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SUBJECT: Uranium Recovery from LAPRE-II Fuel Solution by TBP Extraction

TO: F. L. Culler

FROM: J. R. Flanary

ABSTRACT

A feed preparation and solvent extraction flowsheet has been developed for the recovery and decontamination of highly enriched uranium from the LAPRE-II reactor fuel solution. The fuel solution, uranium(IV) in concentrated H_3PO_4, must be diluted, ferric nitrate added to complex phosphate and supply salting strength, sodium nitrite added to oxidize U(IV) to U(VI) so that uranium may be extracted efficiently with 6% TBP. The flowsheet is designed for operation in noncritically safe equipment.

NOTICE

DISCLAIMER

INTRODUCTION

In a letter from H. M. Roth to J. A. Swartout dated May 4, 1960, it was requested that we evaluate the economic and technical feasibility of processing LAPRE-II fuel solution at ORNL. There are presently available at Los Alamos Scientific Laboratory 94.74 liters of spent fuel solution, for which the following data was supplied:

Volume: 94.74 liters of 96.8% H_3PO_4 solution
Burnup: 5.81×10^{21} total fissions (0.04%)
Beta-gamma activity: 0.5 curies/liter on 2/16/60
Decay time: 1 year on 5/8/60
Analysis: 18.05 M H_3PO_4
0.327 $\overline{M}$ U (93.35% enriched)
0.323 $\overline{M}$ U(IV)
0.004 $\overline{M}$ U(VI)
0.021 $\overline{M}$ Cu
0.015 $\overline{M}$ Fe

In addition, it was requested that the Intermediate-scale Head-end and Solvent Extraction facility (IMMI) in Cell I - Bldg. 4507 be considered as a possible processing site for this material.

SUMMARY

Recovery and decontamination of the uranium contained in the LAPRE-II fuel solution in the IMMI solvent extraction facility appears to be feasible. A flowsheet has been developed for feed preparation and solvent extraction under critically safe conditions. Final concentration of the product by evaporation would be carried out at Y-12. Over-all decontamination of the uranium is expected to be $\sim 10^3$ for β and γ with a uranium loss of $<0.02\%$. For operation in the IMMI facility, limitation of batch size to 300 g U is recommended for criticality control. As an additional criticality safeguard, uranium concentration is limited to 6 g/liter in the flowsheet. Dilution of the fuel solution, 96.8% H_3PO_4 containing 77 g U(IV)/liter, produces a feed solution containing 1.4 $\underline{M}$ H_3PO_4 and 6 g U(IV)/liter. By addition of 1.6 $\underline{M}$ $Fe(NO_3)_3$ and 0.05 $\underline{M}$ $NaNO_2$, uranium(IV) is quantitatively oxidized to uranium(VI) and nitrate salting strength is provided. In addition, the strong complexing strength of phosphate for uranium (VI), which hinders uranium extraction by TBP, is nullified by formation of a ferric phosphate complex. Such treatment yields a stable adjusted feed (FP) below -10°C) for solvent extraction.

Batch extraction studies with synthetic feeds showed that the uranium could be extracted with either 2.5 and 6% TBP; however, 6% TBP is preferred on the basis of uranium extraction efficiency, volumetric throughput, and hydraulic characteristics in keeping with existing process equipment.

Batch countercurrent demonstration of the proposed flowsheet showed that 99.98% uranium recovery is accomplished with 7 theoretical extraction and 5 theoretical stripping stages. Internal reflux of uranium is limited to 6% using 4 M HNO_3 as scrub. Owing to the complexing action of phosphate on plutonium(IV), only 3% of the plutonium was extracted, scrubbed and stripped with the uranium. Three percent of the calculated amount of plutonium expected to exist in the LAPRE-II fuel solution would not exceed the 30 ppb specification for this contaminant in recovered uranium.

CRITICALITY CONSIDERATIONS

Since most of the vessels in the IMMI facility have a noncritically safe geometry, it was decided to employ batch control as the primary criticality safeguard. Batch size was selected as 300 g total U (93.35% enriched) however, the flowsheet was designed for added safety with a nominal uranium concentration of 6 g/liter throughout the system. Both 2.5 and 6% TBP were studied as suitable dilute solvents for the solvent extraction flowsheet. Although 2.5% TBP with maximum extraction capacity of 10.4 g U/liter offers more stringent concentration control, its extraction power for uranium in the strong phosphate-nitrate system is somewhat deificient, leading to an inefficient, unwieldy solvent extraction flowsheet in terms of theoretical stage requirements, relative flow, and throughput. Consequently, 6% TBP is a far superior choice; with a maximum extraction capacity of 24.8 g U/liter.

A brief description of the chemical flowsheet (Fig. 1) and the mode of operation is needed to outline the techniques of criticality control by batch and concentration limitations. The process involves basically 3 steps: feed adjustment, solvent extraction, and final product concentration by evaporation. Setting the batch size at 300 g U and the concentration at 6 g U/liter established the batch volume of adjusted feed as 50 liters. The feed adjustment tank is charged with 46.1 liters of 1.74 M $Fe(NO_3)_3$-0.05 M $NaNO_2$. While the tank is air-sparged, 3.9 liters of fuel solution is metered into the vessel; agitation by air-sparge is continued for 30 min to ensure uniform dilution and promote the oxidation of U(IV) to U(VI) by ferric nitrate and sodium nitrite. The adjusted feed is sampled in duplicate, specific gravity and liquid level are recorded to establish the mass of uranium entering the system.

The adjusted feed (AF) containing 1.4 M H_3PO_4, 1.6 M $Fe(NO_3)_3$, 6 g U/liter, 0.0045 mg Pu/liter, 0.039 curies of mixed fission products/liter, and traces of non-radioactive impurities is steam-jetted to the feed displacement tank, from which it is pumped by displacement to the first of 3 solvent extraction contactors arranged in cascade. The AF stream enters about midsection of mixer-settler "A" where it is contacted with a countercurrent flow of 6% TBP, AX. The uranium is extracted near-quantitatively into the solvent at 5 g/liter; the uranium-bearing solvent stream is scrubbed with a small, countercurrent flow of 4 M HNO_3 before it emerges from the "A" contactor. The relative flow and nitric acid concentration of the scrub were chosen

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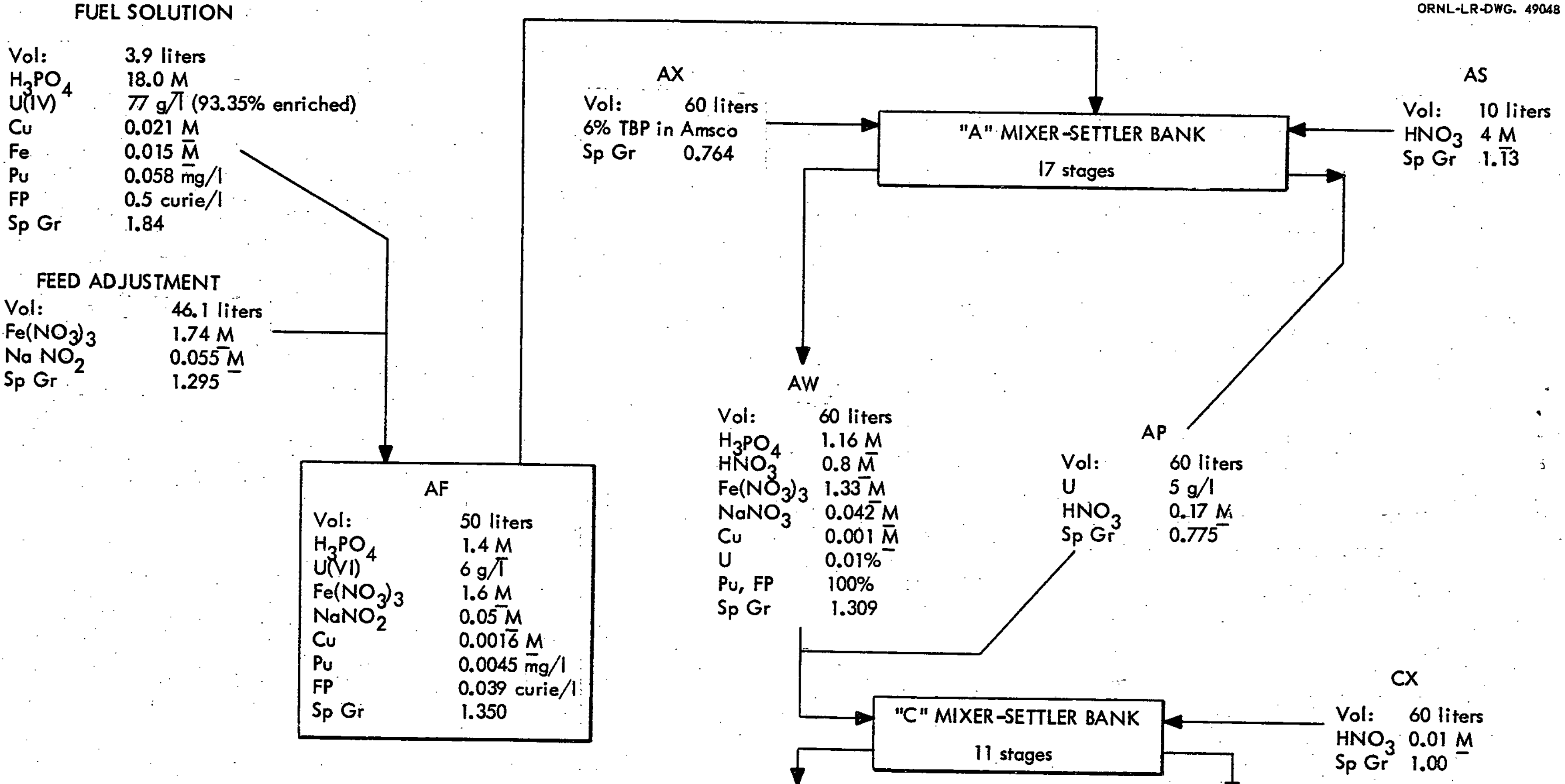

Basis: Batch Operation in the IMMI Facility, 4507 Bldg.
Criticality Control by Batch and Concentration Limitation
Batch Size: 50 Liters of Adjusted Feed at 6 g U/l (300 g U)

Fig. 1. Chemical flowsheet for uranium recovery from LAPRE-II fuel solution.

to (a) provide near-optimum conditions for backwashing extracted fission products, particularly ruthenium, and nonradioactive impurities from the uranium-bearing solvent stream (AP), and (b) limit the reflux of uranium in the "A" contactor to ~10%.

The AP stream cascades into mixer-settler "C" where the uranium is stripped into a countercurrent flow of 0.01 M HNO_3 at a nominal concentration of 5 g/liter. The dilute uranium product (CU) flows into a catch tank. When a batch volume, 50 liters less the calculated volumetric holdup in the system, is accumulated, it is withdrawn by vacuum into a weighed, calibrated shipping container. The gross weight and volume content of the container are recorded, and the product is sampled in duplicate for specific gravity and total uranium determination to establish the mass of uranium removed from the system.

The batch of assayed product solution is transferred to Bldg. 9212 for final concentration in a critically safe evaporator. Meanwhile, another 50-liter batch of adjusted feed is ready to be fed to the solvent extraction cascade.

FEED ADJUSTMENT

The fuel solution from the LAPRE-II reactor is 96.8% H_3PO_4 (18.05 M) containing 77 g total U/liter predominantly as U(IV). Aside from criticality considerations, high dilution and special treatment of the fuel solution is necessary to permit the recovery of uranium by TBP extraction. Simple dilution of the fuel solution to 6 g U/liter with water reduces the phosphate concentration to 1.4 M. Even at this lowered concentration, however, the complexing strength of phosphate for U(VI) is quite high. A synthetic adjusted feed was prepared containing 1.4 M H_3PO_4, 4.8 M $NaNO_3$ to provide high nitrate salting strength, and 6 g U/liter as U(VI). Equilibration of this solution with an equal volume of 6% TBP yielded an extraction coefficient for uranium of only 0.015. By, contrast, extraction under similar conditions in the absence of phosphate yielded U E_a^o of 1150.

It is known that ferric ion forms an aqueous-soluble complex with phosphate. The addition of as much as 1.6 M $Fe(NO_3)_3$ to the diluted fuel solution produces a clear, stable solution with a freezing point below -10°C. Rapid oxidation of U(IV) to U(VI) by the large excess of ferric nitrate occurs at room temperature; 87.2% conversion to U(VI) was obtained within 30 min. Standing for 48 hr produced no additional conversion, nor did a 30 min air sparge of the solution. It was found, however, that addition of 0.05 M $NaNO_2$ promoted complete oxidation of the uranium.

SOLVENT EXTRACTION

The effectiveness of ferric ion as a complexing agent for phosphate to nullify the complexing power of phosphate for uranium was determined by exhaustive batch extraction of synthetic feed solutions with 2.5 and 6% TBP. These feed solutions each contained 1.4 M H_3PO_4 and 6 g U(VI)/liter with varied addition of ferric nitrate and nitric acid. Repetitive extraction with aliquots of solvent were performed on each feed to determine the prevailing extraction coefficient for uranium and the completeness of uranium extraction (Table I).

In Table I, the uranium extraction coefficients obtained with 6% TBP and feeds containing from 1.0 to 1.6 M $Fe(NO_3)_3$ vary from 1.6 to 7.5. These values are from 100- to 500-fold greater than the U E_a^o of 0.015 obtained with 6% TBP and a similar feed containing $NaNO_3$ of equivalent nitrate salting strength substituted for $Fe(NO_3)_3$. Exhaustive extraction of the feed containing 1.6 M $Fe(NO_3)_3$ with 6% TBP proceeds rather efficiently; 99.97% extraction of the uranium is accomplished in five consecutive passes.

Since it is planned to use 4 M HNO_3 as scrub solution in the "A" contactor, the effect of a 20% dilution of the feed stream with the scrub was examined (Table I). Although the U E_a^o is slightly depressed to a nominal value of 4.0, calculation indicates that it is sufficiently large to permit 99.99% extraction of uranium with 5.5 theoretical stages.

Rather poor uranium extraction coefficients were obtained using 2.5% TBP. U E_a^o for the first extraction simulating the feed stage increased from 0.52 to 0.89 as ferric nitrate in the feed was increased from 1.0 to 1.6 M These extraction coefficients are not feasible in a solvent extraction system unless multiple volumes of solvent are used. Such a flowsheet involves unwieldy volumes of solvent, and since the volumetric throughput of a TBP solvent extraction system is limited by low flooding rates in the uranium stripping contactor, the mass throughput becomes extremely low.

A batch countercurrent experiment was conducted to test the proposed solvent extraction flowsheet as regards uranium extraction efficiency, extent of uranium reflux in the scrub section, and hydraulic behavior of the system. In Table 2 are summarized the results of the run conducted with synthetic LAPRE-II feed solution, 6% TBP, and 4 M HNO_3 scrub. The data show that almost 7 batch countercurrent extraction stages of 100% efficiency are required to reduce uranium loss to 0.01%. The uranium extraction coefficient (E_a^o) exceeds 4 in the extraction section, as predicted from batch equilibration data, except at the first and seventh stages. In the seventh stage, the uranium is so dilute that analytical accuracy becomes rather poor. At the first stage, material balance calculations show that the uranium content of the aqueous phase is high by a factor of 1.91, suggesting analytical error.

Uranium extraction in the scrub section is efficiently maintained with a U E_a^o varying from 3.7 to 4.1 with salting strength provided by 4 M HNO_3. Reflux of uranium from the last scrub stage back to the first extraction stage is limited to 6%, owing to the highly favorable extraction factor of 20 (U E_a^o of 4 multiplied by the solvent-to-aqueous volume ratio of 5).

Table I. Uranium Extraction by 2.5% and 6% TBP from Synthetic LAPRE-II Feed Solution as Influenced by Ferric Phosphate - Uranium Phosphate Complexes

Adjusted Feed: 1.4 M H_3PO_4, 6 mg U/ml as U(VI), $Fe(NO_3)_3$ and HNO_3 as shown.
Solvent: 2.5 or 6% TBP in Amsco 125-82

Repetitive extraction of the feed with solvent volumes equal to the feed. Contact time: 2 min; temperature: 25°C

1.0 M $Fe(NO_3)_3$ in Feed	2.5% TBP		6% TBP	
	U E_a^o	% U Extracted	U E_a^o	% U Extracted
Extraction 1	0.52		1.64	
2	0.54		1.79	
3	0.57		1.73	
4	0.42	76.3	2.57	98.8
5	-			

1.4 M $Fe(NO_3)_3$ in Feed	2.5% TBP	
	U E_a^o	% U Extracted
Extraction 1	0.59	
2	0.77	
3	0.88	
4	0.50	
5	0.36	94.7

1.6 M $Fe(NO_3)_3$ in Feed	2.5% TBP		6% TBP	
	U E_a^o	% U Extracted	U E_a^o	% U Extracted
Extraction 1	0.89		4.69	
2	1.29		5.11	
3	1.55		7.50	
4	1.50		6.0	
5	1.40	98.4	3.50	99.97

1.33 M $Fe(NO_3)_3$ - 0.8 M HNO_3 in Feed	6% TBP	
	U E_a^o	% U Extracted
Extraction 1	3.81	
2	4.17	
3	4.0	
4	4.37	
5	5.0	99.98

Table 2. Batch Countercurrent Extraction of Uranium from Synthetic LAPRE-II Feed Solution with 6% TBP

Solution	Relative Volume	Composition
Adjusted Feed	50	6.25 mg U/ml, 4 x 10^3 Pu cts/min/ml, 1.4 M H_3PO_4, 1.6 M $Fe(NO_3)_3$, 0.05 M $NaNO_2$
Scrub	10	4 M HNO_3
Solvent	60	6% TBP in Amsco 125-82

The batch countercurrent run, using 7 extraction and 4 scrub stages, was conducted through 55 equilibrations, (equivalent to 5 volume changes, at room temperature, 25°C.) Contact time per stage was 2 min.

Stage	U, mg/ml Org	U, mg/ml Aq	U E_a^o	Comments
Scrub 4	5.14	1.25	4.1	Uranium reflux from last scrub stage back to the first extraction stage (feed point) is limited to 6%.
2	5.39	1.47	3.7	
Ext 1	5.42	2.09	2.6	U E_a^o in scrub section nearly equivalent to that prevailing in extraction section indicating that 4 M HNO_3 scrub is nearly equal in nitrate salting strength to that of mixed feed-scrub solution.
3	0.48	0.11	4.4	
5	0.032	0.007	4.6	
7	0.001	0.0004	2.5	U analysis of 7th extraction stage aqueous (same as flowing stream AW) is equivalent to 0.008% U loss.
				U analysis of 4th scrub stage organic (same as flowing stream AP) represents 99% material balance for uranium, indicating steady-state is closely approached after 5 volume changes.

A 99% uranium material balance was calculated for the run, based on relative volumes and uranium analyses of the adjusted feed and fourth scrub stage organic (flowing stream AP). Thus, it is certain that the system had reached equilibrium after 5 volumes changes, when sampled.

Mixing of the relatively light solvent (Sp Gr: 0.764) with the heavy feed-plus-scrub aqueous phase (Sp Gr: ~1.30) was somewhat difficult, requiring impeller speeds of 900 to 1000 rpm. To ensure thorough mixing, a 2-min contact time was allowed. Settling was quite rapid as expected; with a maximum of 30 sec required in the extraction section. Settling produced clear phases; no interfacial "crud" was detected.

Analyses showed that the nitric acid extracted by the solvent (AP stream) is 0.17 M. Actually, this value is very constant for acid extraction by the solvent throughout the extraction and scrub sections. There is no appreciable reflux of nitric acid in the system.

Stripping of the uranium from the solvent at low concentration, 5 g/liter, is very efficient, owing to the weak nitrate salting strength which prevails. A portion of the composite AP from the batch countercurrent extraction run was exhaustively stripped with 5 successive aliquots of 0.01 M HNO_3; the solvent-to-strip volume ratio was maintained at 1/1. The uranium E^o_a after the first strip was 0.04; this value prevailed through the second and third strips. After the fourth strip, uranium loss to the solvent was reduced to 0.01%. Calculations show that if the U E^o_a of 0.04 prevailed throughout stripping, which it does not, only 2.8 theoretical stages are needed to reduce uranium loss to 0.01%. Actually, in the countercurrent stripping operation, between 4 and 5 theoretical stages will be required to reduce the uranium loss to 0.01%.

Three percent of the plutonium present in the adjusted feed was extracted with the uranium, carried through the scrub section, and was stripped with the uranium. With excess nitrite in the adjusted feed, plutonium exists as Pu(IV), which in the absence of phosphate would have been quantitatively extracted. Thus, complexing by phosphate aids the removal of this contaminant.

Assuming that the calculated concentration of 0.0045 mg plutonium per liter of adjusted feed from the actual LAPRE-II fuel solution is correct and extraction of plutonium is limited to 3%, the 30 ppb plutonium specification on recovered uranium will be met. However, decontamination greater than that gained by phosphate complexing can be accomplished by addition of ferrous sulfamate to the scrub.

FINAL CONCENTRATION OF URANIUM PRODUCT

From a telephone conversation with F. M. Tench, 9212 Bldg., it was learned that final concentration of the dilute uranium product by evaporation can be conducted at Y-12. If the product solution is 5 g U/liter or less, it can be transferred in noncritically safe containers, or by tanker truck if such method appears convenient.

It is preferred that the total nonradioactive impurities in the product solution not exceed 0.5 wt % of the uranium; however, extraction facilities are available at Y-12 if further purification is needed.

The specification on mixed fission product activity is stated as: total gamma activity per milligram of uranium should not exceed 2 x 10^4 d/min. In view of the relatively small amount of uranium from the LAPRE-II fuel solution as compared to Y-12 processing capacity, this specification may be somewhat relaxed to avoid processing of slightly off-standard product at ORNL. Assuming that the total fission product activity in the uranium product will consist of 50% Ru-106 and 50% Zr-Nb, the specification in terms of scintillation counting becomes 700 Ru gamma cts/min plus 2000 Zr-Nb gamma cts/min per milligram of uranium.

The specification on plutonium in the uranium product is 30 parts per billion parts of uranium.

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