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Chemistry - Separation Processes
for Plutonium and Uranium

AEC Research and Development Report

SCAVENGING OF RUTHENIUM FROM PUREX URANYL NITRATE SOLUTION

by

C. A. Prohaska

Separations Chemistry Division

June 1958

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ABSTRACT

Ruthenium in uranyl nitrate solutions is adsorbed by the solid residue that remains when the solutions are concentrated by evaporation after treatment with thiocarbanilide and thioacetamide.

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SCAVENGING OF RUTHENIUM FROM PUREX URANYL NITRATE SOLUTION

INTRODUCTION

When uranium is recovered from irradiated nuclear fuel by the Purex process(1), the initial product is a dilute aqueous solution of uranyl nitrate; this solution is subsequently concentrated by evaporation. Ruthenium, zirconium, and niobium are the principal contaminants that remain in the recovered uranyl nitrate. Zirconium and niobium can be removed from the concentrated uranyl nitrate solution by adsorption on silica gel at 90°C(1,2). Ruthenium can be removed from dilute solutions of uranyl nitrate by adsorption on carboxylic acid ion exchange resin, after heating the solutions with thiourea.(3)

In previous work on the ion exchange adsorption of ruthenium, it was observed that when certain compounds of sulfur were added to dilute uranyl nitrate solutions, precipitates formed which carried ruthenium(3). The purpose of this investigation was to develop a similar method for scavenging ruthenium from concentrated uranyl nitrate solutions. Such a method, combined with the silica gel treatment for removing zirconium and niobium, might provide an integrated process to remove all three contaminants.

SUMMARY

Laboratory tests showed that ruthenium is effectively scavenged from the uranyl nitrate product of the Purex process by the following procedure. Thiocarbanilide and thioacetamide, 0.04 weight per cent each, are added to the dilute uranium product stream. The treated solution is then concentrated by evaporation. A solid residue remains in the uranyl nitrate solution during and after the evaporation step. The ruthenium is adsorbed on this solid material, and is removed from the solution by filtering.

Ruthenium decontamination factors greater than 35 were observed in the laboratory. Uranyl nitrate from which ruthenium had been scavenged by this method showed normal denitration behavior in laboratory tests and the resulting oxide products were normal in composition and functional behavior, i.e., "reactivity" during reduction and hydrofluorination.

The amounts of chemicals used were not critical. Significant ruthenium decontamination factors were observed when the amount of each chemical added was as small as 0.007 weight per cent. The presence of organic solvent in excess of its solubility in the unevaporated solution interfered with the ruthenium adsorption; it was not established whether this interference would be eliminated if the excess solvent were completely volatilized or decomposed during the evaporation.

DISCUSSION

FEED SOLUTIONS

The feeds for all experiments were solutions of irradiated uranium which had been treated by one or two cycles of a Purex solvent extraction process. For the early experiments, these solutions had been concentrated by evaporation and contained approximately 1.7M uranyl nitrate and 0.3M nitric acid. The feed solutions for some later experiments were taken directly from the dilute uranium product stream of a Purex process and contained approximately 0.2M uranyl nitrate and 0.01M nitric acid. The activity levels in the feed solutions varied considerably, but were of the order of a few thousand scintillation gamma counts per minute per milliliter. The amounts of ruthenium and zirconium-niobium were approximately equal; no other activity was present in significant quantities.

EXPERIMENTAL PROCEDURE

Feed solutions that had been previously concentrated by evaporation were treated with the scavenging materials, diluted with distilled water, evaporated to their original volume on a hot plate, cooled, and filtered. Whatman No. 1 filter paper was normally used, but a bed of fine sand two inches thick also served as a satisfactory filter. Ruthenium analyses of the feed and product solutions were made with a gamma pulse height analyzer. The results of the tests are reported as ruthenium decontamination factors (Ru DF), calculated by dividing the ruthenium concentrations in the original uranyl nitrate solutions by the ruthenium concentrations in the filtrates. When dilute Purex endstreams were used directly as feed solutions, the evaporation and scavenging steps were combined. Many of the scavenging materials used are insoluble in water, and there was usually solid material on the surface of the uranyl nitrate solution before and during the evaporation step, as well as after the evaporation was complete.

RESULTS

The chemicals that had been effective in the previous study were added to concentrated (1.7M) uranyl nitrate solutions which were then diluted by a factor of 2 and reconcentrated to their original volumes, to simulate an evaporation step. The results of these experiments (Table I) show that the ruthenium decontamination factors are very much less when the treatments are applied to concentrated solutions. Substantial improvements were obtained, however, by two modifications: (1) by increasing the dilution of the feed to approximately the original volume of the Purex effluent, the Ru DF for the thiocarbanilide treatment was increased from 1.9 to 4.4, and (2) when thiolacetic acid and thiocarbanilide were added simultaneously to concentrated uranyl nitrate solution, the Ru DF was increased to 17.

Because of the significant increase in the Ru DF when treatments with thiolacetic acid and thiocarbanilide were combined, other combinations of chemicals were investigated in tests in which the favorable (7-fold) dilution of the concentrated feed was also adopted. The results are summarized in Table II. The combinations which gave the best ruthenium decontamination factors were thiocarbanilide and thioacetamide (Ru DF = 26), thiocarbanilide and sodium sulfide (Ru DF = 10), and thiolacetic acid and thioacetanilide (Ru DF = 17).

In the experiments summarized in Table II, significant Ru DF's were observed only when one of the added chemicals contained an ionizable sulfur atom. Thiolacetic acid and thioacetamide are soluble in water, and hydrolyze in acidic solutions to give acetic acid and a bisulfide ion (HS^-). In the next series of tests (Table III) useful Ru DF's were observed when thiocarbanilide was combined with any of four chemicals which yielded bisulfide ions. Smaller, but significant Ru DF's were obtained when thioacetanilide was used instead of thiocarbanilide.

The amounts of chemicals used were not critical. Tables IV and V summarize the effects of varying the amount of either chemical. The process was equally effective whether the feed was concentrated uranyl nitrate solution which had been diluted with distilled water (Table IV), or dilute uranyl nitrate solution which had not been previously concentrated and diluted (Table V).

Significant ruthenium adsorption was observed with both types of dilute feed, provided that no organic solvent was present on the surface of the feed solution. Dilute uranyl nitrate solution taken directly from a Purex process occasionally included a small amount of organic solvent, and this solvent interfered with the ruthenium adsorption by dissolving the thiocarbanilide.

Uranyl nitrate from which ruthenium had been scavenged by this method showed normal behavior during conversion to uranium trioxide. Four of the treated and filtered solutions were evaporated to dryness. The resulting samples of uranyl nitrate were dried at 110°C and denitrated at 270°C. Behavior during heating and denitration was identical with that of reagent-grade uranyl nitrate. The samples of UO_3 obtained from the denitrations were tested in the laboratory for "reactivity ratio"* and sulfur content. The results showed the samples to be normal. The reactivity ratios ranged from 0.82 to 0.99; residual sulfur was below the limit of detection.

The mechanism of this ruthenium adsorption is obscure, but the HS^- ion seems to be necessary. Many combinations of chemicals were tried, but unless a compound containing an ionizable sulfur atom was present, the Ru DF was small. In all cases where a significant Ru DF was observed, a finely divided precipitate, presumably sulfur, was formed at the beginning of the evaporation. By the end of the evaporation, all of the sulfur had been coagulated or oxidized.

The role of the second constituent is not at all clear. A large number of substituted amines and amides were added to concentrated uranyl nitrate solution in combination with thiolacetic acid or thioacetamide. The Ru DF's observed are summarized in Table VI. Thiocarbanilide consistently gave the highest values, but carbanilide, diphenylamine, and thioacetanilide also produced significant adsorption of ruthenium. These chemicals are all insoluble in water, and remain on the surface of the uranyl nitrate solution during the evaporation. Thiocarbanilide and other derivatives of thiourea form complexes with ruthenium which are only very slightly soluble in water[4,5]. Since only tracer quantities of ruthenium were involved, it is not possible from the data

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* UO_3 is subsequently reduced by H_2 to UO_2 and hydrofluorinated to UF_4. The yield through these reactions is taken as a measure of the reactivity of the UO_3. The "reactivity ratio" is the ratio of the yield from any sample of UO_3 to the yield from "standard" UO_3, under carefully controlled conditions.

obtained in this study to tell whether any of these complexes are involved in the adsorption mechanism. Thiourea forms a water soluble complex with ruthenium(5), and no ruthenium adsorption was observed when thiourea and sodium sulfide were added to concentrated uranyl nitrate solution. Indeed, the Ru DF of 18 observed when diphenylamine and thiolacetic acid were added to this uranyl nitrate solution decreased to 1.9 when thiourea was added along with these two chemicals. Ruthenium forms many water soluble complexes with ammonia, amines, and substituted amines, and presumably such a complex would be formed with diphenylamine. It is not known whether ruthenium forms any complexes with carbanilide.

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5. Deford, D. D. The Chemistry of Ruthenium. United States Atomic Energy Commission, NP-1104, May 1948.

TABLE I

Ruthenium Decontamination Factors Observed when Various Chemicals were Added to Uranyl Nitrate Solutions

0.2 gm of indicated chemical
added to 100 ml of indicated solution

	Ru DF when Treated Solution was	
Chemical Added	0.2M Uranyl Nitrate(a)	1.7M Uranyl Nitrate(b)
Benzenethiol	2.6	none
p-Toluenethiol	2.5	1.1
Mercaptosuccinic acid	-	1.1
Thiolacetic Acid	27	1.5
Thioacetamide	21	none
Thioacetanilide	45	none
Thiobenzanilide	131	none
Thiocarbanilide	3.9	1.9
Thiocarbanilide		4.4(c)
Thiourea	none	none
Carbon disulfide saturated with sulfur	none(d)	1.2
Sodium sulfide ($Na_2S \cdot 9H_2O$)	93	1.3
Thiocarbanilide and thiolacetic acid	-	17

(a) Data from DP-291, Table VII. Dilute uranyl nitrate product solution from a Purex process was treated, simmered one hour, cooled, and filtered.

(b) Concentrated uranyl nitrate product solution was treated, diluted to 0.85M U, evaporated to original volume, cooled, and filtered.

(c) For this test only, treated solution was diluted to 0.24M U, before evaporation as in (b).

(d) For this test only, treated solution was stirred at room temperature instead of simmered.

TABLE II

Ruthenium Decontamination Factors Observed when Thiolacetic Acid or Thiocarbanilide were Combined with Various Other Chemicals and Added to Uranyl Nitrate Solutions(a)

Chemical "A"	Ru DF when Chemical "B" was	
	Thiolacetic Acid	Thiocarbanilide
Thioacetamide	-	26
p-Toluenethiol	-	3.7
Benzenethiol	-	3.3
Mercaptosuccinic acid	-	1.6
Thioacetanilide	17	-
Thiobenzanilide	3.0	-
Sodium sulfide ($Na_2S \cdot 9H_2O$)	2.9	10
Carbon disulfide saturated with sulfur	2.6	1.8

(a) Uranyl nitrate product solution from a Purex process, evaporated to 1.7M U, was used as feed. 100-ml samples of the feed were treated with 0.2 gm of each of the specified chemicals "A" and "B," diluted 7-fold to 0.24M U, evaporated to original volume, cooled, and filtered.

TABLE III

Ruthenium Decontamination Factors Observed when Thiocarbanilide or Thioacetanilide were Combined with Various Sources of Bisulfide Ion and Added to Uranyl Nitrate Solutions(a)

Chemical "I" (Source of Bisulfide Ion)	Ru DF when Chemical "II" was	
	Thiocarbanilide	Thioacetanilide
Sodium sulfide, ($Na_2S \cdot 9H_2O$)	10	13
Hydrogen sulfide(b)	10	5.5
Thioacetamide	26	-
Thiolacetic acid	52	17

(a) Uranyl nitrate product solution from a Purex process, evaporated to 1.7M U, was used as feed. 100-ml samples of the feed were treated with 0.2 gm of each of the specified chemicals "I" and "II," diluted 7-fold to 0.24M U, evaporated to original volume, cooled, and filtered.

(b) Hydrogen sulfide gas bubbled through diluted solution for ten minutes.

TABLE IV

Ruthenium Decontamination Factors Observed with Various Amounts of Chemicals Added to Preconcentrated Purex Effluent

Thiocarbanilide Added per 100 ml of 1.7M Uranyl Nitrate Before Dilution(a)	Ru DF when Quantity of Thiolacetic Acid or Thioacetamide was		
	0.05 gm	0.1 gm	0.2 gm
0.01 gm	2.6	-	-
0.02	2.7	-	-
0.05	9.1	-	8.8
0.1	61	21	13
0.2	14	18	26
0.4	-	14	28

(a) Uranyl nitrate product solution from a Purex process, evaporated to 1.7M U, was used as feed. 100-ml samples of the feed were treated with the specified quantities of thiocarbanilide and either thiolacetic acid or thioacetamide, diluted to 0.24M U, evaporated to original volume, cooled, and filtered.

TABLE V

Ruthenium Decontamination Factors Observed with Various Amounts of Chemicals Added to Normal Purex Effluent

Thiocarbanilide Added per 700 ml of 0.2M Uranyl Nitrate(a)	Ru DF when Quantity of Thiolacetic Acid or Thioacetamide was			
	0.05 gm	0.1 gm	0.2 gm	0.4 gm
0.05 gm	-	11	1.8(b)	2.3(b)
0.1	5.8 1.9(b)		1.8(b)	2.7(b)
0.2	9.1	7.0	15 3.6(b)	
0.4	-	20	12	

(a) Uranyl nitrate product solution (0.24M U) from a Purex process was treated with the specified quantities of chemicals, evaporated to one-seventh of original volume, cooled, and filtered.

(b) Organic solvent was present on surface of feed and concentrated product.

TABLE VI

Ruthenium Decontamination Factors Observed
when Various Chemicals were Added to Uranyl
Nitrate Solutions in Combination with Bisulfide Ion[(a)]

Chemicals Added	Ru DF	Chemicals Added	Ru DF
Thiocarbanilide	52	Thiobenzanilide	3.0
Diphenylamine and urea	36	Ethylamine (70% in H_2O)	2.8
Carbanilide	21	Diethylamine	2.8
Thioacetanilide and urea	19	Benzamide	2.5
Diphenylamine	18	Benzylamine	2.3
Thioacetanilide	17	n-Butylamine	2.3
Thiobenzanilide and urea	9.1	Formamide	2.1
N, N-dimethylaniline and urea	7.2	2-Phenylethylamine	2.0
Aniline	6.8	Benzamide	1.9
Benzanilide	5.8	Diphenylamine and thiourea	1.9
N, N-dimethylaniline	5.6	"Dowex" A-1 resin	none
Triethylamine	5.3	Thiourea	none
Triphenylamine	5.2		
Urea	3.2		

(a) The source of the bisulfide ion was thiolacetic acid or thioacetamide. Uranyl nitrate product solution from a Purex process, evaporated to 1.7M U, was used as feed. 100-ml samples of the feed were treated with 0.2 gm of the specified chemicals, diluted to 0.24M U, evaporated to original volume and filtered.

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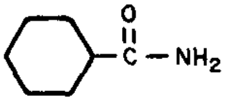
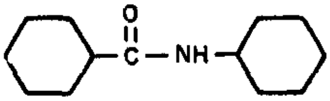
APPENDIX

Structural formulas of some organic chemicals tested in this study:

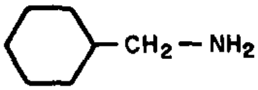
Benzamide



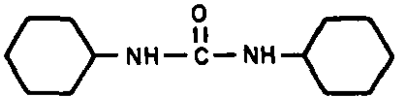
Benzanilide



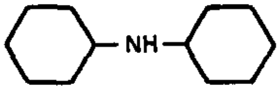
Benzylamine



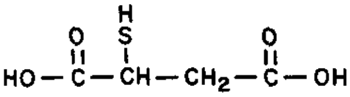
Carbanilide



Diphenylamine

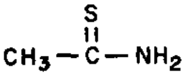


Mercaptosuccinic acid



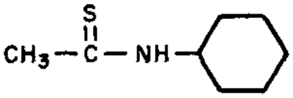
$$HO-\overset{\overset{O}{\|}}{C}-\overset{\overset{\overset{H}{S}}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

Thioacetamide



$$CH_3-\overset{\overset{S}{\|}}{C}-NH_2$$

Thioacetanilide



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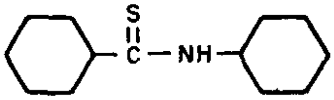

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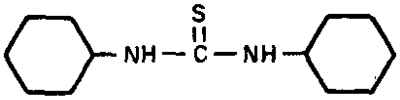
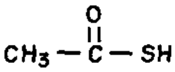


Thiolacetic acid



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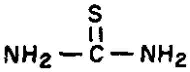

$$NH_2-\overset{\overset{S}{\|}}{C}-NH_2$$

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