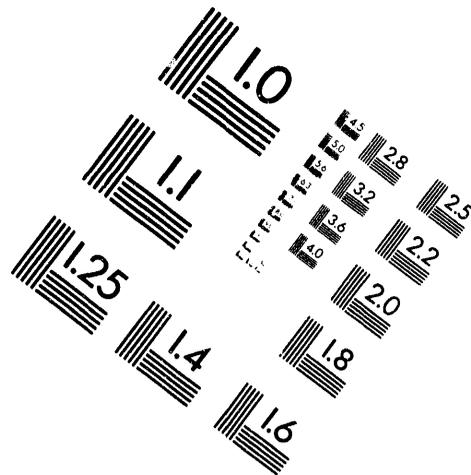
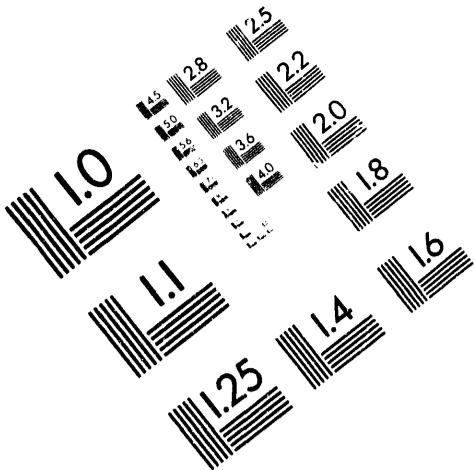




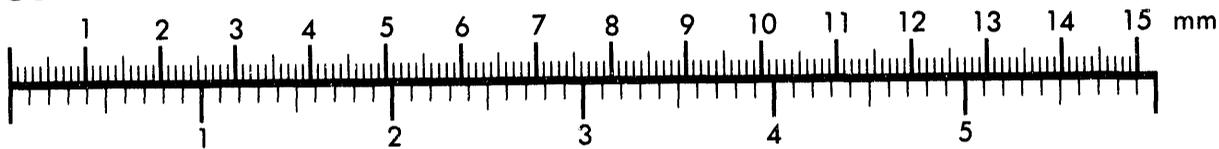
**AIM**

**Association for Information and Image Management**

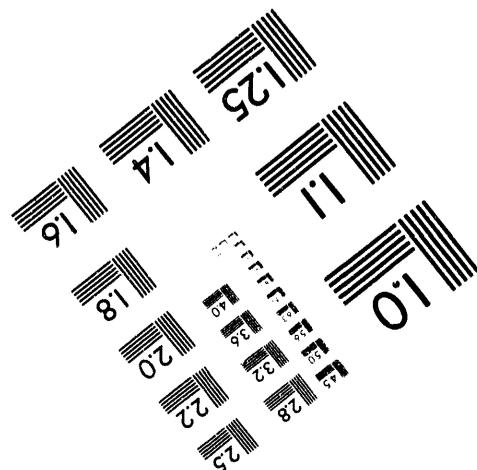
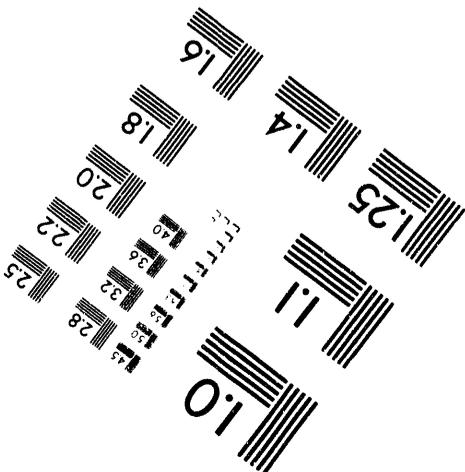
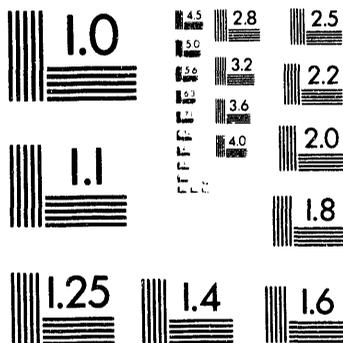
1100 Wayne Avenue, Suite 1100  
Silver Spring, Maryland 20910  
301/587-8202



Centimeter



Inches



MANUFACTURED TO AIM STANDARDS  
BY APPLIED IMAGE, INC.

**1 of 1**



[REDACTED]

DECLASSIFIED

HW-84139

THE USE OF CHEMICAL ADDITIVES TO IMPROVE  
FIRST CYCLE DECONTAMINATION AT PUREX

by

T. R. McKenzie

Separations Chemistry Laboratory  
Research and Engineering  
Chemical Processing Department

September 25, 1964

HANFORD ATOMIC PRODUCTS OPERATION  
RICHLAND, WASHINGTON

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.

500

MASTER

pages, copy no. /  
of 26 copies. [REDACTED]

[REDACTED]  
Excluded from automatic downgrading  
and declassification

Classification Canceled (Change to UNCLASSIFIED)  
By Authority of [REDACTED] Classification Coordinator, [REDACTED] West.  
Date 3/23/93

[REDACTED]

DECLASSIFIED

Copy Number

Distribution

1.	O. F. Beaulieu
2.	R. E. Burns
3.	J. P. Duckworth
4.	C. B. Foster
5.	W. M. Harty
6.	H. H. Hopkins, Jr.
7.	R. E. Isaacson
8.	B. F. Judson
9.	J. B. Kendall
10.	R. J. Kofoed
11.	R. W. McCullugh
12.	T. R. McKenzie
13.	H. C. Rathvon
14.	C. A. Rohrmann
15.	R. J. Sloat
16.	A. E. Smith
17.	S. G. Smolen
18.	R. E. Tomlinson
19.	A. J. Waligura
20.	300 Files
21.	Records Center
22. - 26.	Extra

DECLASSIFIED

THE USE OF CHEMICAL ADDITIVES TO IMPROVE  
FIRST CYCLE DECONTAMINATION AT PUREX

INTRODUCTION

The decontamination cycle (HA) at Purex has occasionally responded favorably to additions of waste rework material. The effect, exhibited in increased extraction of plutonium and improved decontamination from fission products, has become known as the "Tonic effect." Efforts to find the agent or agents in waste rework which are responsible for this effect have not been successful.

Workers at ORNL, principally C. A. Blake<sup>(1)</sup>, found that various materials decreased the distribution ratios of zirconium-niobium and ruthenium activity. This work covered oximes, ketones, and oxalic acid in the Purex HA system. Their work ended with the conclusion that oxalic acid was the most effective of all agents tested.

This paper describes the work by Separations Chemistry Laboratory designed to test these and other additives in the HA system at Purex.

SUMMARY

Several organic compounds including ketones, oximes, and dibasic acids were evaluated as chemical additives to determine their effectiveness in increasing ZrNb<sup>95</sup> and Ru decontamination in the HA column. Of those tested, oxalic acid was the most effective in reducing ZrNb  $E_2^0$ . No successful complexant for Ru was found.

In HA feed point contacts, HAF concentrations of 0.001M, 0.01M, and 0.1M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> reduced ZrNb<sup>95</sup> distribution ratios ( $E_2^0$ ) by factors of 4, 49, and 360, respectively.

  
**DECLASSIFIED**

These results were verified by MBCC (multiple batch counter current) runs simulating the HA column. Improvement in ZrNb<sup>95</sup> DF by factors of 1.6 and 2.8 were obtained at 0.001M and 0.003M oxalic acid. In these runs there was no evidence of increased Pu losses. On the contrary, Pu extraction appeared to be improved by the addition of oxalate.

The possibility of precipitating Pu oxalate in the HA system and in the waste was recognized. Investigation of these possibilities showed that Pu could not be precipitated in the feed or in the column with less than 0.003M oxalate. The half-life of oxalic acid in boiling 1WW at 4.6M and 5.7M HNO<sub>3</sub> was determined to be 40 and 16 minutes, respectively. These rates of oxidation will prevent the accumulation of oxalate and the subsequent precipitation of Pu at this point.

#### EXPERIMENTAL

To determine the most effective additives, a series of exploratory experiments simulating HA feed point contacts was made. The additives used are listed in Table I. The compositions and flows of streams used for the HA system are shown in Table III. This flowsheet was used throughout the study.

During the development program the following procedure was used: The HAF was spiked with activity supplied from plant dissolver solution. The appropriate amount of additive was added (see Table II) to the HAF which was then divided into three equal portions and treated as follows:

- a. No treatment
- b. Refluxed at boiling temperature for 30 minutes
- c. Made 0.01M in NaNO<sub>2</sub> and refluxed for 30 minutes

DECLASSIFIED

The resulting HAF was combined with synthetic 3WB (Back-cycle waste) and HSR (HS scrub) solutions to produce HAFS and was contacted with 30 v/o TBP-Soltrol.

Contact times were five minutes at ambient temperature. The phases were separated by centrifugation and 0.1 ml of the aqueous and 0.5 ml of the organic were mounted using standard wet mount techniques. The mounts were scanned for gamma activity on a 400-channel analyzer. The relative effect of each additive was determined by comparing ZrNb<sup>95</sup> and Ru (total) distribution ratios ( $E_a^0$ ) with control runs. The results are summarized in Table II. The  $E_a^0$  values for ZrNb<sup>95</sup> with improvement factors over the control runs are listed.

In the work with Ru, the average  $E_a^0$  based on analyses of both ruthenium isotopes RuRh<sup>106</sup> and Ru<sup>103</sup> was used. The accuracy of the ruthenium results is questionable due to the variance in ZrNb/Ru activity ratios. Improvement in Ru distribution ratios is considered insignificant, and in the light of results with subsequent MBCC runs, this conclusion appears valid.

Of those additives tested, all except fumaric acid gave some improvement in ZrNb  $E_a^0$ . Oxalic acid proved to be far superior to the other additives so all subsequent work was limited to its use.

A series of MBCC runs was made at ambient temperature. A control run was made using the standard flowsheet employed in the exploratory experiments. This run and two runs with H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in the HAF at 0.001M and 0.003M are shown in Table III. These results show that 50 to 300 percent improvement in ZrNb<sup>95</sup> decontamination can be obtained with low oxalic acid concentrations. It is interesting to note that plutonium losses did not suffer as a result

DECLASSIFIED

of oxalic acid. On the contrary, in every run that was made, Pu losses were slightly lower with oxalic acid than in the control run.

The addition of oxalic acid to a plutonium stream could result in precipitation since the solubility of plutonium oxalate  $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  in water is very low ( $\text{SP} = 4 \times 10^{-22}$ ). It was decided, therefore, to investigate the extent of Pu precipitation, if any, in the HA system as a result of adding  $\text{H}_2\text{C}_2\text{O}_4$ .

The following potential problem areas were evaluated for the following cases:

- Case 1. The precipitation of Pu in the HAF as a function of oxalic acid concentration.
- Case 2. The precipitation of Pu in the extraction section of the HA column as U is removed.
- Case 3. The stability of oxalic acid in the F-6 concentrator where significant Pu content may result from off-standard HA operation.

For the first and second cases, synthetic HAF was prepared at flowsheet Pu concentrations (254 mg/l). Oxalic acid at concentrations of  $10^{-4}\text{M}$  to  $10^{-1}\text{M}$  was added and the solution allowed to stand with gentle agitation for five days. After centrifugation the supernatant liquid was analyzed for Pu, by standard alpha counting techniques, and compared to calculated values. The results of these experiments are summarized in Table IV.

These results show that no precipitation occurs in HAF as a result of adding oxalic acid up to a concentration of  $0.013\text{M}$ . At  $0.065\text{M}$  and  $0.115\text{M}$   $\text{H}_2\text{C}_2\text{O}_4$  precipitation occurred but no Pu was carried by the precipitate. It

DECLASSIFIED

has been shown in subsequent experiments that uranium oxalate precipitates from solutions containing 0.05M  $H_2C_2O_4$ , 1.0M to 4.0M  $HNO_3$  at 100 to 400 g/l uranium. With excess uranium present, the precipitation of uranium oxalate limits the concentration of  $H_2C_2O_4$  remaining in these solutions to less than 0.03M. The precipitates observed in HAF as a result of adding oxalate ( $> 0.06M$ ) are oxalates of uranium rather than plutonium.

In the extraction section of the HA column the U/Pu concentration ratio will be lowered due to the preferential extraction of uranium. Two factors tend to retard the precipitation of plutonium oxalate; namely, the competition from uranium and the removal of Pu by extraction. However, it must be assumed that Pu reflux below the HA feed point would cause Pu concentrations equal to the HAF. This section of the column would contain an equilibrium concentration of 2.5M  $HNO_3$  and be essentially free of uranium. Experiments simulating this condition were carried out. The precipitation of plutonium at 253 mg/l and 651 mg/l in 2.5M  $HNO_3$  as a function of oxalic acid concentration was determined. The results of these experiments are summarized below:

$H_2C_2O_4$ M	Pu Added mg/l	Pu in solution at 72 hours, mg/l	Percent Pu Precipitated
0.03	651	15	97.7
0.01	651	39	94.0
0.005	651	571	12.3
0.003	651	651	0.0
0.001	651	650	0.0
0.03	253	16.4	93.5
0.01	253	39.5	84.4
0.003	253	253	0.0
0.001	253	253	0.0

DECLASSIFIED

The second set of experiments at 253 mg/l Pu was obtained by diluting the first set, so that the  $\text{Pu}(\text{C}_2\text{O}_4)_2$  precipitate was already formed. There was some dissolution of the precipitate under these conditions after 48 hours.

In any event, there will be no precipitation of the Pu as a result of oxalic acid in the HA column provided the oxalate concentration is maintained at 0.003M or below.

For the third case, synthetic LWW solutions were prepared varying only the nitric acid content. The composition of these solutions is shown below:

<u>Constituent</u>	<u>Sol'n I, M</u>	<u>Sol'n II, M</u>
Al	0.125	0.125
Ni	0.015	0.015
Si	0.015	0.015
Cr	0.025	0.025
Na	0.67	0.67
Fe	0.35	0.35
F	0.003	0.003
$\text{PO}_4$	0.015	0.015
$\text{SO}_4$	0.67	0.67
$\text{NO}_3$	5.57	6.68
$\text{H}^+$	4.62	5.73

Oxalic acid was added to these solutions and analyzed by titration with standardized ceric sulfate using a ferroin endpoint.

Solution I exhibited a reducing potential of 0.0023 N and solution II an oxidizing potential of 0.0035 N. The difference was due to the more

[REDACTED]

[REDACTED]

**DECLASSIFIED**

rapid oxidation of Cr(III) to Cr(VI) by the higher nitric acid concentration in solution II. The two solutions were refluxed for two hours at 120-130 C to produce chemical equilibrium. This treatment was successful and both solutions exhibited oxidizing potentials of 0.014 N after this treatment.

After dividing solution I into two equal parts, IA and IB, oxalic acid at 0.044M was added to solution IB and II. All solutions were refluxed at 120-130 C for two hours with samples taken every 15 minutes.

Solution IA, without oxalate, varied from an oxidizing normality of 0.0106 to 0.0156 throughout this period, which indicates an experimental accuracy of  $\pm 7.0\%$  for the titrations.

The results obtained for solution IB and II are summarized in table form below:

Reflux time minutes	Molarity of $H_2C_2O_4$ Remaining	
	Solution IB 5.2M $H^+$	Solution II 5.7M $H^+$
0	0.0422	0.0441
15	0.0337	0.0249
30	0.0214	0.0111
45	0.0196	0.0058
60	0.0142	0.004*
75	0.0116	--
90	0.0078	--
105	0.0073	--
120	0.0063	--

\* Lower limit of analytical procedure

DECLASSIFIED

The half-life of  $H_2C_2O_4$  in boiling LWV at 4.2M and 5.7M  $HNO_3$  is 40 and 16 minutes, respectively. With a residence time for LWV in the F-6 concentrator of 2.5 days, the above rates of oxidation will assure no oxalate accumulation in the waste.

### CONCLUSIONS

Experimental evidence shows that it will be safe to add up to 0.003M  $H_2C_2O_4$  to the HAF at Purex. The addition of oxalic acid will greatly enhance the capabilities of the plant to decontaminate products from Zr-Nb activity. This increased capability may be necessary in the immediate future for the successful handling of the various programs proposed for Purex, which will include hotter feeds than those presently being processed.

In these studies no attempt was made to evaluate the effect of oxalic acid on neptunium. If the neptunium is to be routed to the waste with a high nitrite flowsheet and subsequently recovered from LWV, the addition of oxalic acid should have no effect. Under the present flowsheet, where Np(VI) is maintained with low nitrite, the addition of oxalic acid might change the  $NO_2^-$  requirements necessary, but should not affect the extraction of Np(VI) nitrate.

### REFERENCES

C. A. Blake - ORNL periodicals for the years 1960, 1961, and 1962.

DECLASSIFIED