Anion Exchange of Uranium in Nitrate Solutions

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THE SELECTIVE adsorption of uranium on strong-base (quaternary amine) anion exchange resin—principally as sulfate, chloride, or carbonate anionic complexes—has been used extensively in many diversified processes involving its concentration, purification, and recovery. In recent years the adsorption behavior of sexivalent uranium from nitric acid and nitrate salt solutions has been reported by Kraus and Nelson (*4, 5*) and others (*1-3, 6, 7*).

Anion exchange of sexivalent uranium in nitrate media is analogous to that in chloride solutions. In nitric acid the adsorbability of uranium becomes significant above 2*M* nitric acid, increases with increasing nitrate concentration, attaining a maximum in approximately 8*M* acid, and then drops off appreciably at higher acid concentration (*1, 8*). Uranium adsorbability occurs to an even greater extent from nitrate salt solutions having lower acidities. Such solutions have an added advantage of providing greater resin stability, as decomposition of the resin becomes a serious factor in high nitric acid concentrations.

Because of the general use of the nitrate system in uranium recovery operations at the Oak Ridge Y-12 Plant and the possibility of using anion exchange to economic advantage in miscellaneous processing operations, a study was made of the anion exchange behavior of sexivalent uranium from concentrated nitrate solutions. Such a process would be particularly desirable in that it would enable the recovery of adsorbed uranium from the resin as uranyl nitrate, a product having widespread utility for uranium oxide and metal production.

EXPERIMENTAL

Resin Preparation. The nitrate forms of Dowex 21K and Dowex 1 anion exchange resins used for these studies were prepared by treating a large batch of chloride-form resin in a column with 0.1*M* nitric acid-0.9*M* ammonium nitrate solution until the column effluent tested negative for chloride ion using silver nitrate. The resin was then rinsed with distilled water, filtered, air-dried, and stored in capped bottles to retain residual moisture.

Adsorption Studies. The adsorption of uranium from solutions of various nitrate salts was studied in batch-contacting experiments using a weighed quantity of the moist, nitrate form of resin. For most of the experimental work, a relatively coarse resin particle size (Dowex 21K, 16- to 20-mesh) was used, so as to obtain information regarding the practicality (from a kinetic standpoint) of using a coarse resin for uranium recovery in nitrate media with a Higgins-type, semicontinuous, ion exchange contactor. Although the use of resin having a much finer particle size would have enabled equilibrium conditions to have been attained more rapidly, our experience with the Higgins unit has shown that its successful operation requires the use of rather coarse resin particles for the processing of slurries.

Ten-gram quantities of moist resin were slurried with 500-ml. volumes of uranium-bearing nitrate solution for various contact periods, using magnetic stirring. The resin phases were separated from the solutions by quantitative transfer to fritted-glass filter funnels and rinsed rapidly with the appropriate nitrate solution to remove any residual mother liquor from the resin beads. Adsorbed uranium was eluted from the resin with distilled water which had been acidified with nitric acid to a pH of approximately 1 to 2.

Kinetic Studies. The exchange kinetics between the nitrate form of Dowex 21K resin and uranyl nitrate from 2.0*M* aluminum nitrate solutions were studied in similar batch-type contacting tests. For these tests, 10 grams of moist resin were slurried with 1-liter volumes of solution using magnetic stirring, and small samples were withdrawn for uranium analyses after various contact time intervals by means of a pipet with a fritted-glass tip.

RESULTS

Uranium Adsorption Studies. EFFECT OF NITRATE ION CONCENTRATION. A distribution diagram showing equilibrium resin uranium loadings from aluminum and ammonium nitrate solutions is presented in Figure 1. The adsorption of uranium increases greatly with increasing nitrate ion and uranium concentration. For these data, equilibration contact periods of from 2 to 16 days were employed using Dowex 21K resin (50- to 100-mesh).

Resin uranium loading from 2*M* aluminum nitrate solutions—i.e., 6*M* total nitrate ion concentration—are considerably higher than those obtained from 6*M* ammonium nitrate solutions. Similarly, greater uranium adsorption was shown for 1*M* aluminum nitrate—i.e., 3*M* total nitrate—than for 3*M* ammonium nitrate solutions, indicating a greater ability of Al^{+3} to promote anionic uranium exchange.

EFFECT OF CATION SPECIES. To show the effect of cation species, the adsorption of uranium was studied at constant nitrate ion concentration (Figure 2). Despite the use of 4-day (96-hour) contact periods, these data do not represent equilibrium conditions for the 2*M* ferric or 2*M* aluminum nitrate solutions; and only relative effects of the cation species are indicated. The curves for 6*M* nitric acid and 6*M* ammonium nitrate solutions represent greater than 90% of equilibrium loadings. The rates of uranium adsorption for most of the solutions having relatively high densities and viscosities—i.e., 2*M* ferric or 2*M* aluminum nitrate—were extremely slow with the method of agitation and rather coarse resin beads employed. The uranium adsorption isotherms obtained for the 2.0*M* aluminum

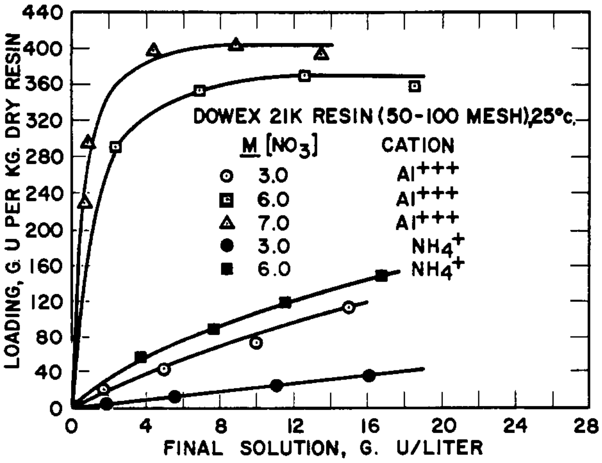

Figure 1. Equilibrium adsorption of uranium from aluminum and ammonium nitrate solutions

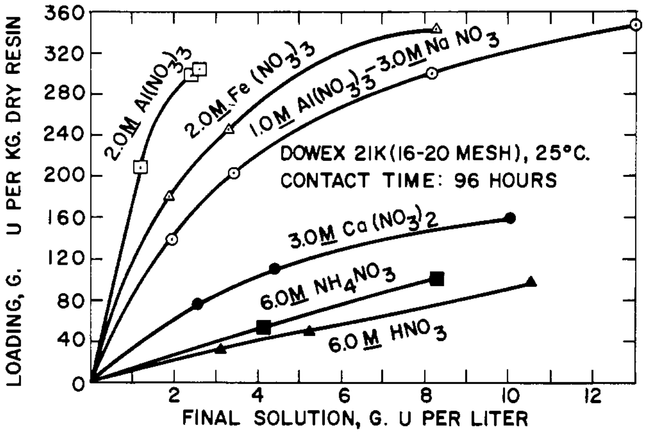

Figure 2. Uranium adsorption from 6.0M total nitrate solutions showing relative effect of cation species

solutions at uranium solution concentrations greater than 3 grams of uranium per liter showed irregular shape—i.e., loading dropped off because of the nonattainment of equilibrium conditions, even after 96-hour contact. These tests demonstrated, however, that resin uranium loadings were high enough for a practical recovery process, if the reaction rate for coarse resin particles could be accelerated.

For 6*M* nitrate solutions, trivalent cations aluminum and iron showed considerably higher resin loadings than divalent calcium, which in turn was higher than monovalent hydrogen or ammonium. This suggested that uranium adsorption was related to total ionic strength. However, although the 3*M* calcium nitrate and 1*M* aluminum nitrate–3*M* sodium nitrate solutions represent equivalent total ionic strengths, the adsorption isotherms obtained were not identical. Foreman, McGowan, and Smith (*3*) have reported on a similar variation in uranium adsorbability with aluminum, calcium, lithium, and ammonium cations at constant nitrate ion concentration and advance the explanation that the smaller abilities of calcium, lithium, and ammonium nitrate to promote anion exchange of uranium follow the degree of hydration of these cations.

EFFECT OF ACIDITY. Various proportions of aluminum nitrate and nitric acid were used for these tests while the total nitrate ion concentration of the solutions was held constant at 6*M* nitrate. The uranium concentration in the starting solutions was 3.4 grams per liter (Figure 3). An increase in the nitric acid acidity of aluminum nitrate solutions produces an adverse effect on resin uranium adsorption, probably because of greater amounts of an uncharged $HUO_2(NO_3)_3$ species in equilibrium with uranyl nitrate and nitric acid at the higher acidities (*3*).

EFFECT OF SULFATE. The effect of sulfate on uranium adsorption from 2.0*M* aluminum nitrate and 6.0*M* ammonium nitrate solutions is summarized in Table I. These data were obtained from equilibrium tests using 50- to 100-mesh Dowex 21K resin. The presence of sulfate ion (added as ammonium sulfate) up to approximately 0.3*M* sulfate did not seriously affect resin uranium adsorption from 2*M* aluminum nitrate. Resin uranium loadings of greater than 300 grams of uranium per kilogram of dry resin were obtained. The presence of 0.4*M* sulfate, added as H^+ or Al^{+3} gave only a slight decrease in uranium adsorption.

As is shown by Table I, adsorption of uranium from 6.0*M* ammonium nitrate solutions appeared to be adversely affected by sulfate ion. Sulfuric acid produced a larger decrease in resin uranium loading than did corresponding ammonium additions. Attempts to add sulfate as $Al_2(SO_4)_3$ to sulfate ion concentration of 0.4*M* were unsuccessful, since precipitation occurred.

Table I. Effect of Sulfate on Uranium Adsorption from 2.0*M* Aluminum Nitrate and 6.0*M* Ammonium Nitrate Solutions

	Equilibrium Solution				
	G.U/1.	*M* SO_4^{-2}	pH (1:25 dilution)	Cation	Loading, G.U/Kg. Dry Resin
2.0*M* $Al(NO_3)_3$[a]	5.7	0.10	3.2	NH_4^+	382
	6.1	0.21	3.2	NH_4^+	361
	6.1	0.32	3.2	NH_4^+	331
	6.6	0.43[b]	3.2	NH_4^+	301
	5.9	0.0	3.2	None	332
	5.7	0.42	1.5	H^+	260
	6.3	0.43	3.1	Al^{+3}	286
6.0*M* NH_4NO_3[a]	9.3	0.0	4.4	None	102
	9.3	0.42	4.3	NH_4^+	72
	9.8	0.42	2.0	H^+	33
	10.0	0.16[b]	3.8	Al^{+3}	15

[a] Dowex 21 K, 50- to 100-mesh. [b] Solution became unstable at room temperature, precipitation occurred.

Table II. Effect of Chloride on Uranium Adsorption from 2.0*M* Aluminum Nitrate and 6.0*M* Ammonium Nitrate Solutions

	Equilibrium Solution				
	G.U/l.	*M* Cl	pH (1:25 dilution)	Cation	Loading, G.U/Kg. Dry Resin
2.0*M* $AL(NO_3)_3$[a]	6.0	0.0	3.1	None	363
	6.6	0.38	3.2	NH_4^+	316
	5.8	0.39	2.3	H^+	388
	6.6	0.37	3.5	Al^{+3}	284
6.0*M* NH_4NO_3[b]	9.3	0.0	. . .	None	97
	9.0	0.40	. . .	NH_4^+	122
	9.1	0.39	. . .	H^+	100
	8.8	0.40	. . .	Al^{+3}	127

[a] Dowex 21K, 50- to 100-mesh. [b] Dowex 21K, 16- to 20-mesh.

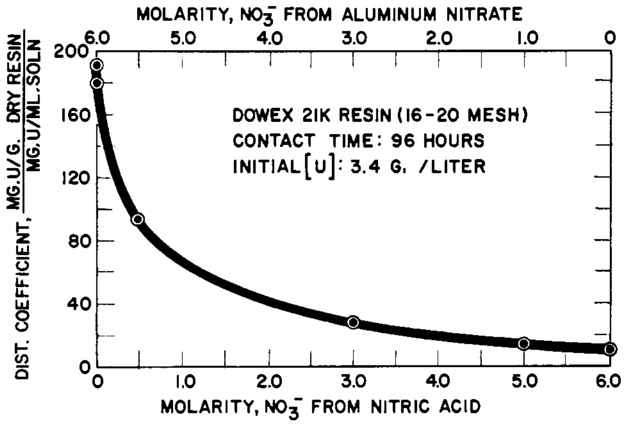

Figure 3 Effect of acidity on uranium adsorption from aluminum nitrate–nitric acid solutions at 6.0M total nitrate

EFFECT OF CHLORIDE. The effect of chloride ion on uranium adsorption from 2*M* aluminum nitrate and 2*M* ammonium nitrate solutions was also studied in equilibrium tests. Chloride ion was added as hydrochloric acid and as ammonium chloride up to approximately 0.4*M* chloride. As shown by Table II, the presence of chloride as HCl had no detrimental effect on uranium adsorption from 2*M* aluminum nitrate and only a slight decline in resin uranium loading was found when the chloride was added as the ammonium or aluminum salt. Similarly, no deleterious effect of 0.4*M* chloride ion, added as NH_4^+, H^+, or Al^{+3} compounds, was found for 6*M* ammonium nitrate solutions.

EFFECT OF ZIRCONIUM AND THORIUM. The presence of zirconium or thorium had a deleterious effect upon uranium adsorption from 2.0*M* aluminum nitrate solutions. A summary of equilibrium adsorption data obtained with Dowex 21K resin (20- to 50-mesh) at 60° C. is shown in

Figure 4. Under the test conditions studied, the separation coefficient for uranium to zirconium ranged from 125 at low zirconium concentration to 62 at high zirconium concentration, indicating the feasibility of separating these elements from 2.0*M* aluminum nitrate solutions. For uranium to thorium, however, the separation coefficient ranged from approximately 1 to 4. Thus, a practical separation of uranium from thorium by anion exchange in 2*M* aluminum nitrate solutions does not appear promising. It is possible, however, that larger differences in the adsorption distribution coefficients for uranium and thorium may exist at other aluminum nitrate molarities or under other conditions, so as to enable separation of these elements; this has not been studied.

Kinetic Studies. EFFECTS OF TEMPERATURE AND RESIN PARTICLE SIZE. Kinetic studies made from 2.0*M* aluminum nitrate solutions have shown that the contact time for attainment of adsorption equilibrium is decreased appreciably by decreasing the resin particle size, decreasing the aqueous uranium concentration, or raising the solution temperature.

A kinetic study employing Dowex 21K resin (16- to 20-mesh) at room temperature with an initial aqueous uranium concentration of 16.8 grams of uranium per liter showed that a contact time of approximately 170 hours was required to attain 90% of equilibrium resin uranium loading. At a lower inital uranium concentration of 5.6 grams of uranium per liter, 90% of equilibrium was attained in 120 hours. With the resin of smaller particle size (20- to 50-mesh), a contact time of only 30 hours was required.

With the coarser 16- to 20-mesh at 55° C., contact times of 30 and 48 hours were required to attain 90% equilibrium at initial aqueous uranium concentrations of 5.6 and 16.8 grams per liter, respectively.

Under the most favorable conditions studied—i.e., 20- to 50-mesh resin at 60° C. with an initial uranium concentration of 5.6 grams per liter—the time required to attain 90% of equilibrium was only about 5 hours.

EFFECT OF CROSS LINKAGE. The degree of resin cross linkage greatly affects the uranium adsorption kinetics from 2.0*M* aluminum nitrate solutions. For this study, 20-gram samples of moist Dowex 1 resin (50- to 100-mesh) having 1, 4, and 10% cross linkage were slurried with 1 liter of solution containing 5.6 grams of uranium per liter, using magnetic stirring. Results confirmed expectations that equilibrium conditions were attained more rapidly with the lower cross linkage resins. Approximately 90% of the equilibrium loading was reached in about 2- and 4-hour contact time for the 1 and 4% cross-linked resins, respectively. Only about 60% of equilibrium was obtained in 12-hour contact time with the 10% cross-linked resin, and the subsequent rate of approach to equilibrium was extremely slow.

After the kinetic study had been completed, the Dowex 1 resins were filtered, rinsed with 2*M* aluminum nitrate, and eluted with nitric acid–acidified water. Resin uranium loadings after 72-hour contact time, together with the large variation of residual moisture content with cross linkage, are shown in Table III. Although the 1% cross-linked resin showed the highest uranium loading on a dry basis, it showed the lowest loading on a wet resin basis because of its high water content and swollen form. Consequently, much larger resin inventories would be required in a process using this resin. The 10% cross-linked resin, while satisfactory from the standpoint of uranium loading, exhibited too slow a rate of exchange. Of the three resins tested, the 4% cross-linked resin appears to have the best combination of kinetic and uranium-loading properties.

Table III. Effect of Cross Linkage on Uranium Adsorption from 2.0M Aluminum Nitrate Solutions

% Resin[a] Cross Linkage	% Water, Wet Resin Basis	Resin Uranium Loadings at 72 Hours, G.U/Kg. Wet resin	Dry resin
1	88	45	380
4	53	150	320
10	31	160	240

[a] Dowex 1 nitrate form, 50- to 100-mesh.

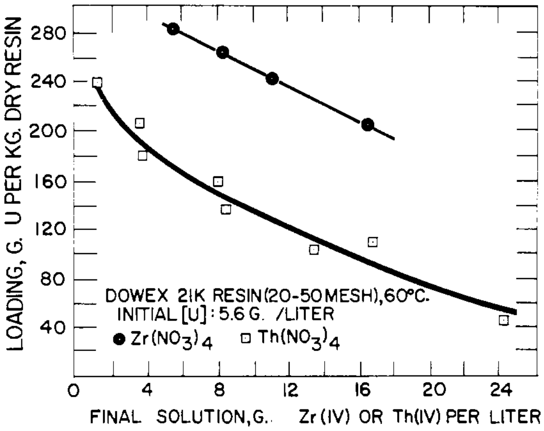

Figure 4. Effect of Zr(IV) and Th(IV) on uranium adsorption from approximately 2.0M aluminum nitrate solutions

CONCLUSIONS

Uranium adsorbability from approximately 2*M* aluminum nitrate solutions is large enough to make recovery and purification feasible. Qualitative data indicate that adsorbed uranium may be rapidly and completely stripped from the resin by treatment with nitric acid–acidified water, yielding a concentrated uranyl nitrate product.

The attainment of adsorption equilibrium conditions from 2*M* aluminum nitrate solutions was extremely slow for the relatively coarse 16- to 20-mesh Dowex 21K resin used. However, adsorption kinetics may be increased appreciably by decreasing the resin particle size, raising the temperature, or making a judicious choice of nitrate salt molarity.

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