OCT 31 1968

UNCLASSIFIED

RECEIVED BY DTIE FEB 6 1969

ARH-SA-20

MASTER

AQUEOUS CITRATE FOR PLUTONIUM-URANIUM PROCESSING

By

R. L. Knights

Separations Chemistry Laboratory
Research and Engineering
Chemical Processing Division

ATLANTIC RICHFIELD HANFORD COMPANY
RICHLAND, WASHINGTON

To be presented at:

Analytical Chemistry Seminar
University of Washington
November, 1968

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Operated for the Atomic Energy Commission by
Atlantic Richfield Hanford Company under Contract #AT(45-1)-2130

UNCLASSIFIED

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

flg

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
CONCLUSIONS	1
EXPERIMENTAL	2
RESULTS	3
URANIUM STRIPPING	3
URANIUM RE-EXTRACTION	4
PLUTONIUM STRIPPING	4
PLUTONIUM RE-EXTRACTION	4
PLUTONIUM-URANIUM PARTITIONING	4
INTERFERENCE IN OXALATE PRECIPITATION	7
DESTROYING CITRATE	7
FURTHER WORK	8
REFERENCE	8

AQUEOUS CITRATE FOR PLUTONIUM-URANIUM PROCESSING

INTRODUCTION

This report describes the work I performed as a Summer Employee with the Atlantic Richfield Hanford Company (ARHCO). ARHCO operates the reactor fuel reprocessing facilities on the Hanford project for the Atomic Energy Commission. The work I did concerns a plutonium-uranium separation scheme proposed for the Plutonium Reclamation Facility.

The system investigated required five extraction steps:

Step

- 1 Extract plutonium and uranium with tributyl phosphate (TBP) into an organic phase (20% TBP in CCl_4).
- 2 Strip plutonium by reduction to plutonium(III).
- 3 Strip plutonium as a fluoride complex (backup to Step 3).
- 4 Strip uranium.
- 5 Clean organic with carbonate wash.

Aqueous citrate was investigated as an agent for stripping uranium from the organic stream in Step 4. Because plutonium and uranium were found to behave differently during citrate stripping, plutonium-uranium partitioning was also explored.

CONCLUSIONS

Citrate solutions provide a means of plutonium-uranium partitioning and processing. However, continuous extraction columns should be used to demonstrate the concepts under continuous conditions.

Additionally, a citrate solution for stripping uranium from

the organic should be quite efficient if pH control can be maintained. Continuous stripping should be tested in a simulated column.

Citrate should cause no interference in the present plutonium-uranium processing flow sheet. In each existing column, the effect of citrate would support the intended characteristics of the column. If some citrate is carried over into other columns, no opposing equilibria are introduced.

A processing scheme based on citrate would consist of five extraction steps:

Step

- 1 Extract plutonium and uranium into organic phase with TBP.
- 2 Strip plutonium into strongly acidic aqueous citrate.
- 3 Strip plutonium as in Step 2 (backup).
- 4 Strip uranium with citrate in optimum pH range.
- 5 Wash organic with carbonate before recycling.

EXPERIMENTAL

PROCEDURES

The organic phase for all work was 20% TBP in CCl_4 . Contacts used volume ratios of aqueous-to-organic (L/V) of 1/3 or 1/5. Mixing time was 1 min with agitation gentle enough to avoid emulsions.

ANALYSES

Plutonium analyses were by alpha counting, and uranium analyses were by x-ray analysis or fluorimetry.

Citrate analysis followed a gravimetric procedure of

oxidation and bromination to pentabromoacetone, which was weighed.⁽¹⁾ The procedure was modified to allow analysis of smaller amounts of citrate by eliminating a preliminary dilution step.

SOLUTIONS

All organics were supplied by Plutonium Reclamation Facility. Cold work used CAX, which was washed with K_2CO_3 and then HNO_3 solutions before use.

Sources of organic are listed below.

<u>Requirements</u>	<u>Composition</u>	<u>Source</u>
No Pu, no U	20% TBP in CCl_4	CAX
High Pu, high U	25 g/liter Pu spiked with U	CAP
Low Pu, high U	<0.001 g/liter Pu spiked with U	COW

RESULTS

URANIUM STRIPPING

Uranium stripping is pH-dependent, as shown below.

pH	>6.5	ppt formation
pH	3-5	optimum U stripping (>95%)
pH	<2, 5	<5% U stripped from organic.

Within the optimum pH range, the uranium will strip completely (>95%) into aqueous citrate. The pH was controlled by neutralizing the acid in the organic with K_2CO_3 and using the buffering effect of a larger amount of sodium citrate than necessary for a 1:1 molar ratio with uranium.

Ratio of aqueous-to-organic:	1/5
Uranium present in organic:	10 g/liter, or 0.04M
Uranium in aqueous after stripping:	0.2M
Sodium citrate in aqueous:	0.5M
K ₂ CO ₃ to yield pH 3 to 5:	5 %

Higher concentrations of K₂CO₃ formed precipitates because the aqueous was too basic.

URANIUM RE-EXTRACTION

Uranium will not strip into an acidic aqueous phase. This property allows the return of uranium to an organic phase following stripping with aqueous citrate (pH 3 to 5). Acidification and contact with new organic gave >95% re-extraction and concurrent concentration up to 80 g/liter uranium.

PLUTONIUM STRIPPING

Stripping plutonium with citric acid in the range pH 3 to 5 is even more efficient than the uranium strip. However, most of the plutonium will also strip into strongly acidic citrate solutions.

PLUTONIUM RE-EXTRACTION

Corresponding to more efficient stripping of plutonium from organic, only about 20% of the plutonium is re-extracted into new organic in a strongly acidic citrate medium. Thus acidifying an aqueous plutonium-uranium-citrate solution will preferentially extract the uranium, leaving most of the plutonium in the aqueous phase.

PLUTONIUM-URANIUM PARTITIONING

The selective stripping of plutonium from an organic plutonium-uranium mixture using aqueous citric acid presents a possible means of partitioning. The results of several experimental contacts are summarized below:

Initial organic: 25 g/liter Pu, 25 g/liter U.
 Contact: L/V = 1/3.

Aqueous		% Stripped	
<u>M</u>		<u>Pu</u>	<u>U</u>
1	HNO ₃	23	11
3	HNO ₃	10	
0.05	citric acid	49	
0.2	citric acid	61, 62	7
0.5	citric acid	78, 62	7, 8
0.5	citric acid-1 HNO ₃	43	4

Repeated contacts of the same organic phase yielded results dependent on composition of the aqueous strippant. Results found using three stripping systems are shown in Figure 1, page 6.

1M HNO₃

Aqueous nitric acid is an unsatisfactory strippant, removing too much uranium and not enough plutonium.

0.5M Citric Acid

The 0.5M citric acid provides excellent plutonium removal, but the uranium exhibits anomalous behavior.

0.5M Citric Acid-1M HNO₃

More strongly acidic 0.5M citric acid-1M HNO₃ assures stable uranium behavior, but plutonium stripping is less complete.

Acidic citrate solutions produce higher plutonium stripping and lower uranium stripping than acid alone.

Contact of the first aqueous phase with new organic confirmed that the uranium was preferentially re-extracted into the organic compared with the plutonium. The percentages

Number of Contacts with same Organic Phase

returned to the organic resemble the percentages that failed to strip on the first contact. Thus the distribution between phases will be the same for extracting and stripping.

Behavior in an actual continuous extraction column will dictate the aqueous composition for optimum partitioning. Maintaining low uranium level in aqueous effluent should present no difficulty, and most attention will probably be paid to decreasing plutonium loss to the organic.

INTERFERENCE IN OXALATE PRECIPITATION

Plutonium is precipitated as the oxalate in the process of reduction to the metal from a nitrate solution. If any citrate is used in the flow sheet for preparing a plutonium product solution, the effect of citrate-plutonium complex on completeness of oxalate precipitation of plutonium requires definition.

Plutonium solution: 230 g/liter in 6N HNO₃

<u>Citric Acid</u>	<u>Pu Unprecipitated</u>
None	0.018 g/liter
<u>2M</u>	0.023 g/liter

The above data shows there is apparently no plutonium-citrate complex formed strong enough to prevent plutonium-oxalate precipitation. The rapidity, color, and appearance were the same in both processes.

DESTROYING CITRATE

In case citrate must be destroyed in situ, several methods of oxidation were explored.

Boiling had no effect on citrate, even boiling for several hours with concentrated HNO₃.

Permanganate oxidation proved effective, except that 7 times the theoretical amount was required for complete removal of citrate. This ratio is the result of work summarized in

Figure 2, page 9. The reaction was rapid once it had begun, presumably after some catalytic amount of Mn^{++} had been formed. Adding permanganate too rapidly precipitated MnO_2 , which eventually dissolved with mixing and heating. Heating the solution allowed more rapid addition of permanganate without precipitate formation.

Dichromate oxidation was also effective, but required a longer time for complete reaction. No precipitate forms on rapid addition. Heating speeds reaction.

FURTHER WORK

- Use continuous extraction columns to determine efficacy of plutonium-uranium partitioning, efficiency of citrate stripping of uranium, and concentration of carbonate necessary for pH control during uranium stripping.
- Investigate the effect of column L/V ratio on the processes, considering the advantage of lower volumes of waste solutions.
- Determine effect of DBP in the organic phase on stripping characteristics of citrate.
- Measure effectiveness of the small amount of carbonate present during citrate stripping in cleaning the organic of DBP.

REFERENCE

1. Welcher, F. J., Ed., Standard Methods Of Chemical Analysis, Vol. II, Part A, p. 596.

R. L. Knights

Calculations:

$$\frac{5.40 \text{ moles KMnO}_4}{1.23 \text{ moles Citric Acid}} = 4.3 \text{ moles KMnO}_4/\text{mole Citric Acid}$$

$$4.3 \times \frac{(5 \text{ equiv/mole KMnO}_4)}{(3 \text{ equiv/mole Citric Acid})} = 7.2 \text{ equiv KMnO}_4/\text{equiv Citric Acid}$$