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CATION EXCHANGE CONCENTRATION OF AQUEOUS $^{233}UO_2(NO_3)_2$ AND CONVERSION TO $^{233}UO_3$

G. A. BURNEY

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CATION EXCHANGE CONCENTRATION OF AQUEOUS $^{233}UO_2(NO_3)_2$ AND CONVERSION TO $^{233}UO_3$

by

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ABSTRACT

A process was developed to isolate ^{233}U from the dilute uranyl nitrate solution that is produced by solvent extraction separation of ^{233}U from irradiated thorium. The uranium is concentrated by cation exchange, precipitated from the cation exchange eluate as ammonium uranate, and finally converted to uranium trioxide by calcination.

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CATION EXCHANGE CONCENTRATION OF AQUEOUS $^{233}UO_2(NO_3)_2$ AND CONVERSION TO $^{233}UO_3$

INTRODUCTION

In the process developed for use in the Savannah River Plant for the production of ^{233}U, irradiated thorium metal or thorium dioxide is dissolved in nitric acid, and the thorium and uranium are separated from each other and from fission products by solvent extraction with tributyl phosphate. The dissolution and solvent extraction processes are described in other reports.(1,2)

Processing steps were required to isolate the ^{233}U from the dilute uranium nitrate solution produced by solvent extraction, and to convert the ^{233}U to UO_3. The process was required to be compatible with existing plant equipment, similar to that described by Orth, et al.(3)

On the basis of prior technology, the following steps were chosen for laboratory testing and development:

- Cation exchange concentration of the uranium. Extensive data were available on the cation exchange absorption of uranium;(4) but the development of an elution procedure compatible with the subsequent precipitation step and compatible with necessary nuclear safety restrictions was required.
- Precipitation of ammonium uranate. Considerable information was available on the precipitation of ammonium uranate;(5,6) however, the precipitation procedure had to be adapted to the existing plant equipment and a method of producing a readily filterable precipitate had to be developed.
- Calcination of ammonium uranate to form UO_3. Optimum conditions for the calcination had to be defined in order to attain complete decomposition of the ammonium uranate without excessive formation of U_3O_8, and in order to avoid explosive conditions in the calcination off-gas equipment.

SUMMARY

Processing steps were developed for the isolation of ^{233}U from the dilute uranium nitrate solution produced by solvent extraction, and for the preparation of UO_3. The uranium is concentrated 10- to 50-fold by cation exchange; ammonium uranate is precipitated by the addition of ammonium hydroxide to the concentrated uranium solution; and finally the ammonium uranate is calcined to UO_3.

In the cation exchange cycle, uranium is absorbed from dilute nitric acid solution on a column of "Dowex"* 50W-X8 resin, and is then eluted with 2M NH_4NO_3-1M HNO_3. Uranium solutions containing ~35 g U/l were obtained when ~75% of the absorbed uranium was eluted in a product fraction; ~15% of the absorbed uranium was eluted as a recycle fraction and ~10% remained on the resin bed as a heel.

Preparation of an easily filterable precipitate of ammonium uranate by the addition of ammonium hydroxide to the concentrated uranium solutions from cation exchange required careful control of the temperature, the concentrations of uranium and ammonium hydroxide, and the rate of addition of ammonium hydroxide (over the range of pH 3 to 6). Dried ammonium uranate was calcined to UO_3 at 500-550°C. At temperatures greater than 600°C, the rate of conversion to U_3O_8 was appreciable. The rate of heating between 150 and 300°C was controlled to limit the rate of evolution of ammonia and hydrogen so that these gases were kept below the lower explosive concentrations in the air purge of the calcination furnace.

The combined losses of uranium from the cation exchange and precipitation steps were less than 1%. Little separation from thorium and other cationic impurities was achieved.

EXPERIMENTAL

Laboratory studies were performed with simulated process solutions prepared from reagent grade chemicals and uranium with natural isotopic composition. Fission product activity was not added. Thorium was added for some tests of its behavior in cation exchange and precipitation.

Ion exchange studies were made in columns 0.75 cm² in area by 38 cm long; previous work(4) demonstrated that scale-up from this size to much larger columns is valid. "Dowex"* 50W and "Amberlyst"** 15 resins were used. The resins were washed with

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* Trademark of Dow Chemical Company

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several volumes of hydrochloric acid to remove metal cationic impurities, then rinsed and graded in water to remove most of the resin beads smaller than 100 mesh. Resin in the hydrogen form was charged to the column. Unless otherwise indicated, ion exchange data were obtained at 23°C.

Inconsistencies in the elution data are attributed to variations in different batches of resin of the same nominal cross-linking and particle size. Resin from the same batch was always used to study a particular variable, except cross-linking and resin type.

Precipitation studies were done in small glass vessels with 2 to 5 grams of uranium per test. The precipitator was heated in a water bath maintained within ±3°C of the stated temperature.

Drying of the ammonium uranate and conversion to uranium trioxide were studied by thermogravimetric and differential thermal analyses. Samples of ammonium uranate were analyzed after heating at different temperatures, and samples of the off-gas from decomposition were collected and analyzed mass-spectrometrically.

DISCUSSION

CATION EXCHANGE CONCENTRATION

The absorption of uranyl ion by cation resin from dilute nitric acid solutions has been studied.(4) The absorption and elution of uranyl ion by sulfonic acid cation exchange resin may be represented by the equation:

$$UO_2^{2+} + 2HR \underset{\text{elution}}{\overset{\text{absorption}}{\rightleftharpoons}} UO_2R_2 + 2H^+$$

where R represents the ion exchange resin, and HR the resin in acid form. The absorption capacity of the resin for uranium depends on the composition of solution in contact with the resin and is conveniently described as the "partial capacity" of the resin for uranium (designated S_u), expressed as a percent of the total exchange capacity of the resin. The total exchange or absorption capacity is a fixed property of the resin. For example, at complete saturation "Dowex" 50W-X8 resin can absorb 236 grams, or 2.0 equivalents of uranium (as uranyl ion) per liter of resin (settled volume in water).

S_u has been related to acid concentration and uranium concentration in feed solutions containing only uranyl and hydrogen cations by correlation with the following parameter:(4)

$$K = \frac{M_H^2}{C_U}$$

where M_H is the molarity of hydrogen ion and C_U is the uranium concentration in grams per liter. The correlation was confirmed by experiments and can be derived from the law of mass action, if simplifying assumptions are made about the relative values of the activity coefficients in the resin and solution phases. The relationship of S_u and K are given in Figure 1 (reproduced from Reference 4). The data represent equilibrium conditions; in practice, the absorption of uranyl ion by resin is very rapid so that equilibrium is closely approached at practical column feed rates.

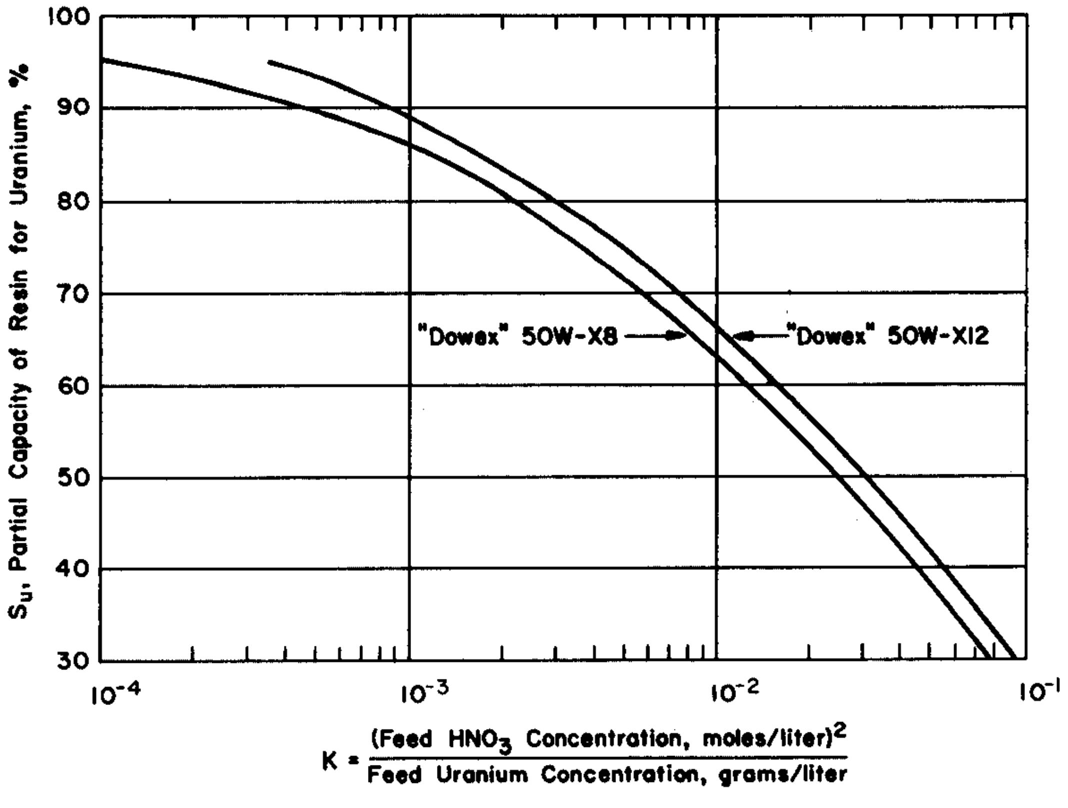

FIG. 1 ABSORPTION OF URANIUM ON "DOWEX" 50W RESIN

The relationship in Figure 1 indicates that, for an efficient cation exchange process for concentrating uranium, the feed solution should contain as low a concentration of nitric acid and as high a concentration of uranium as practical (i.e., small values of K). In the ^{233}U process the acid concentration in the solvent extraction product (the ion exchange feed solution) was limited to 0.25M HNO_3, or greater, to provide flexibility in the solvent extraction operations and to prevent hydrolysis of uranium; the uranium concentration was limited to 5 g $^{233}U/l$, or less, by nuclear safety. For reference, "Dowex" 50W-X8 resin equilibrated with a solution containing 0.3M HNO_3 and 3.6 g U/l will absorb 118 grams of uranium per liter of resin (S_u = 50%).

Calculation of S_u values for actual process feeds was complicated by varying concentrations of ammonium ion in the feed, resulting from the recycle of elution fractions. The selectivity of "Dowex" 50W-X8 for ammonium ion is almost twice that for hydrogen ion.(7) With the assumption that one mole of NH_4^+ is equivalent to two moles of H^+, values of S_u were calculated from the relationship shown in Figure 1 for solutions containing ammonium, hydrogen, and uranyl cations. These calculated values agreed well with experimentally measured quantities of absorbed uranium, as shown in Table I.

TABLE I

S_u for Solutions Containing H^+-NH_4^+-UO_2^{2+}

Feed solution: 0.3M H^+, 3.6 g U/l

	S_u, %	
NH_4^+, molarity	Calculated	Measured
0	50	46
0.025	45	41
0.05	40	37
0.1	32	30
0.2	20	24

Th^{4+} was the only other cation expected to be present in significant concentrations in process feed. Little separation of uranyl ion from Th^{4+}, or other multivalent cations, was expected in a cation exchange cycle operated to concentrate uranium. Although tetravalent ions have such strong affinity for the resin that Th^{4+} in the feed is absorbed in a concentrated band at the inlet of the resin bed, elution tests showed that thorium was not selectively retained when the direction of flow during elution was opposite that during feed absorption. Typical data are shown in Table II for three sequential runs.

TABLE II

Behavior of Th^{4+} in Cation Exchange(a)

	Run 1		Run 2		Run 3(b)	
	mg	%	mg	%	mg	%
U in product	1157	73	1160	75	1161	75
Th in product	29	>100	22	88	25	100
U in recycle	254	17	257	18	253	16
Th in recycle	<2	<8	<2	<8	<2	<8

(a) Run conditions:

29 ml of "Dowex" 50W-X8, 50-100 mesh resin.

1530 mg U and 25 mg Th absorbed downflow in each run.

Elution upflow with 2.8 bed volumes 2M NH_4NO_3-1M HNO_3 at 0.5 ml/(min)(cm^2); 1.2 bed volumes taken as product fraction; 1.6 bed volumes taken as recycle fraction.

(b) Heel elution after Run No. 3 with five bed volumes of 0.5M H_2SO_4 contained 102 mg of U and 2.5 mg of Th.

Separation of Th^{4+} could be achieved in a cation exchange column operated ahead of the uranium concentration column. When the first column approached saturation with Th^{4+}, the absorbed uranyl ion could be eluted, in the same flow direction in which the column was fed, and the uranium absorbed on the second column. The Th^{4+} could be eluted from the first column with strong HNO_3 or $NaHSO_4$.

A number of ion exchange column runs were made in the laboratory to define elution conditions. Only nitric acid and mixed nitric acid-ammonium nitrate solutions were tested as elutriants. In most tests only a fraction of the resin column was loaded with uranium; the remainder was used as a stripping section. The S_U values cited in the following tests relate only to the fraction of the resin loaded with uranium and are not average values based on the total volume of resin in the column. Uranium elution from cation resin is affected by a number of variables; those investigated are discussed in the following sections.

Elutriant Composition

The experimental results illustrated in Figures 2 and 3 show that optimum uranium elution is obtained with 2 to 4M HNO_3 or 2M NH_4NO_3-1M HNO_3. These concentrations of hydrogen ion and ammonium ion are somewhat lower than might be expected for best elution if elution of uranium from cation resin were determined entirely by mass action. Further, increased nitrate complexing of UO_2^{2+} at higher nitrate concentrations might be expected to increase elution efficiency. However, there are at least three possible reasons for less efficient elution with more concentrated elutriants: (1) complexed uranium ions in concentrated nitrate solution might diffuse more slowly in the resin phase; (2) increased resin shrinkage might contribute to slower diffusion rates; and (3) the distribution coefficient decreases initially with increased acid concentration in some cation exchange systems, but eventually goes through a minimum and increases in more concentrated acid solutions.(8)

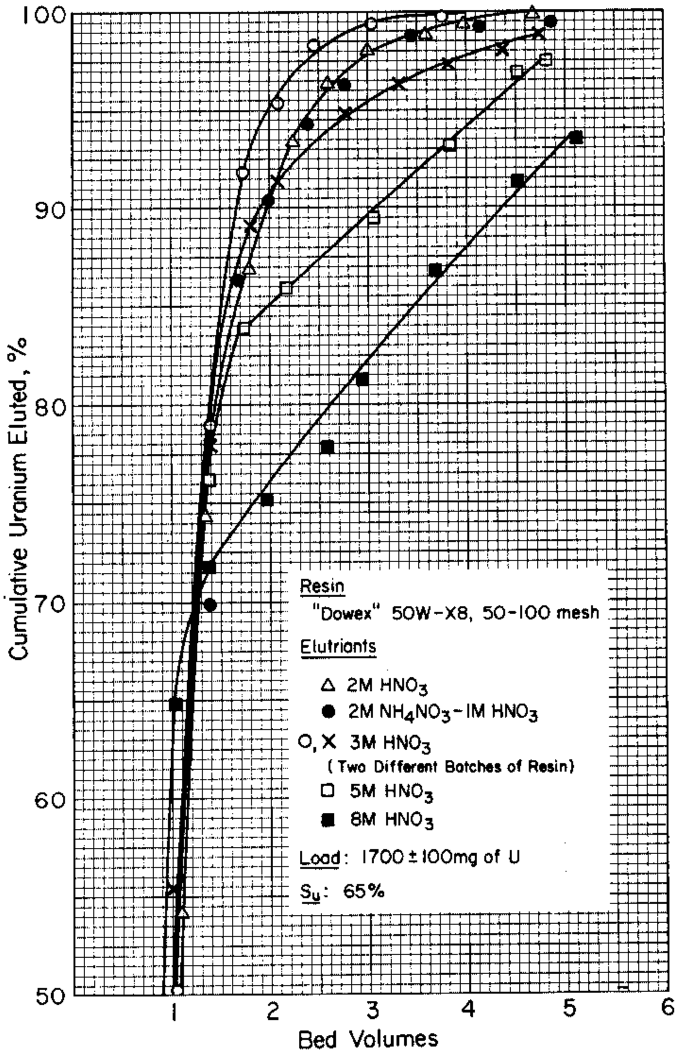

FIG. 2 EFFECT OF ELUTRIANT COMPOSITION ON URANIUM ELUTION EFFICIENCY

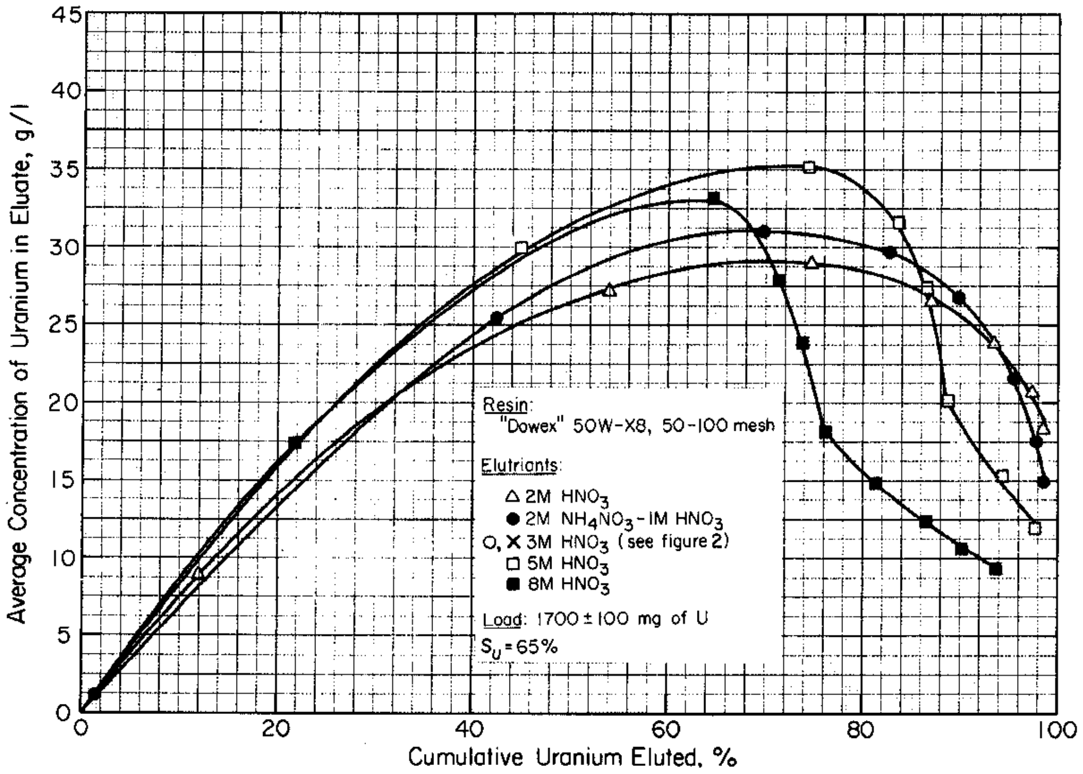

FIG. 3 EFFECT OF ELUTRIANT COMPOSITION ON CONCENTRATION OF URANIUM IN ELUATE

The third phenomenon has been interpreted as a loss of water from the hydration sphere of the exchanging ion in the dehydrating atmosphere of the concentrated acid, and replacement of the solvating species by the sulfonate anion of the resin. This effect would result in direct bonds between the cation and the resin sulfonate anion, increasing the affinity of the cation for the resin.

In an attempt to establish a reason for optimum elution with relatively low concentrations of nitric acid, distribution coefficients were determined for uranium in 0.5 to 12M HNO_3 and in NH_4NO_3-HNO_3 solutions. ^{233}U tracer was added to the nitrate solution, which was mixed with "Dowex" 50W-X8 resin until equilibrium was attained, as indicated by no further change in the distribution coefficient. The data are shown in Table III.

TABLE III

Effect of Solution Composition on Uranium Absorption by "Dowex" 50W-X8 Resin

Solution Composition		UO_2^{2+} Distribution Coefficient
HNO_3, M	NH_4NO_3, M	
0.5		43
1.0		14
2.0		6.1
3.0		3.8
4.0		3.4
5.0		2.2
8.0		2.9
12.0		3.9
1.0	1.0	5.0
1.0	2.0	3.5
1.0	3.0	5.5

The uranium distribution coefficient reached a minimum at ~5M HNO_3 and in 1M HNO_3-2M NH_4NO_3; these results are consistent with the elution results for HNO_3-NH_4NO_3 solutions, but not with those for HNO_3 for which optimum elution occurred at 2-4M. The equilibrium measurements with HNO_3 support the dehydration hypothesis, but the discrepancy between the column and equilibrium tests indicates that a second effect is involved, such as decreased rate of diffusion of the uranyl species.

Figures 2 and 3 compare the elution efficiencies for a number of elutriants. Numerous other elution tests were made, particularly with elutriants containing 1M HNO_3 and greater than 2M NH_4NO_3; but these compositions were all less effective than 1M HNO_3-2M NH_4NO_3. The shape of the elution curves for 5M HNO_3 and 8M HNO_3 in Figure 2 are consistent with a diffusion effect.

Uranium is effectively eluted from cation resin with mixed acetate-citrate solutions at elevated temperature;(4) however the columns that were available for ^{233}U processing were not equipped for heating, so these elutriants were not studied.

Cross-Linking of Resin

Cation resins with greater cross-linking have greater total exchange capacity. The capacities of "Dowex" 50W resins cross-linked with 4%, 8%, and 12% divinyl benzene are given in Table IV.

TABLE IV

Capacities of Cation Exchange Resins

"Dowex"	Total Exchange Capacity,[(a)] equivalents/liter
50W-X4	1.2-1.4
50W-X8	1.9-2.1
50W-X12	2.2-2.4

(a) Resin volumes measured in water.

As shown in Figure 1, for a given feed composition S_u is affected to a limited extent by cross-linking.

A comparison of the elution behavior of these resins is shown in Figures 4 and 5. At constant total uranium load, uranium is eluted more effectively with 3M HNO_3 from "Dowex" 50W-X12 than from -X8 or -X4 resin; there is slightly more tailing with X8,

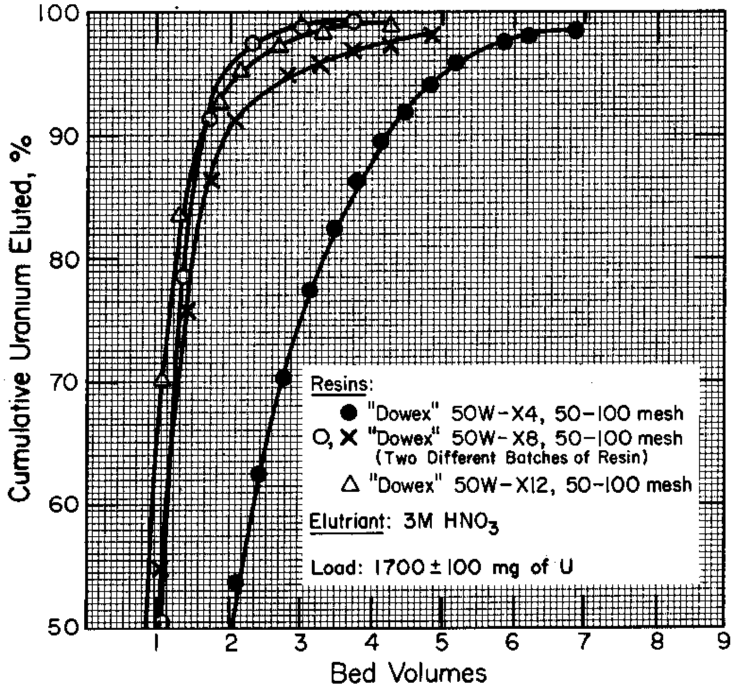

FIG. 4 EFFECT OF RESIN CROSS-LINKING ON URANIUM ELUTION EFFICIENCY

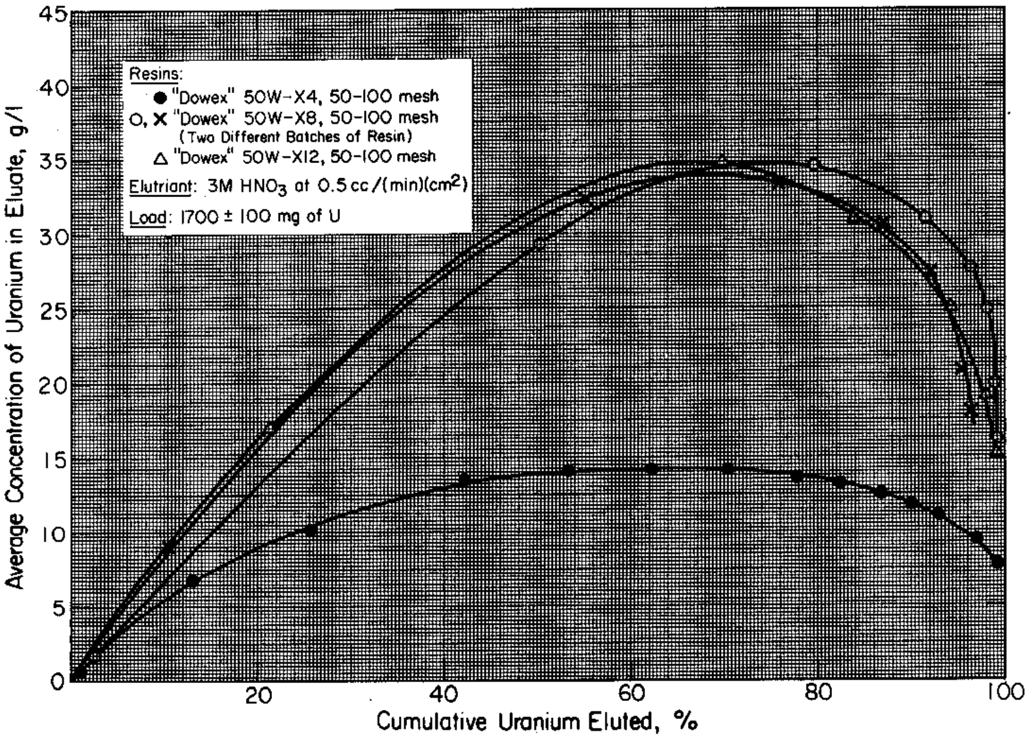

FIG. 5 EFFECT OF RESIN CROSS-LINKING ON CONCENTRATION OF URANIUM IN ELUATE

and elution from X4 is much less effective. The average concentration of uranium in the eluate at 90% elution is 25 to 30 g/l from -X12 or -X8 resin, but is only ~12 g/l from -X4 resin. The elution behavior of these resins apparently reflects (1) the appreciably higher concentration of uranium per unit volume on the X12 resin, and (2) possibly the smaller shrinkage of the X12 resin in the elutriant, which may affect the elution behavior by altering the rate of diffusion of the uranium species in the resin phase.

Uranium Saturation, S_u

Uranium is eluted most efficiently from cation resin that is loaded to maximum uranium saturation, S_u, assuming all other factors constant. Figures 6 and 7 compare elutions from "Dowex" 50W-X8 resin loaded to different values of S_u. Complete elution in the smallest volume resulted with resin loaded to $S_u = 87\%$; much more tailing resulted with resin loaded to $S_u = 35\%$. The average uranium concentration in the eluate at 90% elution was 33, 29, and 11 g/l, respectively, for 87, 65, and 35% saturation.

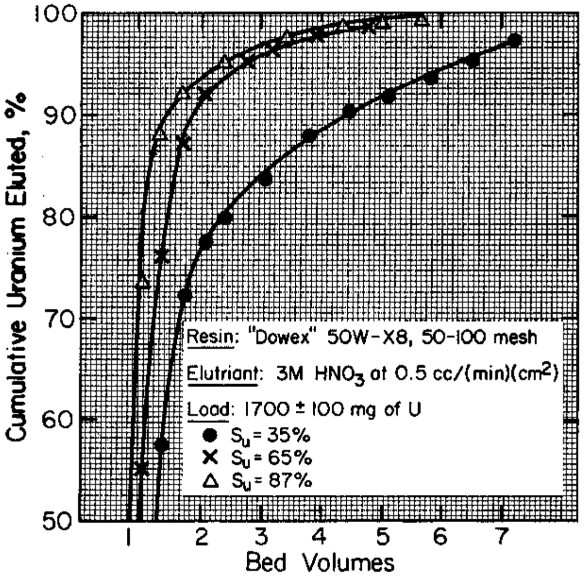

FIG. 6 EFFECT OF S_u ON URANIUM ELUTION EFFICIENCY

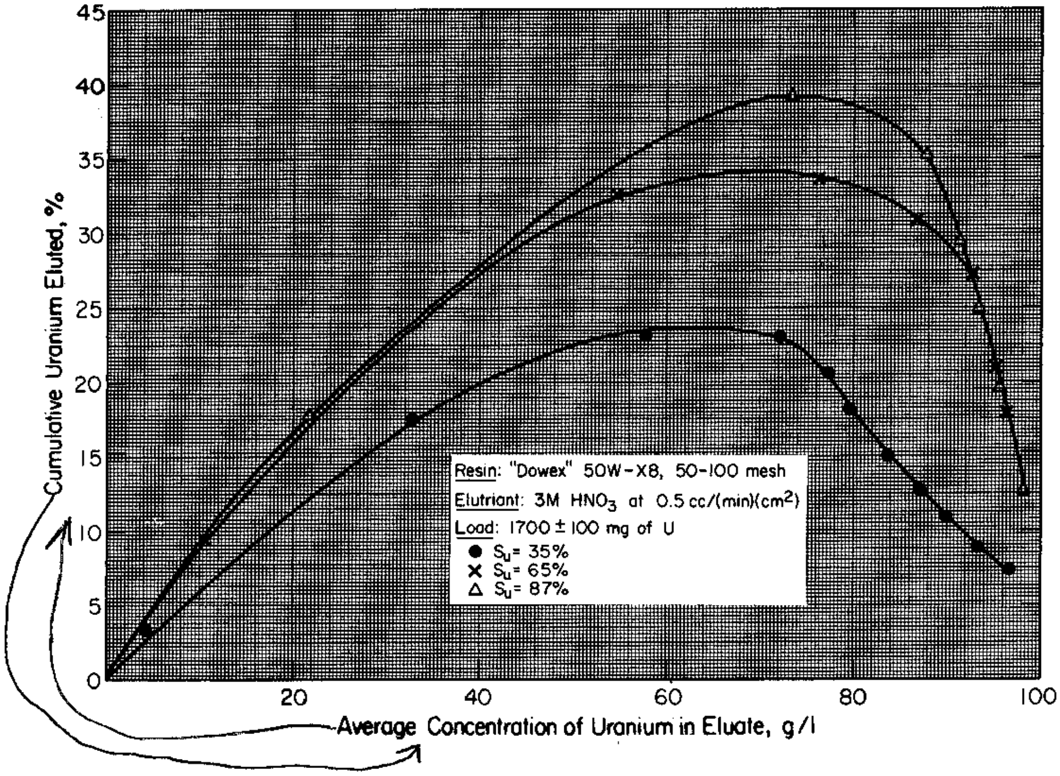

FIG. 7 EFFECT OF S_u ON CONCENTRATION OF URANIUM IN ELUATE

Total Uranium Load at Constant S_u

The elution behavior of columns with varying total uranium load on the resin bed, but at constant S_u in the uranium band, is complex. Although increasing the length of the uranium band (total load) results in higher peak concentrations during subsequent elution, the average concentration of uranium in the product at 90% removal may actually be decreased. For example, in laboratory tests a "Dowex" 50W-X8 bed 15 inches long was loaded with constant feed (constant S_u) in three successive runs: (I) 7-1/2" uranium band, (II) 10-3/4" uranium band, and (III) 15" uranium band. The peak concentrations and corresponding percent of the total uranium eluted were: (I) 38 g/l at 70% elution, (II) 45 g/l at 68% elution, and (III) 39 g/l at 52% elution. However, at 90% removal for each loading, the average uranium concentration was ~25 g/l for tests II and III, but ~34 g/l for test I. These factors are important in optimizing the loading-elution cycle for column operation.

Elutriant Flow Rate

Uranium removal is improved somewhat by decreasing the elutriant flow rate. At elutriant flows of 0.25, 0.5, and 1.0 ml/(min)(cm^2), average uranium concentrations in the eluates were 36, 33, and 30 g/l, respectively, when "Dowex" 50W-X8 (50-100 mesh) was loaded to S_u = 65% and eluted with 3M HNO_3.

Temperature

There was no appreciable difference between the efficiency of elution from "Dowex" 50W-X8, 50-100 mesh resin (S_u = 65%) with either 3M HNO_3 or 1M HNO_3-2M NH_4NO_3 elutriants at 23°C and that at 55°C.

Direction of Elutriant Flow

Elution is more effective when the direction of elutriant flow is opposite to the direction of feed flow, unless the entire bed is saturated with uranium. Under the condition for which the uranium band occupied only slightly more than half the length of the resin bed at S_u = 65%, elution in the same direction as feed absorption yielded an average uranium concentration of only ~16 g/l at 90% elution; whereas elution in the opposite direction yielded ~30 g/l at 90% elution.

Types of Resin

Elution of uranium with nitric acid elutriant is not as efficient from "Amberlyst 15" resin as from "Dowex" 50W-X8 or -X12. The "Amberlyst" resin particle size was 20-50 mesh, compared with 50-100 mesh for the "Dowex" resin; some improvement might result with smaller beads of resin.

The "Amberlyst" resin has been reported to have pores between 200 and 600 Å, with little change in pore size when the resin is contacted with solutions of very different composition or when the resin beads are dried. If resin shrinkage were responsible for slower diffusion and less efficient elution from "Dowex" 50W resin, elution from "Amberlyst" resin with 8M HNO_3 should be quite effective. However, little difference was observed when "Amberlyst" resin was eluted with 3M or 8M HNO_3. This fact supports the theory that loss of hydration in more concentrated elutriant controls elution efficiency.

PRECIPITATION OF URANYL ION WITH AMMONIUM HYDROXIDE

An insoluble precipitate of uranium is produced when excess ammonium hydroxide is added to a solution containing uranyl ions. The compound is commonly described as ammonium diuranate $(NH_4)_2U_2O_7$, but recent work shows that the diuranate is usually not the compound precipitated.(5,6) Four compositions have been reported in the ternary system UO_3-NH_3-H_2O by Cordfunke:(5)

I. $UO_3 \cdot 2H_2O$ (orthorhombic structure) at pH 3

II. $3UO_3 \cdot NH_3 \cdot 5H_2O$ (orthorhombic structure) at pH 5

III. $2UO_3 \cdot NH_3 \cdot 3H_2O$ (hexagonal structure) at pH 6 to 7

IV. $3UO_3 \cdot 2NH_3 \cdot 4H_2O$ (hexagonal structure) at pH >8

In addition, the precipitates contain nitrate and sulfate ions when these ions are present in solution.

In a typical precipitation, when NH_4OH is added to NH_4NO_3-HNO_3-$UO_2(NO_3)_2$ solution, precipitation initially occurs at pH 3 to 3.5, presumably with the formation of precipitate type I which is partially converted to type II at higher pH. The conversion to types III and IV is reported to be very slow. At pH 7.5 to 8 a product of different settling characteristics and color is formed, and the uranium solubility is less than 0.1 mg/l. Typical compositions of uranium precipitates obtained in this work from the addition of NH_4OH to NH_4NO_3-HNO_3-$UO_2(NO_3)_2$ solution, and after washing with dilute ammonium hydroxide are given in Table V.

TABLE V

Composition of Uranium Precipitates

	% by Weight			
	U	NH_3	H_2O	NO_3^-
As precipitated	58	5.2	12	13
Washed with 0.5M NH_4OH	71	2.2	10	1.3
Washed with 0.5M NH_4OH-0.5M NH_4NO_3	66	3.2	9	6.2

Filterability

In laboratory tests, the filterability of the slurry was affected by a number of variables, particularly the uranyl and ammonium ion concentrations in the feed, the rate of addition and concentration of the ammonium hydroxide, and the temperature. The data in Table VI show the effect of feed composition on the "filtration factor", which is defined as the time required to filter a given volume of slurry divided by the time required to pass an equal volume of water through the same filter.

TABLE VI

Effect of NH_4NO_3 AND $UO_2(NO_3)_2$ Concentrations on Filtration

55°C, 7M NH_4OH added at a constant rate in one hour

Composition of Feed			Filtration Factor
NH_4NO_3, M	HNO_3, M	U, g/l	
1	1	37.5	1.9
2	1	37.5	1.9
3	1	37.5	32
1	1	75	3
2	1	75	31
4	1	75	~100

The effect of NH_4OH addition rate on filtration of the uranate cake is shown in Table VII. In other tests the rate of addition of NH_4OH before a precipitate forms was shown to be unimportant if mixing was adequate; but the addition rate after a precipitate forms, over the range pH 3 to 6.5, must be carefully controlled.

TABLE VII

Effect of NH_4OH Addition Rate on Filtration

55°C, 7M NH_4OH added to 2M NH_4NO_3-1M HNO_3-37.5 g U/l

Minutes for 7M NH_4OH Addition	Filtration Factor
30	11
60	1.9

Dilute Uranium Solutions

NH_4NO_3-HNO_3 solutions containing only 1 to 5 g U/l result from total elution of the uranium "heel" from a cation resin bed. To obtain filterable precipitate, a lower concentration of NH_4OH and slower addition of NH_4OH during initiation of precipitation are required, as shown in Table VIII.

TABLE VIII

Effect of Uranyl Ion Concentration on Filtration

55°C; 7M NH_4OH added at constant rate over 30 minutes to 2M NH_4NO_3-1M HNO_3 containing $UO_2(NO_3)_2$

$UO_2(NO_3)_2$, g U/l	Filtration Factor
37.5	1.5
10	22
2	>40

55°C; 7M NH_4OH added rapidly to 2M NH_4NO_3-1M HNO_3-2 g U/l to neutralize to pH 3, then 1M NH_4OH added slowly

$UO_2(NO_3)_2$, g U/l	Minutes for 1M NH_4OH Addition	Filtration Factor
2	10	>15
2	30	2

Sulfate solutions are quite effective for uranium heel elution, and a filterable precipitate is produced by adding NH_4OH to the sulfate eluate; however, the precipitate contains 15 to 20% sulfate. The sulfate could be removed by calcination temperature, but under such conditions the product

Effect of Thorium

Thorium in the precipitation feed has a deleterious effect on the filterability of the precipitate. The filtration factor is approximately doubled when thorium is 1% of the uranium concentration, tripled with 3% thorium, and 20-fold greater with 10%. There is also an accompanying 25 to 50% decrease in bulk density of the cake with 3 to 10% thorium present.

Recommended Procedure

The procedure recommended for precipitation of ammonium uranate is as follows:

- Add the eluate from cation exchange to the precipitator and heat to 60 ±5°C.
- Add NH_4OH (any concentration) rapidly with good mixing until most of the acid is neutralized (pH 3), but no stable precipitate persists.
- Add the remaining NH_4OH slowly with good mixing to pH 7.5 to 8. (The exact concentration of NH_4OH to be added depends on the uranium concentration in the eluate.)
- Digest the slurry for at least 5 minutes.
- Filter the slurry (cooling not necessary).
- Wash the cake with several volumes of dilute NH_4OH.

An alternative method for the precipitation of uranium from nitrate solutions was tested to a limited extent. This method consisted of reducing the uranyl ion to U(IV) and precipitating U(IV) oxalate. The method was not satisfactory, however, and its investigation was abandoned. Details are reported in the Appendix.

CALCINATION OF AMMONIUM URANATE TO URANIUM TRIOXIDE

A detailed study of the thermal decomposition of ammonium uranate was not made; but thermogravimetric analysis showed a region of stability for the desired UO_3 product between 450 and 600°C, as shown in Figure 8. At temperatures greater than 600°C, conversion to U_3O_8 occurs.

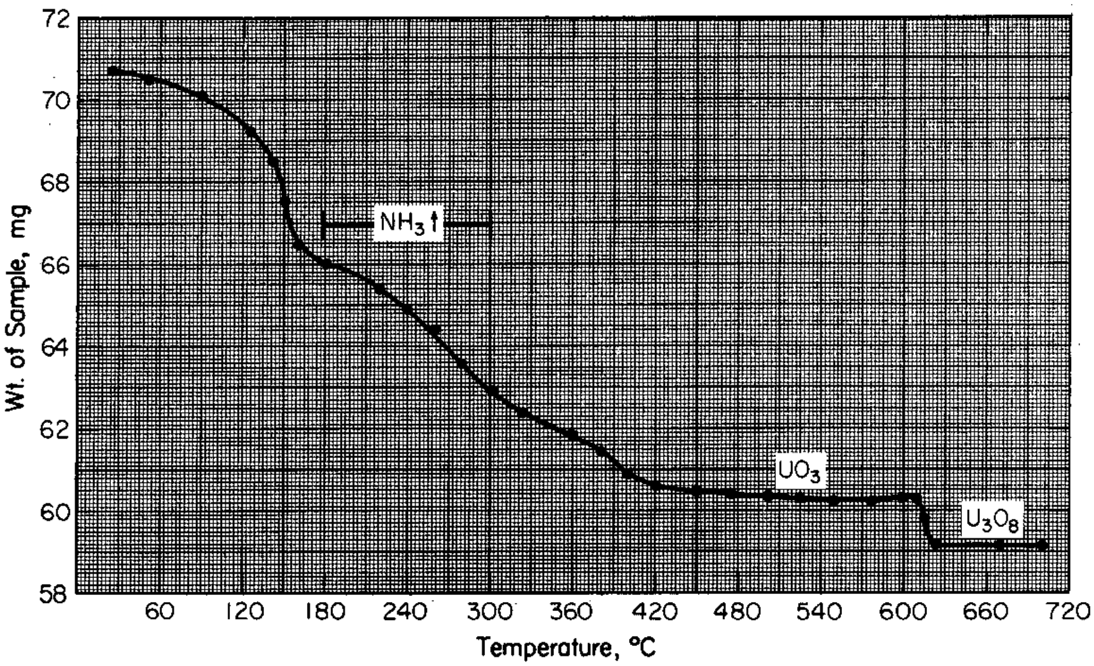

FIG. 8 CONVERSION OF AMMONIUM URANATE TO URANIUM TRIOXIDE

Ammonium nitrate retained by the precipitate is a potential explosion hazard for large-scale calcination operations. Differential thermal analysis showed that the solid "as precipitated" (Table V), which contained 13% nitrate, exhibited an exotherm at approximately 300°C that was attributed to NH_4NO_3; the solid containing <2% nitrate that was produced by washing with 0.5M NH_4OH exhibited an endotherm at approximately 200°C. Therefore, no uncontrollable temperature effect is possible during calcination of NH_4OH-washed precipitate.

Another potential hazard in the large-scale calcination of ammonium uranate is the possibility that explosive concentrations of NH_3, or H_2 formed by decomposition of NH_3, might exist in the off-gas from the calcination furnace. Laboratory tests indicated that during the decomposition ammonia was released mainly between 150 and 300°C; however the off-gas from the decomposition in this temperature range contained only a few percent of the theoretical amount of ammonia. Mass spectrographic analysis showed the major decomposition products to be N_2O and N_2 with only marginally detectable quantities of H_2 and NH_3.

Because the thermal decomposition reaction is probably heterogeneous and because the conditions in the plant equipment might vary, these conservative assumptions were made in specifying the calcination conditions: (1) that all the ammonia generated by decomposition is converted to hydrogen, and (2) that the uranate contains one mole of ammonia per mole of uranium (analytical values of the ratio approximated 0.5). Thermogravimetric analyses showed that the rate of weight loss of the precipitate in the critical temperature range (150-300°C) is constant when the heating rate is constant. The rate of decomposition in this range is not rapid, probably because of the endothermic nature of the reaction. On the basis of these observations, the rate of heating between 150 and 300°C was so specified that the calculated evolution of hydrogen was compatible with the available rate of air purge through the furnace to maintain less than the explosive limit of 4% H_2 in the atmosphere.

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APPENDIX

PRECIPITATION OF U(IV) OXALATE

U(IV) oxalate was precipitated from HNO_3 and NH_4NO_3-HNO_3 solutions by the addition of oxalic acid. Uranyl ion was reduced to U(IV) by the addition of "Hydrosulfite AWC"*, a compound of sodium sulfoxylate with formaldehyde ($NaHSO_2 \cdot CH_2O \cdot 2H_2O$). The advantages of oxalate precipitation over uranate precipitation were expected to be (1) better separation from many cationic impurities, and (2) fewer controls for the production of an easily filterable precipitate.

The procedure developed for precipitation involved the addition of oxalic acid to the eluate from cation exchange, then the addition of the reductant. U(IV) oxalate was slowly precipitated from the nitrate solution under homogeneous precipitation conditions as the uranyl ions were slowly reduced to U(IV). For example, in 2-3M nitrate solution containing 35 g U/l, approximately 99% of the uranium was precipitated in 2-3 hours at 25°C when the reductant concentration was 0.2M. The precipitate filtered rapidly.

Only a few precipitations were made because the reductant was quite unstable in nitric acid; optimum precipitation conditions were not established. At room temperature in 2-3M HNO_3, free sulfur was slowly produced; at greater than 4M HNO_3 and at 50-60°C oxidation of the reductant was very rapid.

No other chemical reductants were tested, because none are known that are compatible with the existing process equipment and product specifications.

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