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Chemistry–Separation Processes
for Plutonium and Uranium

THE EFFECT OF ACIDITY AND REDUCING AGENTS ON RUTHENIUM SOLVENT EXTRACTION BY TRIBUTYL PHOSPHATE IN THE 25 PROCESS

R. Flanary
L. D. Frashier

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Chemical Development Section

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1.0 ABSTRACT

Results of tracer studies suggest that, in tributyl phosphate extraction processes designed to recover and purify fissionable material, minimum ruthenium extraction should be obtained from feeds at least 2 M in nitric acid or at least 1 M acid-deficient. Ruthenium decontamination was decreased by preheating the feed and increased by pretreatment with reducing agents. A pretreatment using 0.06 M ferrous ion and 0.5 M urea with 1 hr simmering at 85°C should increase ruthenium decontamination about 10-fold in the 25 process. If other process considerations dictate the use of a low-acid feed, decontamination from ruthenium may be improved by using 3 M nitric acid as the scrubbing solution. Apparently, the scrubbing process is quite time-dependent; a solvent holdup time of about 15 min may be needed in the scrub section for maximum decontamination.

2.0 INTRODUCTION

This study was undertaken to learn more about the behavior of ruthenium in the tributyl phosphate solvent-extraction phase of the 25 process. Ruthenium is one of the most difficult products to separate from irradiated reactor fuels when these fuels are processed to recover fissionable material, and has proved to be the limiting fission product contaminant in U^{235} recovered by the hexone extraction process used at the Idaho Chemical Processing Plant. A special tail-end ruthenium-scavenging procedure had to be added to the process in order to meet the U^{235} product activity specifications. Work on development of the Purex process through the pilot plant stage at ORNL showed that the uranium product activity specifications

might not be met consistently with two cycles of tributyl phosphate extraction because of inadequate separation of ruthenium from

duced to

The data presented in this report were obtained in experiments utilizing Ru^{106}-Rh^{106} tracer and are valid for the conditions outlined. However, it should be pointed out that past experience has shown that results obtained with tracer activities cannot in every case be duplicated under process conditions where macro amounts of fission products are present and the previous environment of the fission products is different.

3.0 EXPERIMENTAL PROCEDURES

The experiments were carried out by equilibrating 25-ml aliquots of a synthetic aqueous phase, containing Ru^{106} tracer, with equal

volumes of organic solvent for a given time. The mixture was allowed to stand until the phases had separated, and the activity of 1-ml samples of each phase was then determined in a gamma scintillation counter. All distribution coefficients were measured at room temperature, approximately 25°C.

The aqueous phase contained 1.8 M aluminum nitrate, nitric acid, and Ru^{106} tracer obtained from the Operations Division at ORNL. The tracer was obtained as a 7 M nitric acid solution, and the principal activity measured was the gamma emitting 0.5-min Rh^{106}, the decay product of 1-year Ru^{106}. The solvent was 6% tributyl phosphate in a hydrocarbon diluent, Amsco 125-90W, and had been previously purified by calcium hydroxide treatment(1) and sulfonation.(2)

4.0 EFFECT OF EXTRACTION CONDITIONS

4.1 Effect of Acidity on Extraction

The results of a series of batch equilibrations of 6% TBP solvent in Amsco diluent with aqueous feed solutions of various acidities show that the ruthenium distribution coefficient (O/A) is a maximum at about 0.03 M nitric acid. Within the range of conditions employed in these experiments, minimum ruthenium distribution coefficients were observed with feeds 2 to 2.5 M in nitric acid or 1.2 M acid-deficient (see Table 1 and Fig. 1). The experiments were made by contacting aliquots of the aqueous phase, 1.8 M aluminum nitrate plus Ru^{106} tracer, and various concentrations of nitric acid or sodium hydroxide with equal (25 ml) volumes of the solvent. Previous to each equilibration, the aqueous phase had been allowed to simmer for 3 hr at 85°C. After 5 min equilibration, the phases were separated and analyzed for gamma activity.

Table 1

Effect of Acid Concentration on Ruthenium Extraction by TBP

Solvent: 6% TBP in Amsco 125-90W
Aqueous phase: 1.8 M aluminum nitrate, Ru^{106} tracer, acidity adjusted with nitric acid or sodium hydroxide; heated 3 hr at 85°C prior to extraction[a]
Phases: 25 ml each, equilibrated 5 min; then separated and analyzed for gamma activity

Nitric Acid (M)	Ruthenium Distribution Coefficient, O/A	Nitric Acid (M)	Ruthenium Distribution Coefficient, O/A
-1.23	0.00014	0.14	0.22
-0.47	0.0025	0.20	0.16
-0.22	0.0065	0.40	0.045
-0.10	0.020	0.70	0.0097
-0.00	0.16	1.00	0.0029
0.03	0.34	1.50	0.00065
0.06	0.32	2.00	0.00026
0.09	0.25	2.50	0.00014

(a) Acid concentrations are nominal since the values represent the nitric acid or sodium hydroxide added to the aluminum nitrate solutions and not actual pH determinations. The most acid deficient solution tested showed a pH of approximately 2 with pH paper.

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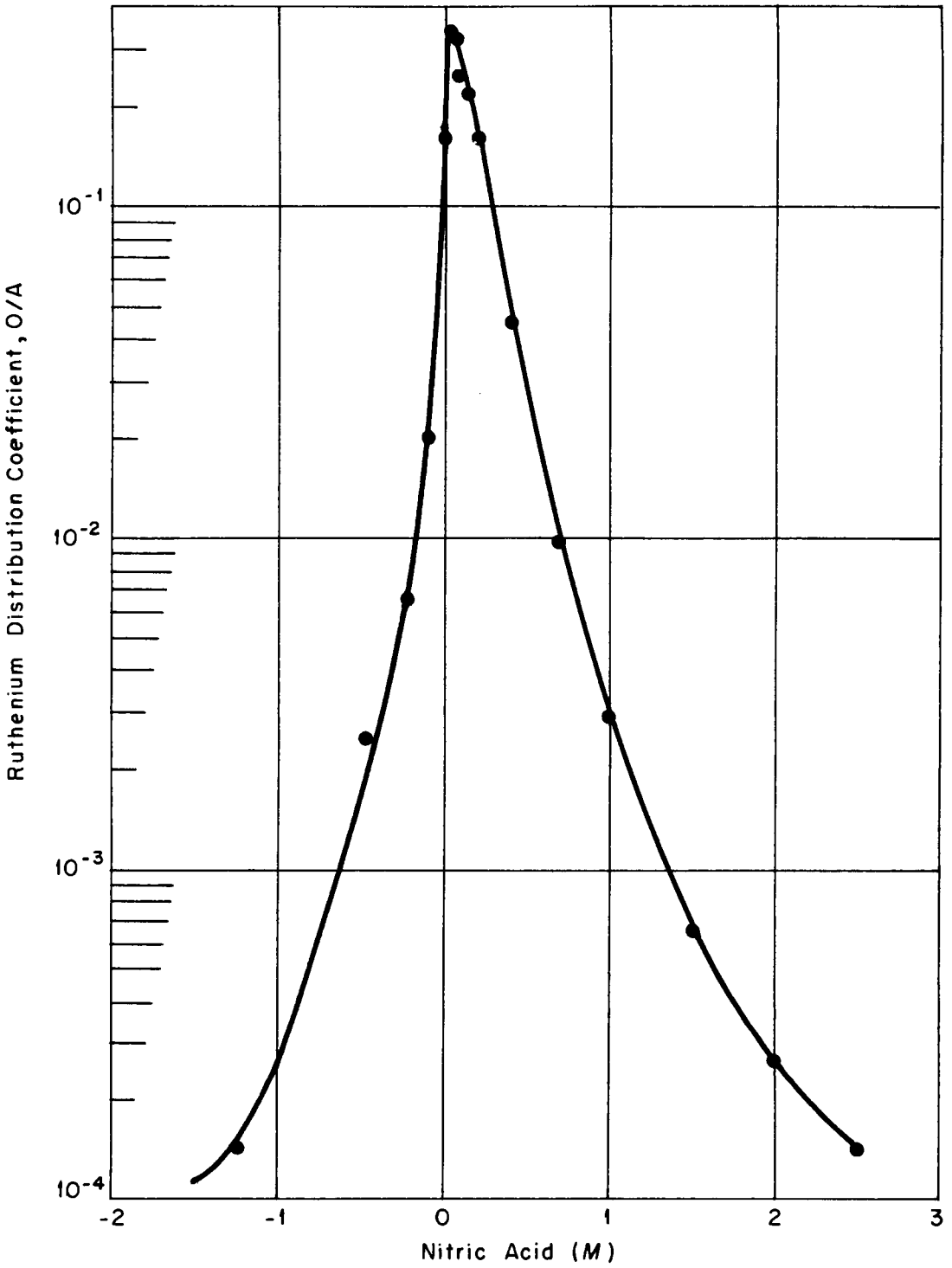

Solvent: 6% TBP in Amsco 125-90W

Aqueous phase: 1.8 *M* aluminum nitrate, Ru^{106} tracer, acidity adjusted with nitric acid or sodium hydroxide; heated 3 hr at 85°C prior to extraction; phases, 25 ml each, equilibrated 5 min, then separated and analyzed

Fig. 1. Effect of Acidity on Ruthenium Distribution Coefficient.

5.0 EFFECTS OF FEED PRETREATMENTS

5.1 Effect of Feed Preheating

When the feed was low in acid concentration and was heated at 85°C prior to the extraction, the ruthenium distribution coefficient (O/A) in the extraction increased as the heating time increased, from 0.062 at 0 hr to 0.41 at 23.5 hr (see Table 2). The feed was a 1.8 M aqueous solution of aluminum nitrate with a nitric acid concentration of 0.03 M, i.e., the acidity for maximum ruthenium extraction (see Sect. 4).

During the heating the ruthenium was apparently converted to a more extractable form. This could not be due to the formation of higher oxidation states since the tracer solution (7 M nitric acid) is more strongly oxidizing than the 0.03 M nitric acid feed solution used. A possible explanation is the formation of an extractable ruthenium polymer or colloid.

The extraction is not rapidly reversible. This is in agreement with previous work in hexone solutions.[3]

Two runs were made with ruthenium tracer in 1 and 3 M sodium hydroxide with no aluminum nitrate present. The aqueous phase was heated 3 hr at 85°C. The ruthenium distribution coefficient (O/A) was 5×10^{-4} in both cases.

5.2 Effect of Sodium Nitrite

During Purex process development at ORNL it was established that ruthenium decontamination across the second solvent extraction cycle (uranium purification) could be increased about 20-fold by simmering the second cycle feed solution 3 hr at 85°C in the

Table 2

The Effect of Feed Preheating on Ruthenium Extraction by TBP

Solvent: 6% TBP in Amsco 125-90W
Aqueous phase: 1.8 M aluminum nitrate, Ru^{106} tracer, 0.03 M nitric acid; simmered at 85°C for time indicated
Phases: 25 ml each, equilibrated 5 min; then separated and analyzed for gamma activity

Heating Time (hr)	Ruthenium Distribution Coefficient, O/A
0.0	0.062
0.25	0.27
0.50	0.29
1.00	0.36
3.00	0.34
23.5[a]	0.41

(a) After the experiment was completed, the organic phase from this extraction was re-equilibrated with stock aqueous solution containing no ruthenium. The distribution coefficient (O/A) was 3.1, indicating that the ruthenium extraction was essentially nonreversible. The aqueous phase from the initial extraction was re-equilibrated with fresh solvent. The distribution coefficient (O/A) was 0.21, indicating the existence of a second, less extractable species of ruthenium.

presence of 0.005 M sodium nitrite. Owing to the unsatisfactory decontamination of uranium from ruthenium experienced with the hexone extraction 25 process at the Idaho Chemical Processing Plant, the application of the nitrite feed pretreatment to this process was investigated at ORNL. Treatment of the Idaho 25 process second and third cycle feed solutions with sodium nitrite was shown to increase the ruthenium decontamination factor by more than 100.

Four experiments with 1.8 M aluminum nitrate solutions of acidities ranging from 0.1 to 0.6 M were run to determine the effect that pretreating the feed with 0.05 M sodium nitrite would have on the extraction of ruthenium by TBP. The distribution coefficients were not significantly different from those for control solutions with no nitrite added. The reason for the difference in the results is not understood.

5.3 Effect of Reducing Agents

In general, lower oxidation states of an element are more ionic, whereas higher states are more covalent and therefore more extractable into organic solvents. Results of experiments with reducing compounds indicate that simmering the aqueous feed for 1 hr in the presence of 0.06 M ferrous ion and 0.5 M urea should significantly improve the ruthenium decontamination (see Table 3). The solution must be simmered to accelerate the reduction reaction. In several runs in which the simmering was omitted, the ruthenium distribution was unchanged by the additives after 3 hr standing at room temperature.

The effect of urea in depressing the ruthenium extraction after several hours standing at room temperature was observed by

Table 3

Effect of Urea and Ferrous Ion on Ruthenium Extraction by TBP

Solvent: 6% TBP in Amsco 125-90W
Aqueous phase: 1.8 M aluminum nitrate, Ru^{106} tracer; simmered 1 hr at 85°C
Phases equilibrated 5 min; then separated and analyzed for gamma activity

HNO_3 (M)	Iron Salt	Fe^{++} (M)	Urea (M)	Ruthenium Distribution Coefficient, O/A
0.03	---	0	0	0.36
0.03	$Fe(NO_3)_2$	0.06	1.0	0.002
0.03	$Fe(NO_3)_2$	0.06	0.5	0.007
0.12	$Fe(NO_3)_2$	0.06	1.0	0.009
0.12	$Fe(NO_3)_2$	0.02	1.0	0.027
0.12	$Fe(NH_2SO_3)_2$	0.06	0.5	0.028
0.12	$FeSO_4$	0.02	0.2	0.25

Elliot and Miles[3] for hexone solvent. Several other additives were tested for their effect on the extraction of ruthenium. In all tests the aluminum nitrate concentration was 1.8 M, the nitric acid was 0.03 M, the additive was 0.10 M, and the solution was simmered at 85°C for 1 hr. The solvent was 6% TBP in Amsco 125-90W. Mercurous and mercuric nitrates, cobaltous nitrate, nickelous nitrate, phosphorous acid, and hydrogen peroxide had no appreciable effect on the ruthenium extraction. Sodium metabisulfite and oxalic acid each decreased the distribution coefficient slightly.

6.0 EFFECT OF ACIDITY OF SCRUBBING SOLUTION

Extracted ruthenium was more efficiently backwashed from the solvent with 2 or 3 M nitric acid than with 1 M aluminum nitrate (see Table 4). Ruthenium scrubbing appeared to be very time dependent. Apparently, the ruthenium species extracted at low acidity is slowly converted to a less extractable form when contacted with a high-acid solution. This phenomenon may explain why rather small gains in the ruthenium decontamination factor were observed in the scrub section of batch countercurrent batteries or compound pulse columns where the solvent residence time was 3 to 6 min. If a solvent holdup time of about 15 min is needed for effective ruthenium scrubbing, the scrub section would probably have to be concatenated to provide sufficient length of column in a building with limited head room.

Table 4

Effect of Contact Time and Scrub Composition on Ruthenium Retained by TBP

Solvent: 6% TBP in Amsco 125-90W, previously equilibrated with stock aqueous phase [1.8 M $Al(NO_3)_3$, 0.12 M HNO_3, Ru^{106} tracer], heated at 85°C for 1 hr; equilibrated solvent and scrub stirred together for time indicated

Scrub Solution	Concentration (M)	Ruthenium D.C., O/A		
		Contact Time 1 min	Contact Time 6 min	Contact Time 16 min
$Al(NO_3)_3$, Na_2SO_4	1, 0.02	0.60	0.30[a]	0.21
HNO_3	1	0.30		
HNO_3	2	0.17		
HNO_3	2.5	0.15	0.066	0.032
HNO_3	3.0	0.11	0.19[a]	0.010[a]
HNO_3	5.0	0.12	0.044	0.010
HNO_3, $Fe(NH_2SO_3)_2$	3.0, 0.05	0.11	0.046	0.020

(a) Total time 2 to 4 min longer owing to sampling technique.

7.0 RUTHENIUM SORPTION BY ION EXCHANGE RESINS

In a solution which is 1.8 M in aluminum nitrate and 0.03 M in nitric acid the Ru^{106} tracer is very rapidly sorbed by the cation exchanger Dowex 50. When 2 g of resin in hydrogen form was added to 50 ml of solution, the solution activity dropped to 3.5% of its initial value within 5 min. A solution of the same composition gave no measurable exchange with the anion exchanger Dowex 1.

An attempt was made to sorb the tracer from a basic solution, but there was no measurable exchange with either Dowex 1 or Dowex 50. For use in the experiments ruthenium tracer was added to 1 M sodium hydroxide and heated for 3 hr at 85°C.

Apparently, the ruthenium species existing in low-acid media are predominantly cationic in nature, and those existing in basic solution exhibit a colloidal behavior unaffected by prolonged heating.

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