UNCLASSIFIED

BNWL-CC-2461

BATTELLE NORTHWEST

BATTELLE MEMORIAL INSTITUTE PACIFIC NORTHWEST LABORATORY

POST OFFICE BOX 999 / RICHLAND, WASHINGTON 99352

COPY AND SERIES NO.

DATE

February 1970

MASTER

TITLE AND AUTHOR

PILOT PLANT DEMONSTRATION OF THE PLUTONIUM
RECLAMATION FACILITY CC, CR, AND CX COLUMNS

W. F. Bonner and G. L. Richardson

CONTRACT

☐ - 1830☐ - 1831

PROJECT NO.

RESERVED FOR TECH. INFO. USE

D I S T R I B U T I O N

NAME	COMPANY	LOCATION	NAME	COMPANY	LOCATION
SJ Beard	ARHCO	2704E-200E	WF Bonner	BNW	308 - 300
LI Brecke	ARHCO	234-5 200W	DG Bouse	BNW	325 - 300
LE Bruns	ARHCO	234-5 200W	LA Bray	BNW	325 - 300
MH Campbell	ARHCO	234-5 200W	RE Burns	BNW	324 - 300
AH Case	ARHCO	234-5 200W	RL Moore	BNW	325 - 300
RP Corlew	ARHCO	Fed. Bldg.	LD Perrigo	BNW	324 - 300
MH Curtis	ARHCO	234-5 200W	GL Richardson (10)	BNW	324 - 300
RE Isaacson	ARHCO	2704-Z 200W	EJ Wheelwright	BNW	325 - 300
MJ Klem	ARHCO	234-5 200W			
LM Knights	ARHCO	234-5 200W			
GC Oberg	ARHCO	202-A 200E			
RE Olson	ARHCO	234-5 200W			
RL Walser	ARHCO	202-A 200E			
WL Schick	ARHCO	234-5 200W			
WW Schulz	ARHCO	222-s 200W			
MJ Szulinski	ARHCO	2704-Z 200W			
JA Teal	ARHCO	234-5 200W			
RE Tomlinson	ARHCO	2704-E 200E			
JT Christy	AEC	Fed. Bldg.			
OJ Elgert	AEC	Fed. Bldg.			

Tech. Information (3)
Tech. Pubs. (2)

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ROUTE TO	PAYROLL NO.	COMPANY	LOCATION	FILES ROUTE DATE	SIGNATURE AND DATE
	NOTICE				NOTICE
PORTIONS OF THIS REPORT ARE ILLEGIBLE. It has been reproduced from the best available copy to permit the broadest possible availability.			PORTIONS OF THIS REPORT ARE ILLEGIBLE. It has been reproduced from the best available copy to permit the broadest possible availability.		

UNCLASSIFIED

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
SUMMARY AND CONCLUSIONS	2
EQUIPMENT	3
MATERIALS AND OPERATING PROCEDURE	4
RESULTS	8
CC COLUMN	8
Dispersion Characteristics	8
Extraction Performance	10
Nitrite Effects	12
Variable CAP Flow Rate	16
CR AND CX COLUMNS	16
Operating Characteristics	16
CR Column Stripping Efficiency	18
CX Column Stripping Efficiency	19
Uranium Solubility in the CX Column	20
APPENDIX	
Table I Stream Compositions	
Table II Concentration Profiles	
Table III Operating Conditions and Results	

PILOT PLANT DEMONSTRATION OF THE PLUTONIUM RECLAMATION
FACILITY CC, CR, AND CX COLUMNS

W. F. Bonner and G. L. Richardson

INTRODUCTION

This report describes a series of pilot plant solvent extraction column runs in support of the Hanford Plutonium Reclamation Facility (PRF). The PRF has been testing a flowsheet for partitioning uranium from plutonium in the CC (plutonium stripping) column. This is accomplished by the addition of a short uranium scrub section to the top of the column and by providing sufficient reductant to the strip solution to assure complete reduction of Pu(IV) to Pu(III). However, the Plant tests showed that the flowsheet as originally conceived permitted excessive Pu(IV) reflux in the CC column, leading to high uranium contamination in the plutonium product, solids buildup in the column, and eventually high plutonium in the uranium product.⁽¹⁾ Attempts to stabilize the Pu(III) by the use of hydrazine failed because of sporadic gassing caused by reaction of hydrazine with nitrous acid introduced with the feed.

Flowsheet changes, demonstrated in the Applied Chemistry Laboratory, BNW, have been proposed for rectifying these difficulties.⁽¹⁾ These involve the addition of a second strip stream containing hydroxylamine nitrate ("HN") reductant about 4 ft below the solvent feed stream inlet and minimizing the nitrite addition to the feed. Further pilot plant testing was required to demonstrate that uranium could be adequately scrubbed from the plutonium product by the short (eight ft) scrub section available, that the gassing problem could be controlled by the use of hydroxylamine nitrate, and that the uranium leaving CC column solvent

could be adequately removed by the succeeding CR and CX columns. The uranium behavior and the dispersion and operating characteristics of these three columns (with plutonium absent) were investigated as described in this report.

SUMMARY AND CONCLUSIONS

Pilot plant uranium losses in the CAIS (plutonium product stream from the CC column) were below 0.04 g/liter, the maximum allowable contamination level, at near optimum pulsing conditions with up to 8 g/liter uranium in the CAP (CC column solvent feed stream). The maximum allowable uranium concentration in the PRF CAP was estimated to be only 5.4 g/liter, however, because of the inefficient removal of uranium from the solvent in the succeeding unpulsed CR and CX uranium stripping columns. A higher uranium concentration in the CAP would result in recontamination of the plutonium product by uranium recycle in the washed solvent used for the CCS (uranium scrub solution).

Gassing from the nitrite-hydroxylamine reaction, as well as from air addition to the column, had little effect on column performance. Addition of 3/4 in. Kynar[®] rings between the scrub section sieve plates, to simulate the current plant cartridge, slightly improved scrubbing efficiency. Decreasing the HNO_3 in the organic scrub stream from 0.5 to 0.1M increased the uranium in the plutonium product stream from 0.004 to 0.08 g/liter.

[®] Pennwalt Chemicals Corp - tradename for polyvinylidene fluoride.

The CR and CX columns, operating unpulsed with aqueous phase continuous and an aqueous/organic (A/O) flow ratio of 0.33, were capable of stripping 10-20% and 92-96%, respectively, of the column feed uranium. The uranium concentration in the stripped organic, however, was 2-4 times the desired specification limit. Operation with the organic phase continuous or with an A/O ratio of 0.67 had only a small effect on uranium removal. Supplying a 2.25 in., 40 cycle/min pulse to the CR column improved the uranium and acid removal 30-50%, while addition of a pulse to the CX column decreased the uranium loss at least three-fold. Pulsed operation of the CX column produced stripped organic solvent which was well within specifications.

EQUIPMENT

Battelle's pulse column demonstration unit in the 324 Building was used for the pilot plant studies.

CC Column

The PRF CC column was simulated by a 3 in. diameter glass column containing a 21 ft tall cartridge composed of 2 in. spaced, 23% free area sieve plates with 1/8 in. holes.

Following Run 7, 3/4 in. Kynar Raschig rings were packed between the plates of the 9 ft tall scrub section. The rings were placed such that the space above every sixth plate as well as a one foot section above the CAP feed point contained no rings. During replacement of the cartridge, about half of the plates were accidentally bent, some as much as 45° below horizontal. The bent plates appeared to have had negligible effect on column operation.

The CCS stream entered at the top of the cartridge while the CAP stream entered 9 ft below the CCS stream. The CCXF stream entered 3 ft below the CAP entry, and the CCX entered at the bottom of the cartridge.

The column contained sample ports and thermocouples at 3 ft intervals in the cartridge section and was equipped with enlarged disengaging sections at both ends. During operation, the interface was located in the bottom disengaging section 1 ft above the connection to the air pulser.

Flooding could be detected visually and inferred from static pressure readings at the bottom of the column.

CR and CX Column

The CR and the CX columns were simulated by a 4 in. diameter glass column packed with 7 ft of 1 in. Kynar Intalox[®] saddles. Disengaging sections at each end of the column were also 4 in. diameter. A 1 in. diameter pulse leg from an air pulser entered at the bottom, about 18 in. below the packing support. Packing supports were required above as well as below the packing to prevent packing pulsations during pulse operation. The organic feed entered one inch above the packing while the aqueous feed entered one inch below the packing.

MATERIALS AND PROCEDURE

Flowsheet

The basic flowsheet followed in this study, Figure 1, was derived from Figure 1 of ARH-1343.⁽¹⁾ The major change made for the pilot plant studies was the omission of plutonium. The salting effect of Pu(III) nitrate was simulated

[®] Tradename of U.S. Stoneware Co.

by adding an equivalent amount of nitrate (as NaNO_3) to the CCXF stream. Variations from the pilot plant flowsheet are summarized in Tables I and II in the Appendix.

Feed Stream Compositions

The nominal feed compositions corresponded with those shown in the flowsheet with the exceptions noted in Table I in the Appendix. Detailed uranium and HNO_3 analyses of the feed and effluent streams are presented in Table I.

The initial solvent was carbonate-washed, 20 volume percent TBP (tributyl phosphate) in CCl_4 . Washing was accomplished by contacting the organic with an aqueous 5% Na_2CO_3 solution in the CC column. The solvent was again washed prior to Runs 5 and 14.

Solvent feeds were prepared by adding concentrated aqueous uranyl nitrate (UNH) and/or HNO_3 solutions to the bottom of the feed tanks so that they bubbled through the solvent feed. The tanks were mixed by air sparging during and after the additions and allowed to settle at least 30 minutes before the run began.

Evaporation of the CCl_4 caused a gradual increase in the concentration of the TBP to about 22%. Prior to Run 12, CCl_4 was added to the solvent to reduce the TBP concentration to the original 20%. At the end of the program the TBP concentration had increased to 23%.

Gassing

Nitrous acid (as $\text{NaNO}_2 + \text{HNO}_3$) was added to the CAP stream in Run 3 to simulate the gassing observed in the PRF CC column. Difficulty was encountered in pumping the

* HN = HYDROXYLAMINE NITRATE

FIGURE 1. PILOT PLANT FLOWSHEET

CAP to the column because of vapor locking in the pump. Subsequent runs used air introduced in the bottom of the column at various rates, measured in standard cm^3 (scc)/min, to simulate gassing. Nitrite addition was tried again in Runs 12 and 13 by pumping 9M NaNO_2 directly into the CAP feed stream.

Run Length

Runs normally lasted for at least three throughputs of the continuous phase. Less time was allowed when changes were made which did not greatly upset the column concentration profiles. Three or more effluent samples were taken during the last quarter of the run to assure that steady-state had been attained.

Runs 24 and 25 were duplications of Runs 14 and 17, respectively. The run times for Runs 24 and 25 were about twice as great as for the prior runs to assure that steady-state was achieved.

Sample Analysis

Uranium and nitric acid analyses of run samples were performed by the Z Plant Analytical Laboratory Subsection, ARHCO. Uranium analysis was obtained by a fluorometric technique which is usually accurate to $\pm 20\%$. Equipment necessary for the more accurate X-ray absorptiometric method was not available at the time of the study. Uranium and nitric acid material balances ranged from 60 to 140%. The poor balances were apparently due to inaccuracies in the analytical methods. Two phase samples (from intermediate column taps) were pre-equilibrated before analysis.

Nitrite analyses were performed during the run. The analysis was performed spectrophotometrically by the use of the diazotization reaction with Amino G acid and formation of a purple azo dye with alpha-naphthylamine.

Calculation of Transfer Units

Transfer unit heights were calculated on an overall raffinate film basis by the method of Colburn.⁽²⁾ Average distribution ratio values for these calculations were obtained from batch equilibrations of the intermediate CC column samples or from published data.⁽⁶⁾

RESULTS

CC COLUMN

A total of 13 runs were made in the pilot plant CC column to investigate the effect of pulsing conditions and gassing on the dispersion characteristics and uranium scrubbing performance.

Dispersion Characteristics

Stripping Section

The CC column operated stably at the flow rates shown in Figure 1 up to pulse frequencies of 115 cycles/min with a 1 in. pulse amplitude. At these pulsing conditions, the dispersion in the lower, stripping section was extremely tight with small (1/16-1/32 in. diameter) organic droplets. A similar, but slightly more open, dispersion was obtained with a pulse of 70 cycles/min at a 1.5 in. amplitude. The dispersion was considerably less intimate at a frequency of 80 cycles/min and an amplitude of 1 in.

In each of the above cases the dispersion described refers to the section of the column slightly below the CAP feed point. A coarse dispersion (mixer-settler operation) predominated at the feed point. Below this the organic droplet size progressively decreased as the dispersion intimacy increased until the above described dispersion was obtained. The distance below the CAP feed point to where the tight dispersion began ranged from about 1 ft at 115 cycles/min to 3 ft at 80 cycles/min (1 in. amplitude).

Scrub Section

Without packing between the plates, a very loose dispersion of 1/16-1/32 in. diameter organic droplets was obtained in the scrub section at each of the investigated pulsing conditions. The dispersed phase holdup with the maximum pulsing conditions tolerable to the stripping section was well below that necessary to obtain optimum efficiency.

The addition of 3/4 in. Kynar Raschig rings between the scrub section sieve plates increased the size of the organic droplets (1/16 in. to 1/8 in.) due to organic coalescing on the rings. The dispersion was still very loose, but the film contact on the rings may have improved the scrubbing efficiency slightly.

Flooding

The CC column flooded first near the bottom of the column. Flooding consisted of a coalescence of the organic phase forming a local phase inversion which occupied approximately 1/3 of the column area as the organic pulsed down the column. The flooded region slowly moved up the column and would have eventually filled the entire stripping section if the test had been continued long enough. No flooding was observed in the scrub section with or without the rings.

Gassing

Air introduced to the column to simulate gassing from the nitrite-hydroxylamine reaction helped stabilize the column operation. In one test, a flooded condition in the column was quickly remedied by the introduction of 600 scc/min of air. The only apparent deleterious effect of gassing was entrainment of solvent in the CAIS product stream. An aqueous product sample was found to contain about 0.5% entrained organic at 4800 scc/min air flow.

Extraction Performance

Transfer Unit Heights (HTU's)

The scrub section uranium HTU's were found to be mildly sensitive to pulsing conditions. The HTU's, tabulated in Table III in the Appendix and plotted in Figure 2, show that, over the range investigated, the HTU was an inverse function of the product of pulse amplitude times pulse frequency (af). The HTU's ranged from 1.1 ft at an af product of 115 in./min to 1.7 ft at an af product of 80 in./min. On the basis of prior investigations, it is believed that the HTU would increase at a greater rate for af products lower than 80. HTU's were the same or slightly lower when the Kynar Raschig rings were inserted between the plates.

The effect of gassing (simulated by air) on extraction efficiency was minor. The HTU was increased by about 15% at an air flow of 600 scc/min, but was unaffected or lowered slightly by air rates of 1200 and 4800 scc/min.

FIGURE 2. CC COLUMN SCRUB SECTION TRANSFER UNIT HEIGHT VS AMPLITUDE-FREQUENCY PRODUCT.

Distribution Ratios and Concentration Profiles

Uranium equilibrium concentrations throughout the CC column are plotted in Figure 3 and tabulated in Table II. The average calculated distribution ratio (E_a) value, 7.53, was used in HTU calculations for each run. This value is consistent with the scrub section E_a values proposed by Bruns. (1)

Low Acid CCS Stream

Decreasing the HNO_3 in the CCS stream by a factor of 4 in Run 13 increased the scrub section uranium HTU by a factor of 3. The PRF reported a "fish egg" emulsion at the top of the column when operating with a low acid CCS stream. No such emulsion was observed during the CC column runs.

Nitrite Effects

Sodium nitrite is added to the CA column feed to adjust the plutonium valence. The resulting nitrous acid is quite extractable and appears in the CAP at a concentration estimated at 0.1 to 0.2M. This must be destroyed by reaction with hydroxylamine or hydrazine before Pu(IV) can be reduced to Pu(III) in the CC column. The reaction generates considerable amounts of gas, as discussed below.

Gassing with Hydroxylamine

Hydroxylamine nitrate reacts with nitrous acid according to the following equation: (3)

FIGURE 3. URANIUM EQUILIBRIUM DATA-
CC COLUMN SCRUB SECTION

Considerable gassing was expected in the nitrite-addition runs from generation of N_2O ; however, no gassing was observed during the first 30 minutes of the nitrite runs (Runs 3, 12, and 13). A reaction was evidently taking place, however, because the column temperature at the nitrite entry point (CAP feed point) steadily increased as the run progressed. Mild gassing began when the temperature reached 40 °C at the CAP feed point. The gas volume increased as did the temperature until a steady-state volume, estimated at 600 scc/min, was reached at a feed point temperature of 47 °C.

This phenomenon can be explained by the N_2O solubility in CCl_4 , as illustrated below:

The stoichiometrically limiting reagent in the above reaction as it occurs in the column is nitrous acid. The nitrous acid flow rate was about 130 mmols/min which can produce 130 mmols/min or 2910 scc/min of N_2O gas. The solubility of N_2O in CCl_4 ⁽⁴⁾ at 25 °C is 4.285 scc N_2O per ml of CCl_4 and at 40 °C is 3.565 scc N_2O per ml CCl_4 . The total organic flow below the CAP feed point was 844 ml/min of 80% CCl_4 . Assuming that the TBP dissolved the same amount of N_2O as did the CCl_4 , 3610 scc/min could have been absorbed at 25 °C; and 3000 scc/min could have been absorbed at 40 °C. Since this is about the amount of N_2O produced, it appears that any further increase in temperature will cause gassing.

The maximum column temperature occurred in the region of maximum gas formation, which was approximately 1 ft below the nitrite feed point. This was also the region where the organic feed droplets had been reduced to $\leq 1/16$ in. diameter and where maximum mass transfer of the nitrite to the aqueous phase would occur. Since the nitrite distribution coefficient at these conditions is about 10, the reaction must occur quickly, the rate being mass transfer controlled, or gassing would have occurred farther down the column.

Gassing with Hydrazine

Gassing problems in the PRF were greatly increased by the addition of hydrazine to the system. (1) The reaction of hydrazine with nitrous acid, represented as:

shows that both N_2 and N_2O gas are produced. The hydroxylamine-nitrite reaction previously discussed yields only N_2O . Because N_2 does not dissolve in the organic as does N_2O , considerably more gassing with hydrazine than with hydroxylamine would be expected.

The observed amount of gassing, however, was indistinguishable for pilot plant runs with and without hydrazine (Runs 12 and 13). The reason for this may be that the concentration of hydrazine at the feed point was 6-fold less than that of hydroxylamine. Even though the hydrazine reaction is regarded the faster of the two, the law of mass action indicates that the dominant reaction would be with hydroxylamine. Alternatively, the rate of hydrazine addition was only 58 mmol/min, which would produce a maximum of 630 scc N_2 /min from complete reaction with HNO_2 . Approximately 2200 scc/min of N_2O would be generated from the combined N_2H_4 -HN- HNO_2 reaction, and this amount should be completely soluble in the solvent. Thus, in this case the amount of visible gas (N_2) generated if a preferential N_2H_4 - HNO_2 reaction took place would be about the same as the amount of N_2O observed in N_2H_4 -free runs.

N_2O Removal From Solvent

Gassing during Run 12 was no more severe than in Run 3 even though the organic feed used in Run 12 should have

been saturated with N_2O from Run 3. This phenomenon is believed to result because the solvent was washed with an aqueous Na_2CO_3 solution prior to Run 12. Reaction of N_2O with Na_2CO_3 should yield aqueous-favoring sodium hyponitrite, $Na_2(NO)_2$, thus removing the N_2O from the organic. It is also believed that contact of the saturated organic solvent with K_2CO_3 in the CX column would produce the same result.

Variable CAP Flow Rate

The CAP flow rate in the PRF fluctuates considerably because of the action of the interface controller on the preceding CA column. These conditions were simulated during Run 12 by intermittent control of the CAP feed stream. The pulsed feed consisted of 3 minutes of no flow alternated with 3 minutes of flow at twice the normal average flow rate. As shown in Table III in the Appendix, the uranium HTU and waste loss were comparable to those attained in Run 1. The gassing and feed pulsing had little, if any, detrimental effect.

CR AND CX COLUMN

A total of 12 CR and CX column runs were made in the pilot plant to demonstrate the performance of a packed column for removing uranium and nitric acid from the spent CC column solvent.

Operating Characteristics

Nonpulsed Operation

The operating characteristics of the CR and CX columns in the range of conditions investigated were found to be

similar. Channeling of the organic was evident when operating either column with the aqueous phase continuous. A temporary threefold rate increase of the feed streams in either column induced frothing. The resulting "fish egg" emulsion flowing down the column not only reduced channeling but increased the organic holdup and degree of dispersion, indicating possible improved efficiency by increased flows.

Bottom interface operation without pulsing produced almost exclusively film contact with the organic phase completely wetting the Kynar saddles. With organic phase continuous (top interface) operation, a very loose dispersion of 1/8-1/16 in. diameter aqueous droplets was observed. Some of the aqueous phase wet the column walls and streamed upward. Flooding did not occur during any of the runs, including the pulsed runs below.

Pulsed Operation

Pulsing the column contents decreased the size of the droplets, tightened the dispersion, and increased the dispersed phase holdup. For both CR and CX columns with bottom interface (aqueous continuous) operation, pulsing drew the organic phase from the packing in 1/8-1/16 in. droplets which quickly coalesced on adjacent packing. The aqueous phase droplets were 1/16-1/32 in. diameter with organic phase continuous.

The maximum af product attainable with the existing air pulse system was 90 in./min at a 2.25 in. pulse amplitude. This was considerably below the pulse energy input necessary to get an optimum dispersion at the flow rates tested.

CR Column Stripping Efficiency

Without pulsing, the aqueous continuous CR column, operating with an A/O ratio of 0.35, removed 10 to 20% of the uranium and 80 to 90% of the HNO_3 from the CRF. As can be seen from the table below, doubling the aqueous flow rate increased the uranium removal to 60% and the

EFFECT OF MAJOR PARAMETERS ON CR COLUMN PERFORMANCE

Run No.	Pulsed	Interface Position	A/O Flow Ratio	Organic Effluent Conc; % of CRF		HNO_3 HTU, *
				Uranium	HNO_3	
14	No	Bottom	0.34	92	18	4.9
15	No	Bottom	0.66	38	8	3.5
16	No	Top	0.33	67	14	4.1
20	Yes	Top	0.38	55	8	3.2
21	Yes	Bottom	0.37	72	13	3.9
24	No	Bottom	0.36	83	12	3.9

* HNO_3 distribution ratio assumed to be 0.058, an average value⁽⁶⁾ for the range of acidities in the pilot plant tests.

HNO_3 to 90% of that in the feed. Operation with organic phase continuous and normal aqueous flow was slightly more efficient than aqueous-continuous operation.

Pulsing the CR column at 2.25 in. amplitude and 40 cycles per minute increased the uranium removal to 30-45% of the feed uranium and slightly increased HNO_3 removal. The more intimate dispersion obtained with the organic phase continuous again was slightly more efficient for uranium removal than the aqueous continuous case. The major limitation to uranium

removal was apparently the uranium reflux caused by the high acid content of the feed. Additional column height or increased pulse input would be required for improved uranium removal.

CX Column Stripping Efficiency

The CX column, operating unpulsed with bottom interface and an A/O ratio of 0.35, removed 92-96% of the feed uranium. As can be seen from the table below, increasing the A/O ratio to 0.67 had little effect on stripping efficiency. In contrast to the CR column, operation with the organic phase continuous was definitely less efficient than aqueous-continuous operation (only 84% of the feed uranium was removed).

EFFECT OF MAJOR PARAMETERS ON CX COLUMN PERFORMANCE

<u>Run No.</u>	<u>Pulsed</u>	<u>Interface Position</u>	<u>A/O Flow Ratio</u>	<u>U in Organic Effluent, % of CxF</u>	<u>Uranium HTU,* ft</u>
17	No	Bottom	0.36	4.2	2.9
18	No	Top	0.36	16.0	8.6
19	No	Bottom	0.66	6.7	3.4
22	Yes	Top	0.36	8.3	3.7
23	Yes	Bottom	0.35	0.04	1.2
25	No	Bottom	0.32	7.9	3.6

*Uranium distribution ratio assumed to be 0.

Supplying a 2 in. amplitude, 45 cycle/min pulse to the column lowered the uranium loss. Operation with an A/O ratio of 0.33 and bottom interface removed 99.96% of the feed uranium. Top interface operation stripped only 92% of the uranium.

The stripped organic from all CX runs was slightly acidic ($0.002-0.004M\ H^+$).

The combined effect of the observed CR and CX extraction efficiency on the proposed PRF flowsheet is illustrated as follows: With the CR and CX columns operating in series, unpulsed, with aqueous phase continuous, and an A/O ratio of 0.33, the organic leaving the CX column will contain about 7% of the uranium in the CR column organic feed. Thus, to obtain the tolerable maximum of 0.3 g/l uranium in the recycled stripped CX column organic, a maximum of 4.3 g/liter uranium can be allowed in the CR feed. This means that 5.4 g/liter uranium can be tolerated in the CAP stream (after correction for dilution by the CCS stream) without excessively recontaminating the plutonium CAS product with uranium recycled with the CCS. This represents a uranium processing rate in the PRF of about 8 kg/day at a nominal CAP rate of 60 liters/hr.

A dramatic improvement with pulsing can be expected, as was demonstrated in Run 23. The CX column, operating pulsed with a continuous aqueous phase, reduced the organic uranium concentration from 3.6 g/liter to 0.001 g/liter. Under these conditions feeds containing many times the above uranium concentration could be processed.

Uranium Solubility In The CX Column

Neither precipitation of uranium carbonate compounds nor gassing was observed during steady-state operation of the CX column. However, a milky, yellow precipitate formed in the aqueous layer near the interface during routine conversion from CX to CR operating conditions as the entering high acid CRF contacted the remaining CXX carbonate solution.

The precipitate did not redissolve but remained suspended

and overflowed with the aqueous effluent. Precipitation was not accompanied by gassing. The precipitate was assumed to be uranium hydroxide or sodium uranate.

Several special titrations were made to determine the uranium precipitation threshold in sodium and potassium carbonate solutions. Carbonate concentrations of 0.37M (5% K_2CO_3) and 1.5M were titrated with 1.6M uranyl nitrate-0.6M HNO_3 solution until a definite precipitate was observed. In all cases, the titrated solutions remained clear until the "free" carbonate*/uranium mole ratio had decreased below 4. The threshold ratio for a faint precipitate haze to appear was slightly lower with Na_2CO_3 and decreased with decreasing carbonate concentration. For initial 0.37M $CO_3^{=}$ solutions, the threshold free carbonate/uranium ratio for definite precipitation to occur was 3 for K_2CO_3 and 2 for Na_2CO_3 . Only a slight amount of precipitate formed at this threshold, and CX column operation should be unaffected by its presence. The data indicate that increasing the carbonate concentration in the CXX should increase the amount of uranium that can be held in solution by a proportional amount up to the solubility product limit (to at least 1M carbonate).

The assumption that the free carbonate/uranium ratio was controlling was confirmed in additional titrations where most of the excess acid in the uranium solution was neutralized first by NaOH. The same threshold precipitation values were obtained as before.

*Free carbonate is defined here as moles of total carbonate minus moles of HCO_3^- formed by reaction with HNO_3 .

The uranium solubility limits correspond to the values where the uranium present exceeds the amount necessary to form the dicarbonate complex, $\text{UO}_2(\text{CO}_3)_2^=$, in the sodium system and the tricarbonate complex, $\text{UO}_2(\text{CO}_3)_3^{-4}$, in the potassium system. (5) The titration behavior for the two systems also differed in that a precipitate continually formed and redissolved (until the end point was reached) on addition of uranium to the potassium carbonate, while no precipitate was observed in the sodium carbonate system until the precipitation threshold was exceeded.

The titration system was quite highly buffered by the bicarbonate and uranyl-carbonate complexes. Gross precipitation did not occur until the pH was reduced below 6 by U-HNO_3 addition ($\text{free CO}_3^=/\text{U} < 2.0$). Little or no gassing from CO_2 was observed up to this point, nor was any expected because of the preferential formation of bicarbonate by acid addition. The use of KHCO_3 as a buffer additive, as proposed in the PRF flowsheet (1) does not appear to be required in the absence of free hydroxide in the system. In fact, the uranium solubility would be decreased slightly by the increased potassium content because of the solubility product effect as discussed in Reference 5.

It seems evident that no precipitation problems will occur with either the sodium or potassium carbonate system until all of the carbonate is complexed either as HCO_3^- or $\text{UO}_2(\text{CO}_3)_3^{-4}$ and that only minor precipitation will occur until the free $\text{CO}_3^=/\text{U}$ ratio drops below 2.0. [i.e., all carbonate complexed as HCO_3^- and $\text{UO}_2(\text{CO}_3)_2^=$].

Typical titration data for the K_2CO_3 system are presented in the following table. Titration data for Na_2CO_3 were similar; but the threshold for haze formation, cloudiness, etc, occurred at slightly lower free $\text{CO}_3^=/\text{U}$ mole ratios.

TITRATION OF K_2CO_3 BY URANYL NITRATE

100 ml 0.37M K_2CO_3 (5% K_2CO_3) titrated with 1.44M $UO_2(NO_3)_2$,
0.043M HNO_3 , 0.50M $NaNO_3$.

Volume U Solution, ml	U	HCO_3^-	free $CO_3^{=}$	$CO_3/U^{(a)}$	Approx. pH	Appearance
6.0	0.082	0.002	0.347	4.26	10.5	Clear ^(b)
7.2	0.097	0.003	0.342	3.54	10	Very faint haze
7.45	0.100	0.003	0.341	3.41	8.4	Hazy
8.7	0.115	0.003	0.337	2.93	7.5	Cloudy
9.5	0.125	0.004	0.334	2.67	7	Very cloudy but translucent
Added 1.5M HNO_3 at this point						
9.5	0.114	0.132	0.177	1.55	5.5	Heavy yellow ppt. ^(c)

(a) Mole ratio of $(free\ CO_3^{=})/(U)$, where $(free\ CO_3^{=}) = (CO_3^{=}) - (HCO_3^-)$.

(b) Precipitate formed on uranium addition, but quickly redissolved.

(c) Probably $UO_2(OH)_2$ or Na_2UO_4 .

ACKNOWLEDGEMENT

The valuable guidance and assistance of J. FL Bruns of
Atlantic Richfield Hanford Company is gratefully acknowledged.

REFERENCES

1. L. E. Bruns, "Plutonium-Uranium Processing in the Plutonium Reclamation Facility by Coextraction-Partition", ARH-1343. Sept. 25, 1969.
2. A. P. Colburn, "Simplified Calculation of Diffusional Processes", Ind. and Eng. Chem., Vol. 33, 1941, pp. 459-467.
3. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume VIII, Longans, Green, and Co., London, 1947, p. 289.
4. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Supplement II to Volume VIII, John Wiley and Sons, New York, 1967, p. 201.
5. C. A. Blake, et.al, "Studies in the Carbonate-Uranium System", J. Amer. Chem. Soc., Vol. 78, 1956, pp. 5978-5983.
6. D. R. Olander, Lucien Donadieu, and Manson Benedict, "The Distribution of Nitric Acid Between Water and Tributyl Phosphate-Hexane Solvents", AIChE Journal, Vol. 7, No. 1, March 1961, p. 152.

TABLE I

STREAM COMPOSITIONS

TABLE I

STREAM COMPOSITIONS

I. Nominal Feed Stream Compositions

A. CC Column

Run No.	CCS		CAP (CCF)			CCX			CCAF		
	HNO ₃ , M	U, g/l	HNO ₃ , M	HNO ₃ , M	HNO ₃ , M	HNO ₃ , M	NN, M	N ₂ H ₄ , M	HNO ₃ , M	HNO ₃ , M	NN, M
1,2	0.5	8	0.15	0		0.15	0.4	0	2.5	0.15	1.2
3	0.5	8	0.15	0.15		0.15	0.4	0	2.5	0.15	1.2
5-11	0.5	8	0.15	0		0.15	0.4	0	2.5	0.15	1.2
12	0.5	8	0.15	0.18		0.15	0.4	0.1	1.25	1.5	0.6
13	0.1	8	0.15	0.18		0.15	0.4	0	1.25	1.5	0.6

B. CR Column

Run No.	CRF	
	U, g/l	HNO ₃ , M
14-16	8	0.3
20	5	0.3
21	7	0.3
24	9	0.3

C. CX Column

Run No.	CXF from Run No.		CXF, K ₂ CO ₃
17	14		5
18	15		5
19	16		5
22	20		5
23	21, 22		5
25	24		5

II. Analyzed Stream Compositions

A. CC Column

Run No.	CCS		CAP		CCX		CCXF		CAIS		CCW	
	HNO ₃ , M	U, g/l	HNO ₃ , M	HNO ₃ , M	HNO ₃ , M ^(a)	HNO ₃ , M ^(b)	U, g/l	HNO ₃ , M ^(c)	U, g/l	HNO ₃ , M ^(c)	U, g/l	HNO ₃ , M
1	0.568	7.85	0.165	0.494	1.02	0.0015	1.34	4.85	0.069			
2	0.568	7.85	0.165	0.494	1.02	0.004	---	5.54	0.061			
3	---	16.1	---	0.494	1.02	0.0216	1.08	7.66	---			
5	0.498	8.70	0.219	---	1.02	0.083	1.38	8.63	0.199			
6	0.498	8.70	0.219	---	1.02	0.067	1.39	---	---			
7	0.498	8.70	0.219	---	1.02	0.018	1.25	---	---			
8	0.498	---	---	---	---	0.039	1.34	6.54	0.245			
9	0.498	---	---	---	---	0.057	1.34	5.08	0.767			
10	0.498	---	---	---	---	0.025	1.20	5.02	0.916			
11	0.498	---	---	---	---	0.015	1.27	4.9	0.063			
12	0.535	6.9	0.163	0.503 ^(d)	2.26 ^(e)	0.0038	1.41	5.8	0.065			
13	0.011 ^(f)	7.32	0.209	0.936	2.51 ^(e)	0.078	1.10	4.94	0.159			

B. CR Column

Run No.	CRF		CRO-CXF		CRU	
	U, g/l	HNO ₃ , M	U, g/l	HNO ₃ , M	U, g/l	HNO ₃ , M
14	5.52	0.329	5.09	0.0607	4.55	1.10
15	8.12	0.368	3.12	0.0294	5.38	0.567
16	8.12	0.368	5.48	0.0520	8.69	0.986
20	4.0	0.337	2.20	0.0277	6.20	1.03
21	6.67	0.390	4.79	0.0505	5.77	1.17
24	6.01	0.311	4.97	0.0390	3.61	0.944

C. CX Column

Run No.	CXF		CXO		CXA	
	U, g/l	HNO ₃ , M	U, g/l	HNO ₃ , M	U, g/l	
17	6.49	0.057	0.20	0.003	11.5	
18	2.30	0.025	0.80	0.003	6.21	
19	6.0	0.067	0.40	0.004	8.2	
22	2.70	0.049	0.224	0.002	14.2	
23	3.63	0.045	0.0015	0.003	9.7	
25	4.8	0.062	0.38	0.004	15.5	

(a) Includes 0.4M hydroxylamine (NN) analyzed as HNO₃.(b) Includes 1.2M hydroxylamine analyzed as HNO₃ in Runs 1 through 11.(c) Includes CCX and CCXF hydroxylamine analyzed as HNO₃.

(d) Contained additional 0.10M hydrazine.

(e) Includes 0.6M hydroxylamine analyzed as acid.

(f) CCS also contained about 0.1 g/l U.

TABLE II

CC COLUMN CONCENTRATION PROFILES

Analyses of two-phase, equilibrated samples

Run No.	18 ft*				15 ft*				12 ft*			
	UE _a ^O	U, g/l		HNO ₃ , M Aqueous	UE _a ^O	U, g/l		HNO ₃ , M Aqueous	UE _a ^O	U, g/l		HNO ₃ , M Aqueous
		Aq.	Org.			Aq.	Org.			Aq.	Org.	
1	8.07	0.0057	0.046	0.98	6.88	0.032	0.220	0.940	6.92	0.569	3.94	0.892
2									6.88	0.516	3.55	1.02
5	8.3	0.136	1.13	1.08	7.56	0.408	3.08	0.956	6.14	1.42	8.72	1.04
6	16.0	0.015	0.24	0.898	9.39	0.076	0.714	1.07	7.47	0.889	6.64	1.04
7	4.96	0.025	0.124	1.20	7.92	0.207	1.64	1.13	10.5	0.836	8.74	1.20
8	8.47	0.163	1.38	1.16	5.93	0.511	3.03	1.12	2.10	1.74	3.65	1.04
9	5.83	0.211	1.23	1.06	4.06	0.831	3.37	1.08	5.63	1.39	7.82	1.24
10	4.45	0.124	0.552	1.10	6.38	0.406	2.59	1.29	1.64	1.22	2.00	1.12
12	19.4	0.012	0.233	1.10	17.8	0.182	3.24	1.22	8.40	1.04	8.72	1.16
13	12.9	0.22	2.83	1.08	12.4	0.70	8.7	1.20	8.66	0.86	7.45	1.20
Run No.	9 ft*				6 ft*				3 ft*			
	UE _a ^O	U, g/l		HNO ₃ , M Aqueous	UE _a ^O	U, g/l		HNO ₃ , M Aqueous	UE _a ^O	U, g/l		HNO ₃ , M Aqueous
		Aq.	Org.			Aq.	Org.			Aq.	Org.	
1	4.84	1.79	3.67	0.829	1.27	5.13	6.54	0.617	1.18	6.45	7.60	0.574
5	2.75	5.05	13.9	0.946	4.36	1.91	8.33	0.886	9.14	0.66	6.03	0.737
7	16.0	1.29	20.6	0.966								
13	8.03	0.965	7.75	1.50								

* Distance in ft from the bottom of the cartridge. The 12 ft sample is taken at the CAP feed point and the 9 ft sample at the CCXF feed point.

TABLE III
OPERATING CONDITIONS AND RESULTS

TABLE III
OPERATING CONDITIONS AND RESULTS

A. CC Column (i)

Run No.	Pulse Freq., Cycles/Min.	Feed Rates, l/hr (e)				Scrub Section A/O	Air Flow Rate Sec/Min (e)	Run Length, Min.	U in CAIS		Scrub Section U HTU ft. (d)
		CCS	CAP	CCXF	CCX				% of CAP	% of Fd.Pt. Ag.	
1	115	18.1	70.9	8.1	32.0	2.21	0	300	0.012	0.35	1.1
2	70	18.1	70.9	8.1	32.0	2.21	0	90 (a)	0.027	0.77	1.3
3	80	20.5	72.1	7.5	31.7	1.91	0	165	≤1.46 (f)	≤21.6 (g)	≤5.6 (g)
5	80	17.6	72.4	5.2	30.4	2.02	0	195	≤0.56 (f)	≤5.85	≤2.5
6	80	17.6	72.4	5.2	30.4	2.02	1070	120 (a)	≤0.45 (f)	≤7.54	≤2.8
7	80	17.6	72.4	5.2	30.4	2.02	2130	105 (a)	≤0.12 (f)	≤2.06	≤1.5
8 (j)	80	17.0	71.9	4.5	28.2	1.92	0	180	0.26	7.64	1.7
9 (j)	80	17.0	71.9	4.5	28.2	1.92	1070	85 (a)	0.39	4.10	2.2
10 (j)	80	17.0	71.9	4.5	28.2	1.92	2130	80 (a)	0.17	2.05	1.8
11 (j)	80	17.0	71.9	4.5	28.2	1.92	8530	35 (a)	0.10	1.5 (g)	1.7 (g)
12 (j)	115	17.0	75.1	16.2	30.8	2.74	0	190	0.026	0.36	1.1
13 (j)	100	16.6	71.0	10.5	29.8	2.51	0	300	0.63	9.1	2.8

B. CR Column (k)

Run No.	Pulse Freq., Cycles/Min.	Ampl. in.	Feed Rates, l/hr (e)		Flow Ratio A/O	Interface Position	Run Length, Min.	U in CNF		HNO ₃ in CNF		HNO ₃ HTU, ft. (h)
			CRF	CRX				% of CRF	% of CRF	% of CRF	% of CRF	
14	0	0	92.5	31.5	0.341	Bottom	263 (b)	92		18		4.9
15	0	0	89.4	59.0	0.660	Bottom	166 (a)	38		8.0		3.5
16	0	0	95.7	32.0	0.334	Top	165	67		14		4.1
20	40	2.25	84.5	31.9	0.377	Top	215	55		8.2		3.2
21	40	2.25	86.3	31.5	0.365	Bottom	381 (b)	72		13		3.0
24	0	0	88.2	32.1	0.364	Bottom	420	83		12		3.9

C. CX Column (k)

Run No.	Pulse Freq., Cycles/Min.	Ampl. in.	Feed Rates, l/hr (e)		Flow Ratio A/O	Interface Position	Run Length, Min.	U in CXO		U HTU, ft. (d)
			CRF	CRX				% of CRF	% of CRF	
17	0	0	85.0	30.8	0.362	Bottom	212 (b)	4.2		2.9
18	0	0	89.0	32.3	0.363	Top	148 (a)	16.0		8.6
19	0	0	92.7	60.9	0.657	Bottom	198 (a)	6.7		3.4
22	45	2	87.8	31.2	0.355	Top	176	8.3		3.7
23	45	2	88.8	30.9	0.349	Bottom	415	0.04		1.2
25	0	0	90.0	29.2	0.323	Bottom	410	7.9		3.6

(a) Continuation of preceding run after changing operating conditions.

(b) Includes 1 hr at 3 times normal flows to speed establishment of equilibrium concentrations.

(c) A 9M HNO₃ stream was added to the CAP just before entry to the column at an equivalent PRF rate of 1.5 l/hr. This provided a stoichiometric 0.18 ± 0.02M HNO₂ concentration in the CAP.

(d) Calculated using average U distribution ratios of 7.53 in the CC column scrub section and 0 in the CX column.

(e) Pilot Plant flow rates corrected to correspond to the equivalent rates in the PRF 4 in. diameter CC column and 6 in. diameter CR and CX columns.

(f) May not have been at steady state. Sequential samples showed a decreasing uranium content with time.

(g) Estimated feed point aqueous concentration was 1 g/l, the value calculated from stage calculations.

(h) Calculated using an average HNO₃ distribution ratio of 0.058.

(i) 3 in. i.d. glass column with 21 ft. tall cartridge of 2 in. spaced, 23% free area stainless steel sieve plates (1/8 in. holes). The column was operated with a bottom interface. Pulse amplitude = 1 in., except 1.5 in. in Run 2.

(j) 3/4 in. Kynar Raschig rings inserted in scrub section to simulate PRF cartridge.

(k) 4 in. i.d. glass column containing 7 ft of 1-in. Kynar Intalox saddles.