsco			
U, gram/batch	344																				
U, gram/liter			5.46			1.56		5×10^{-4}	1.29			5×10^{-5}	1.09		3.9×10^{-4}	4.35			4.35	200	
ss, gram/batch	5430 ⁽¹⁾																				
ss, gram/liter			86.2			24.6		24.6													
H ₂ M	12.0	6.0	4.69		13.0	4.17		3.85	0.30			0.58	0.004	0.01		0.02				0.8	
SO ₂ M	6.0		4.29			1.22		1.22													
NO ₂ M		6.0	0.62		13.0	3.00		2.68	0.30				0.01	0.01	0	0.06		0.06	2.5		
Al(NO ₃) ₃ M									0.70		0.70										
NH ₄ OH M									0.60			0.60									
NH ₄ NO ₃ M																					
SP, gr	1.335	1.187	1.3	1.0	1.367	1.18	0.78	1.17													

- (1) About 50 grams of steel wool was charged to the dissolver to initiate the dissolution of stainless steel.
- (2) Consists of two consecutive water rinses.
- (3) Includes jet dilution.
- (4) The actual dissolver performance was 3.3 batch dissolutions per day; however only the solution from 2.9 batch dissolutions per day was processed through the solvent extraction system.

The chemical reactions which took place after the nitric acid was added to the dissolver are:

Silicon dioxide, also present in the fuel elements, was insoluble in both acids and left the dissolver as finely divided solids. No provisions were made to clarify the feed during this campaign; however, a feed clarification step would be desirable during any future campaign using this process.

Solubility was another factor that governed the preparation of the flowsheets for this process. The concentration of stainless steel in sulfuric acid was limited to about 120 grams per liter to avoid any possible precipitation problems⁽³⁾. Furthermore, the composition of the adjusted dissolver product had to be in a range as shown in Figure 3 to guarantee long term stability. This relationship is based on the results of previously reported laboratory work⁽³⁾.

FIG.3 STABILITY OF NITRATE - CONTAINING STAINLESS STEEL SOLUTIONS⁽³⁾

During processing, either one heavy element or two light elements were charged into the dissolver along with steel wool to initiate the stainless steel-sulfuric acid reaction. The steel wool was required because the Carpenter-20 material of the dissolver has a passivating effect on stainless steel. The stainless steel was dissolved in an excess of boiling 6M acid, usually 300 percent of the stoichiometric amount of acid required, over a set period of time, initially about four hours. As the campaign progressed, this dissolution time was changed as necessary to obtain a high throughput rate and yet guarantee complete dissolution.

After completion of the sulfuric acid dissolution, 6M nitric acid (a slightly larger volume than theoretically required) was slowly added to the dissolver contents to dissolve the slurry of uranium dioxide. This mixture was maintained at the boiling temperature for an additional hour. The contents of the dissolver were then transferred to a coarse feed vessel for feed adjustment with concentrated nitric acid and for sampling to obtain uranium input data prior to the solvent extraction step in the process. Adjustment with nitric acid was necessary because additional nitrate ion was required during the subsequent extraction step for salting the uranium into the organic phase. This additional nitric acid also increased the stability of the dissolver product solution and inhibited corrosion on subsequent stainless steel equipment.

Before being recharged with fuel elements, the dissolver was rinsed with water sufficiently to guarantee that the nitrate ion concentration in the dissolver during the subsequent sulfuric acid dissolution would be less than 0.01M. This was necessary because nitrate ion passivates stainless steel to sulfuric acid even in the presence of steel wool.

The dissolver product from up to ten charges of fuel elements was accumulated in the coarse feed adjustment vessel before a uranium input sample was taken; this was done to minimize the amount of analytical work required during the campaign. After sampling, the contents of the coarse feed adjustment vessel were transferred to a vessel which was used to feed the extraction or A column in the solvent extraction process.

In the solvent extraction system, the adjusted dissolver product was introduced near the top of the A column. Here the uranium and some acid were extracted into the organic phase, thereby accomplishing a separation from the fission products and other metallic components of the fuel elements. The extractant used was ten volume percent TBP in a kerosene diluent, Amsco. The organic stream containing the uranium flowed to the scrub or B column where it was contacted with a scrub or IBS stream, principally aluminum nitrate, to remove fission products and nitric acid. The spent scrub stream was contacted with an extraction or IBX stream, ten percent TBP in Amsco, in the lower part of the B column to extract any uranium picked up in the top section of the column. Essentially all uranium entering the B column left with the product or IBP stream to flow into the strip or C column. Here the uranium was stripped back into an aqueous phase. In the last wash or D column the aqueous stream from the C column was washed with Amsco to remove traces of TBP before the aqueous stream was concentrated in an evaporator. The concentrated uranium product then was stored for future processing through two hexone extraction cycles.

With respect to nuclear safety during processing, there was no significant problem with the VBWR fuel. The stainless steel dissolver and the extraction system used for this process were geometrically safe under all circumstances. The only vessel in the entire system requiring administrative control to guarantee nuclear safety was the coarse feed adjustment vessel which has a non-safe diameter. Therefore, following the considerations described in Appendix B, the combined total mass of U-235 allowed in the feed adjustment vessel and in the dissolver, ie, the dissolution system at any time was limited to 5.5 kg.

The amount of U-235 leaving the dissolution system (ie, the amount of U-235 transferred from the coarse feed vessel, E-102) was carefully determined by analytical and volumetric measurements. It was estimated that the uncertainty in the measurement was less than six percent of the cumulative measured content of U-235 in that vessel. For the overall material balance, the unirradiated U-235 value for the fuel elements (instead of the estimated irradiated value) as shown in Table 1 was

used to calculate the amount of U-235 entering the system. This intentional bias in the actual amount of U-235 charged to the dissolution system provided an additional margin of safety to guarantee that the maximum amount of U-235 in the dissolution system did not exceed 5.5 kg. When the cumulative unaccounted U-235 (due to neglect of burn-up in input measurements, to measurement uncertainty, and to residual U-235 in the dissolver) plus a new charge of U-235 approached 5.5 kg, a heel cleanout was made.

A heel cleanout of the dissolver was performed by making a regular two-step acid dissolution with no additional fuel elements added to the dissolver. A cleanout of the course feed adjustment vessel was performed simultaneously by washing that vessel with 300 liters of 13M nitric acid. This acid was sampled and then used to adjust the composition of successive batches of dissolver product.

IV. DISCUSSION OF RUN

1. Fuel Dissolution

1.1 Performance

A total of 153 fuel elements containing 37.0 kg of uranium (32.8 kg of U-235) and approximately 514 kg of stainless steel were processed during the run. In addition 8 kg of uranium in an uranyl sulfate solution were processed through the solvent extraction system but not the dissolution system. Data relative to the dissolution of the elements are summarized in Table II. These data are for batches of feed material transferred to the solvent extraction system, and each set of data represents the dissolver product generated from dissolving eight to ten charges of fuel. In effect, each set of data represents two-plus days of operation and show average conditions for such an operating period.

The throughput rates achieved in the dissolution part of the process, after the first few days of operation, ranged from about 15 to 18 kg of stainless steel per day for both one- and two-element fuel charges. Throughput was limited to a significant extent by the batching chores of the process (ie, dissolver rinsing, fuel charging, and solution transfers) as well as by the fuel dissolution rates. The average cycle time shown in Table II represents the average time spent per fuel charge to rinse the dissolver, charge the fuel, and then transfer solutions into the course feed vessel. Although the cycle time for two-element charges to the dissolver averaged about eight hours as compared to about five hours for the one-element charges, the overall throughput rate for all elements was about the same.

For the one-element charges, the dissolution time with sulfuric acid was gradually reduced from about 4.0 to 2.5 hours with no adverse effect on the dissolution. With the two-element charges, the sulfuric acid dissolution time was varied between three and four hours depending on how well the dissolution proceeded as indicated by the specific gravity of solution in the dissolver. In one other technique used to optimize dissolution conditions, the sulfuric acid was reduced from 300 to 250 percent of stoichiometric requirements for the two-element charges. Dissolution rate, presumably a function of the quantity of acid used in the dissolver, was not significantly affected by this change.

TABLE II

SUMMARY OF THE VBWR FUEL ELEMENT DISSOLUTION PROCESS

Fuel Charge (No.)	Elements per Charge	Feed Batch (No.)	Average Cycle Time (hours)	Average Volume Per Dissolution (liters)	Coarse Feed Composition			Throughput Rate	
					Uranium (g/l)	SO ₄ ⁼ (M)	SS (g/l)	U (kg/day)	SS (kg/day)
1-8	1	1	8.8	262	1.535	0.97	14.1	1.10	10.1
9-16	1	2	7.3	210	2.175	1.13	17.6	1.50	12.1
17-26	1	3	6.9	204	1.730	1.09	18.1	1.23	12.9
27-34	2	4	8.7	232	1.540	1.36	23.7	0.98	15.1
35-40	2	5	8.6	229	1.525	1.35	24.0	0.97	15.3
41-46	2	6	7.1	242	1.440	1.13	22.5	1.18	18.4
46A-54	2	7	7.2	232	1.370	1.17	20.7	1.19	18.0
55-64	1	8	5.4	204	1.385	1.12	16.7	1.26	15.2
65-74	1	9	5.2	195	1.260	1.14	19.4	1.13	17.4
75-83	1	10	5.1	197	1.235	1.12	19.2	1.15	17.9
84-92	1	11	5.0	189	1.280	1.18	20.0	1.15	18.0
93-99A	1	12	5.6	192	1.125	1.00	17.0	1.07	16.2
99B-107	1	13	5.2	199	0.875	1.02	15.3	1.00	17.5
108-116	1	14	5.1	192	1.100	1.16	20.0	1.00	18.2
117-124A	1	15	5.1	209	0.860	1.06	16.4	0.95	18.1
Average:									
E-102 batch									
No. 4 - 7			7.9	233	1.463	1.25	22.6	1.07	17.9
E-102 batch									
No. 8 - 15			5.2	198	1.324	1.10	17.9	1.10	17.4

In general, the dissolution process was entirely satisfactory. In three of the fuel charges (No. 99, 102, and 121) out of a total of 124, the stainless steel did not dissolve significantly in the first batch of sulfuric acid fed into the dissolver, probably due to the presence of nitrate ion. In these cases, after the dissolver was jetted free of acid and water rinsed, the stainless steel dissolved readily in a second batch of sulfuric acid.

It was necessary to make three dissolution-system cleanouts (dummy dissolutions 46A, 99B, and 124A) during the campaign because of the uncertainty in the uranium accountability measurements resulting from an arbitrary assumption used in the dissolver "heel" calculations. Totals of only two and three grams of uranium were removed from the dissolver and course feed adjustment vessel, respectively, during these cleanouts. Clearly, the assumed combined error in volume and analytical measurements (six percent of the total uranium processed) was extremely conservative for this process. In any future operation, it may be possible to choose a smaller error value and thereby decrease the number of cleanouts to obtain a higher overall throughput rate.

1.2 Operating Problems

The only significant problem encountered during the dissolution part of the processing involved an occasional pressurization of the dissolver when two elements per charge were dissolved. The pressurization generally occurred very briefly when nitric acid was started into the dissolver in the second step of the dissolution. This problem was minimized later in the campaign by carefully regulating the nitric acid input rate to the dissolver.

2. Solvent Extraction

2.1 Performance

Overall uranium recovery from the first solvent extraction cycle was 99.69 percent; logarithmic gross fission product decontamination factors for the product exceeded 4.6. Total uranium losses to the extraction, scrub, and strip column raffinate streams were 93.2, 2.1, and 44.5 grams, respectively. The overall daily throughput rate for the solvent extraction

system averaged 0.97 kg of uranium or 11.1 kg of stainless steel, and the waste generation rate for the run averaged 267 gallons per kg of uranium dissolved. Approximately 89 percent of the waste from the run was generated as raffinate from the extraction column. The remainder was generated as raffinate from the scrub column and a solvent wash mixer-settler.

The average throughput rates achieved for various batches of feed introduced to the system along with other information relative to the solvent extraction processing are shown in Table III. For part of the run (feed batches 9-14), when uranyl sulfate solution from Atomics International, Inc., was being processed through solvent extraction along with dissolver product from the VBWR elements, uranium throughput rates were as high as 1.6 kg per day. These high uranium throughput rates were a result of an increased uranium concentration in the feed, not a result of any significant change in the flow rates to the extraction system.

As shown in Table III, essentially two-thirds of the total uranium loss occurred in the raffinate stream from the extraction column. Analysis of the plant data indicates much of the uranium loss to this raffinate stream was caused by two related factors: erratic flow rates of streams to the extraction column and a high concentration of silicon solids in the dissolver product. During processing, there were alternate means for transferring the aqueous dissolver product stream to the extraction column--an airlift and a feed metering pump; however, satisfactory flow control was impossible with either. Better control was achieved with the airlift; hence, it was normally used. However, solids eventually plugged the airlift which necessitated using the pump for the latter part of the run.

The aqueous feed rate to the extraction column, as shown in Table III, ranged from 0 to 80 l/hr* with a standard deviation on a batch-to-batch basis varying from 4.5 to 13.3 l/hr. Flow control for the organic stream

* The zero flow rate of the aqueous feed stream for feed batch No. 1 occurred when it was impossible to control or throttle the feed metering pump; ie, the flow was either nothing or greater than 50 liters/hour. At this time, use of the pump was discontinued and the A column was fed with an airlift. The zero flowrates for feed batches 12 through 15 occurred when the airlift plugged.

TABLE III

SUMMARY OF COLUMN PERFORMANCE AND FEED RATE VARIATIONS

Feed Batch	Extraction Column Feed Rates								Volume Flow Ratio, IAF IAX	Uranium Losses in Columns (grams)			Average Processing Rate (kg/day)							
	Aqueous Stream, IAF (liters/hour)				Organic Stream, IAX (liters/hour)					A	B	C	U	SS						
	Ave	Std Dev	Low	High	Ave	Std Dev	Low	High												
1(a)	31.7	13.3	0	80	31.3	3.0	26	42	1.01 ± 0.44	6.479	0.399	13.714	1.17	10.7						
2(a)	34.5	11.1	16	63	33.6	2.3	29	39	1.03 ± 0.34	4.418	0.031	2.847	1.80	14.6						
3(a)	30.4	10.3	13	57	32.7	2.4	26	38	0.93 ± 0.32	0.735	0.032	1.905	1.26	13.2						
4(b)	25.5	7.6	10	61	31.5	2.5	25	36	0.81 ± 0.25	13.749	0.032	1.454	0.94	14.5						
5(b)	23.8	6.7	7	43	32.1	2.6	26	38	0.74 ± 0.22	4.349	0.046	1.294	0.87	13.7						
6(b)	26.7	10.0	11	64	32.6	1.9	25	36	0.82 ± 0.31	0.164	0.045	0.613	0.92	14.4						
7(b)	29.4	7.5	11	54	32.8	3.9	26	41	0.90 ± 0.25	0.521	0.035	0.336	0.97	14.6						
8(a)	33.6	5.2	29	54	32.0	3.5	28	39	1.05 ± 0.20	3.072	0.033	0.316	1.12	13.5						
9(a)	32.0	4.5	24	40	31.2	1.8	27	34	1.03 ± 0.16	0.720	0.023	0.290	1.51(c)	14.9						
10(a)	33.8	9.2	22	65	31.0	1.9	25	34	1.09 ± 0.30	6.754	0.021	0.593	1.61(c)	15.6						
11(a)	27.7	6.0	18	44	32.3	3.5	27	40	0.86 ± 0.21	2.497	0.031	0.417	1.23(c)	13.3						
12(a)	32.5	11.5	0	62	31.9	3.0	26	39	1.02 ± 0.37	20.878	0.114	3.703	1.58(c)	13.3						
13(a)	26.7	10.0	0	50	32.4	3.7	26	39	0.82 ± 0.32	11.971	0.031	0.646	0.93(c)	9.8						
14(a)	24.2	8.7	0	47	33.3	4.0	26	40	0.73 ± 0.28	0.652	1.190	14.192	1.11(c)	11.6						
15(a)	31.0	8.1	0	45	31.5	4.0	25	40	0.98 ± 0.29	16.223	0.032	2.177	0.64	12.2						
TOTAL											93.182	2.095	44.500							
Ave: (Batch 4 - 7)										26.5	8.1			32.2	2.8		0.82 ± 0.26		0.93	14.3
Ave: (Batch 8 - 15)										31.5	9.8			31.9	2.9		0.99 ± 0.32		1.27(c)	12.9

(a) Processing with flowsheet on Figure 1.

(b) Processing with flowsheet on Figure 2.

(c) Includes uranyl sulfate solution from Atomics International, Inc.

was significantly better. The rate ranged from 25 to 42 l/hr, with a standard deviation varying between 1.8 and 4.0 l/hr. Along with these widely varying flow rates, the volume ratio of the aqueous and organic streams also varied; the standard deviation of this ratio varied from 0.16 to 0.44. During periods of exceptionally erratic flow rates, the uranium concentration in the raffinate stream was over an order of magnitude higher than during periods of steady flow. Ten percent of the raffinate produced during the run contained over 66 percent of the total uranium losses from the A column.

As the run progressed, accumulation of silicon solids in the feed tanks became increasingly troublesome. The solids increased the feed flow control problems and periodically plugged the feed lines. Water used to flush the plugged lines introduced an adverse effect to the process in that the water diluted the feed and lowered the salting strength in the extraction column which resulted in higher uranium losses. The feed containing the high concentration of silicon solids contained less than 24 percent of the uranium recovered during the run; however, greater than 53 percent of the uranium losses encountered during the run were incurred while processing this material. In addition, 32 hours of processing time were lost while the plugged lines were flushed.

In spite of the annoying problems with erratic flow rates and silicon solids, many portions of the run were relatively trouble-free; during these times, the flowsheets shown on Figures 1 and 2 typified the process. Using these flowsheets, uranium distribution coefficients as shown on Figure 4, and the height of the columns, a value for the height equivalent to a theoretical stage, HETS, was calculated for the extraction and stripping columns. Respective values were 3.4 and 6.2 feet. The value of 3.4 feet for the extraction column is consistent with values ranging from 2.4 to 3.7 feet reported⁽³⁾ for pilot plant studies involving similar types of solutions. During trouble-free plant operation the extraction column had 6.2 theoretical stages and the stripping column had 2.1 stages.

FIG. 4 DISTRIBUTION OF URANIUM BETWEEN AQUEOUS SULFATE PHASE AND TEN VOLUME PERCENT TBP PHASE

2.2 First-Cycle Decontamination Factors

Fission product decontamination for the uranium product was entirely satisfactory as shown by the data in Table IV. These data were obtained from two sets of samples of feed solution to the extraction column and of first cycle product taken during widely spaced periods of the run and during periods of trouble-free operation.

TABLE IV

FIRST CYCLE LOGARITHMIC DECONTAMINATION FACTORS

<u>Total Gamma</u>	<u>Total Beta</u>	<u>Ru-106</u>	<u>Cs-137</u>	<u>Pu</u>	<u>Co-60</u>	<u>Ce-144</u>
4.8	4.4	3.4	6.1			
4.6	5.2		4.8	0.8	5.1	4.4

2.3 Waste Volume

While processing with the flowsheet shown on Figure 1 (one-element dissolutions) about 277 gallons of waste were produced per kg of uranium processed; with the flowsheet on Figure 2 (two-element dissolution) about 233 gallons of waste per kg of uranium were produced to result in the overall average waste generation rate of 267 gallons per kg of uranium. About 89 percent of the total waste generated consisted of raffinate from the extraction column; the remainder consisted of the raffinate from the scrub column and the wash solution from the first stage solvent-wash mixer-settler. The raffinate from the extraction column was segregated from the other wastes for storage.

Analysis of the data indicates that 45 of the 267 gallons of waste per kg of uranium originated from the second dissolver water rinse used with each charge of fuel. During the campaign, this water rinse was added to the dissolver product to minimize uranium losses. Had this water been discarded to process equipment waste (PEW) for concentration, the uranium losses would have increased from 0.31 to 0.43 percent. It is believed that for any future use of this process, the merits of minimizing uranium losses at the expense of increasing the volume of waste should be economically evaluated. (To avoid corrosion and stability problems, sulfate wastes from this process are never concentrated.) Using present economics, the results of this campaign indicate that the second dissolver rinse should either be concentrated prior to mixing with the dissolver product or discarded to the PEW system.

2.4 Operating Problems

The most serious problem encountered during the VBWR campaign involved the erratic flow rates to the extraction column as already discussed. Other problems involved the flooding of an aqueous wash column in the extraction system and an inadvertent transfer of some uranium to a PEW tank--a large vessel in the process building used for temporary storage of waste solutions.

The column flooding problem involved a 1.28-inch ID column packed with 1/4-inch raschig rings. This column was used to wash TBP and its

degradation materials from the aqueous product. At flowsheet rates, the column consistently flooded; therefore, the volume ratio of the organic and aqueous phases in this unit was reduced from 1/10 to 1/48. A mock-up of the column showed that the 1/4-inch packing was the cause of the problem and that the problem could be eliminated by replacing the packing with 3/8-inch raschig rings or by pulsing the column and continuing to use the existing packing. Neither approach was practical for this run.

The uranium loss to the PEW tank occurred early in the run and was linked to maloperation of the first cycle product evaporator. Normally, the uranium product was concentrated to flowsheet specifications in the evaporator and then transferred to an intermediate jacketed storage vessel, F-125, until a sufficient quantity was accumulated for transfer to inter-cycle storage vessels in N Cell. On some occasions the product in F-125 was more dilute than desired; consequently an attempt was made to concentrate this uranium product in F-125. The boiling rate in this small diameter vessel was difficult to control and, during one period of time, enough vapor was generated to carry almost 1600 grams of uranium up into a vent line connected to the PEW tank. All of the PEW solution containing this uranium was transferred to J Cell; the uranium was eventually recovered by processing through a solvent extraction system. Further problems of this type were avoided by using the evaporator solely to concentrate product solutions.

V. RECOMMENDATIONS FOR FUTURE OPERATIONS

There is now no intent to ever employ the small scale equipment used during this run for processing other stainless steel alloyed fuels. An electrolytic dissolver is currently being installed at the Savannah River Plant for processing this type of fuel. However, should an incentive ever develop to process stainless steel fuel at ICPP using a sulfuric acid process, some consideration should be given to employing a slightly different flowsheet than the one used for the VBWR fuel. Furthermore, should the equipment in F Cell be employed for any type of processing, certain equipment modifications should be made. Our recommendations follow.

1. Flowsheet Modifications

The most obvious area for flowsheet improvement involves waste generation. During this campaign approximately 267 gallons of first cycle waste were generated per kg of uranium processed. It is believed that this rate can be decreased to less than 100 gallons per kg of uranium for fuel similar to VBWR fuel by discarding some of the dissolver rinse solutions (at the expense of a small increase in overall uranium loss) and by using less acid during the dissolution step.

An example is shown in Table V of one possible flowsheet that may be used for the processing of stainless steel fuels using a sulfuric acid process. For simplification, it was assumed the fuel would be similar to the VBWR heavy elements. Furthermore, it was assumed that less sulfuric acid than that amount used on this campaign could be used for dissolution. This assumption is based on reported relationships⁽⁴⁾ that indicate no significant decrease in dissolution rate (for Type 304 stainless steel) results from using 200 percent instead of 400 percent of the stoichiometric sulfuric acid requirements. Use of a smaller amount of sulfuric acid would permit the charging of two elements per batch dissolution.

The result of these changes is an aqueous feed stream containing more sulfate, stainless steel, and uranium and less nitrate than the

TABLE V

RECOMMENDED FLOWSHEET FOR PROCESSING STAINLESS STEEL FUEL ELEMENTS^(a)

	Metal ^(b) Charged	Dissolver Reagents		Dissolver Product	Water ^(c) Rinse	Coarse Feed Adjustment	Coarse ^(d) Feed	Fine Feed, ^(d)		
		H ₂ SO ₄	HNO ₃					IAF	IAX	IAR
Liters/batch		48.5	10	58.5	40	28	130	136		
Liters/hour								14.2 ^(e)	32	14.2 ^(e)
HNO ₃ , M			13.0			13.0				
H ₂ SO ₄ , M		6.0								
Uranium, g/l				10.1			4.54	4.34		2x10 ⁻³
Uranium, g/batch	590									
H ⁺ , M				3.78			4.50	4.30		
SO ₄ ⁼ , M				4.97			2.24	2.14		
NO ₃ ⁻ , M				0.57			3.05	2.92		
ss, g/l				129			58	55.4		
ss, g/batch	7540									
TBP, %									10	

(a) Assuming fuel elements similar in composition to the heavy VBWR elements.

(b) Charge 50 grams of steel wool with each fuel element to catalyze the stainless steel dissolution. Two fuel elements constitute a single batch dissolution.

(c) Dissolver rinses consist of three 40-liter batches of water to reduce residual nitrate ion concentration in dissolver below 0.01M. The second and third rinses are sent to waste.

(d) Includes four percent jet dilution.

(e) Based on 2.5 dissolutions per day.

feed streams processed during this run. In order to achieve satisfactory extraction of this type of feed stream, an aqueous to organic ratio of 0.44 was used in the recommended flowsheet. One other benefit with the recommended flowsheet is that a greater throughput rate could be obtained, 1.5 kg of uranium daily as compared to the 1.1 kg attained during the VBWR campaign.

A comparison of various facets of the VBWR flowsheet and the recommended flowsheet is shown in Table VI.

TABLE VI
COMPARISON OF VBWR FLOWSHEET WITH RECOMMENDED FUTURE FLOWSHEET

	<u>VBWR Flowsheet (a)</u>	<u>Future Flowsheet</u>
Metal charged: Uranium, g	295	590
Stainless steel, g	3770	7540
Sulfuric acid used, percent of stoichiometric	300	200
Nitric acid dissolvent, M	6	13
Dissolutions, No./day	3.7	2.5
Volume of coarse feed, liters/batch	197	130
Process rate, kg U/day	1.1	1.5
Feed rate, liters/hr	31.5	14.2
Aqueous-to-organic ratio in A column	0.99	0.44
Waste generation rate, gal/kg U	206 ^(b)	74
<hr/>		
(a) Data represents processing with flowsheet on Figure 1.		
(b) The actual rate was 277 gal/kg U.		

2. Equipment Modifications

Recommended equipment modifications are as follows:

- (1) The wash or D column in F Cell could be a bottleneck for any type of processing. Throughput can be increased by providing a means to pulse this column or by replacing the existing packing with 3/8-inch raschig rings.
- (2) A means should be considered to continuously remove solids from dissolver product. This recommendation is applicable for much

of the solvent extraction processing at ICPP and, if adopted, could alleviate a recurring problem for various fuels.

- (3) The erratic flow rates experienced during this campaign with the solvent extraction system are extremely undesirable. A means should be provided to control all flow rates either with instrumentation or dependable feed metering devices.

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APPENDIX A--DESCRIPTION OF MAJOR PIECES
OF EQUIPMENT USED IN PROCESSING VBWR FUEL

APPENDIX A--DESCRIPTION OF MAJOR PIECES OF EQUIPMENT USED IN PROCESSING VBWR FUEL

1. Dissolver

The dissolver is a jacketed pipe-like vessel, six inches in diameter, 24.5 feet in height, and fabricated of Carpenter-20 stainless steel. It has an operating volume of 100 liters. The top section of the vessel acts as a slug chute. In the lower section, approximately sixteen inches from the vessel bottom, is a star-shaped crash plate to absorb the shock of falling fuel elements. Two jackets are provided; the lower for both heating and cooling, the upper for cooling only. Near the top a spray ring is provided for decontamination.

2. Dissolver Off-Gas Scrubber

The dissolver off-gas scrubber has two parts: a lower surge tank section and an upper packed section. The lower section is two feet in diameter with a two-foot straight shell, and is of adequate size to hold a 100-liter batch of scrub solution which is recirculated through the upper packed section. The packed section is six inches in diameter and seven feet in height and is packed with 1/2-inch by 1/2-inch Type 304 stainless steel raschig rings.

3. Columns

The extraction, scrub, and strip columns are pulse plate type columns fabricated of Type 347 stainless steel. The plates are perforated with one-eighth inch holes, giving a free area of about 24 percent, and are spaced on two-inch centers. The plates are supported by a 0.75-inch solid rod centered vertically in the column. The wash column is packed with 1/4-inch by 1/4-inch Type 304 stainless steel raschig rings. The size and capacity of the columns are shown in Table A-I.

TABLE A-I
SIZE AND CAPACITY OF COLUMNS

<u>Column</u>	<u>Function</u>	<u>Plate or Packing Height (feet)</u>	<u>Inside Diameter (inches)</u>	<u>Flooding Capacity (liters/hour)</u>
A	Extraction	21.06	3.000	122
B	Dual: Scrub	5.58	2.023	51
	Extract	12.25	1.310	20
C	Strip	13.06	2.023	53
D	Wash	10.00	1.278	---

4. Product Evaporator

The product evaporator is a standard thermal recirculation type, fabricated of Type 347 stainless steel and containing 1.89 square feet of heating surface. Above the thermal leg is an eight-inch diameter de-entrainment section, 32 inches in height. The top eight inches of the de-entrainment section is packed with 1/2-inch stainless steel raschig rings. An overflow is furnished at the top of the four-inch diameter thermal leg to prevent buildup of product solution in the de-entrainment section, whose eight-inch diameter is too large to assure the prevention of a critical incident.

APPENDIX B--NUCLEAR SAFETY CONSIDERATIONS

APPENDIX B--NUCLEAR SAFETY CONSIDERATIONS

Equipment used to process the VBWR fuel, with exception of the feed vessels shown on Figures 1 and 2, is geometrically safe. The feed vessels are four feet in diameter with a capacity of about 2900 liters; administrative control is necessary to prevent the accumulation of a critical mass of U-235 in these vessels. Nuclear safety calculations indicated that 5.6 kg of U-235 was the minimum mass of uranium that could produce a k_{eff} of 0.90. An optimum concentration of 23 grams U-235 per liter is required for the 0.90 k_{eff} with this mass. Based on these results, the maximum amount of uranium in any non-geometrically safe feed vessel was limited to 5.5 kg of U-235. The only vessel in the process with the possibility of exceeding this limit is the coarse feed adjustment vessel because the chemistry of the process prevents the accumulation of 5.5 kg of uranium in other vessels.

In determining the minimum uranium mass for a k_{eff} of 0.90, the following assumptions were used in the nuclear safety evaluation:

1. All uranium transferred from the dissolver to the feed adjustment vessel would be in the form of undissolved UO_2 in an aqueous slurry.
2. Water instead of nitric acid would be used to adjust the composition of the dissolver product in the feed adjustment vessel and thus prevent dissolution of UO_2 .
3. All uranium entering the coarse feed adjustment vessel would settle uniformly toward the bottom of the vessel, and during settling the uranium concentration would pass through the optimum resulting in a condition of maximum reactivity.

In the evaluation, to simulate settling, the uranium concentration in the solution was increased mathematically from an initial concentration of 6.4 to a practical limit of 128 grams per liter with a constant stainless steel concentration. This condition simulates a half-reflected slab of uranium dioxide particles uniformly suspended in stainless steel solution in the bottom of the vessel with a slab of reflector on top.