**An Investigation of the Applicability
of the
New Reillex™-HPQ Anion Exchange Resin System
for
Technetium/Rhenium and Uranium
in the
Hanford Waste Tanks**

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An Investigation of the Applicability of the New Reillex™-HPQ Anion Exchange Resin System for Technetium/Rhenium and Uranium in the Hanford Waste Tanks

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ABSTRACT

The results of the investigation of the sorption behavior of ReO_4^- on the Reillex™-HPQ in 1.00 M sodium nitrate and variable pH between 2 and 12 are reported. The system for determining K_d is the same as previous milestones. The definition and the determination of K_d' is represented by Eq. 1.

$$K_d' = \frac{\text{mmol of } \text{ReO}_4^-/\text{g dry resin}}{\text{mmol of Re(VII)/mL of solution}} = \frac{\frac{[\text{ReO}_4^-]_{\text{tot}} - [\text{ReO}_4^-]_{\text{sol tot}} \times V_{\text{sol}}}{\text{mass dry resin}}}{\frac{[\text{ReO}_4^-]_{\text{sol tot}} \times V_{\text{sol}}}{V_{\text{sol}}}} \quad (1)$$

From Eq. 1 the value of K_d' at pH 2.83 is 99.00 and the value at pH 11.56 is 78.61.

The results of the investigation of the sorption behavior of ReO_4^- on the Reillex™-HPQ and Reillex™-HP resins in 1.00 M sodium hydroxide and variable sodium nitrate have been determined. The system for determining K_d is the same as reported in previous milestones. The data can be fit to Eq. 1. The non-linear least squares fit of the

$$K_d' = \frac{\frac{\text{ReO}_4^-}{\text{NO}_3^-} K}{[\text{NO}_3^-] + \frac{\text{OH}^-}{\text{NO}_3^-} K [\text{OH}^-]} \quad (1)$$

data results in values of $\frac{\text{ReO}_4^-}{\text{NO}_3^-} K^{\text{HPQ}} = 155 \pm 66 \text{ mL/g}$ and $\frac{\text{OH}^-}{\text{NO}_3^-} K^{\text{HPQ}} = -0.026 \pm 0.19$ on the Reillex™-HPQ. Results from the Reillex™-HP resin indicate values of $\frac{\text{ReO}_4^-}{\text{NO}_3^-} K^{\text{HP}} = 111 \pm 10 \text{ mL/g}$ and $\frac{\text{OH}^-}{\text{NO}_3^-} K^{\text{HP}} = 3.73 \pm 0.41$.

The same experiment using the Reillex™-HPQ and Reillex™-HP resins in 1.00 M sodium nitrate and variable sodium hydroxide were determined from the least squares fit of the data resulting from Eq. 2.

$$K_d' = \frac{\frac{\text{ReO}_4^-}{\text{NO}_3^-} K}{1 + \frac{\text{OH}^-}{\text{NO}_3^-} K [\text{OH}^-]} \quad (2)$$

The sorption characteristics of ReO_4^- on the Reillex™-HP resin at a constant 1.00 M

sodium nitrate and sodium hydroxide concentration varying from 0.100 to 5.00 M can be described from the previous equation. This is assuming that both NO_3^- and OH^- are sorbed by the resin. The results from this experiment indicate values of ${}^{\text{ReO}_4^-}_{\text{NO}_3^-} K^{\text{HP}} = 148 \pm 73 \text{ mL/g}$ and ${}^{\text{OH}^-}_{\text{NO}_3^-} K^{\text{HP}} = 6.63 \pm 5.37$.

The sorption behavior of ReO_4^- on the Reillex™-HPQ resin at a constant 1.00 M sodium nitrate and sodium hydroxide concentration varying from 0.100 to 5.00 M can not be described by assuming that both NO_3^- and OH^- anions are sorbed by the resin. With increasing sodium hydroxide concentration, the values of K_d' increase. The results are consistent with the data in the March Milestone.

The K_d values for ReO_4^- on Reillex™-HPQ resin have been determined in 1.00 M NaOH after resin has been in contact with 5.00 M NaOH at 60 °C for up to 120 hours. The average value for 17 samples is $152 \pm 23 \text{ mL/g}$. The uncertainties are the estimated one standard deviation of the mean. The value of K_d reported in the previous section is $165 \pm 91 \text{ mL/g}$. After the first 0.50 hours, the K_d value is $105 \pm 14 \text{ mL/g}$ with no apparent trend with time. The uncertainty in the data due to the error in measuring the rhenium concentrations in the solutions using Atomic Absorption spectrophotometry precludes a definite conclusion. But, the tentative conclusion is that there is no degradation of the resin in 120 hours at 60 °C, as indicated by a change in K_d values.

The K_d value found for uranyl carbonate in 0.103 M NaNO_3 was $21.9 \pm 1.4 \text{ mL/g}$. Atomic Absorption spectrophotometry was used to determine the concentration of the uranium carbonate solutions. However, the method proved to be very inaccurate and s. Hence, the values reported for K_d are only estimates.

Breakthrough experiments have been performed with 0.020 M $\text{UO}_2(\text{NO}_3)_2$ in varying nitric acid solutions. Reillex™-HPQ columns in the nitrate form were prepared using a 1.00 cm diameter column with heights of 20.5 cm and 50.9 cm. The flow rate was kept between 0.50 cm/min and 1.00 cm/min for all experiments. The uranium content was analyzed by UV/Vis absorption spectra. Furthermore, for the 50.9 cm columns, the amount of deionized water necessary to remove the UO_2^{+2} was determined. Elution and K_d' studies have shown that maximum sorption occurs at a nitric acid concentration of about 7 M. For the breakthrough studies, this trend holds true. A plot of 50 % breakthrough vs. bed volume produces a bell shaped curve with maxima at 4.36 BV at 8 M for the 20.5 cm column and 4.49 BV at 7 M HNO_3 for the 50.9 cm column.

INTRODUCTION

This Milestone Report is for the period June 1, 1994 to September 31, 1994. This is the Fourth Milestone and it is the Final Report for this year. It is to report on the following work.

- Results of the measurements of the exchange capacity and K_d values for ReO_4^- on Reillex™-HPQ as a function of nitric acid and hydroxide concentration, temperature, and ten months time will be reported.
- Results of the breakthrough volumes for UO_2^{2+} on Reillex™-HPQ chromatography columns as a function of carbonate ion concentration in high nitrate ion concentrations and various column sizes will be reported.

The actual work accomplished in this time frame is listed below.

- The sorption behavior of ReO_4^- on the Reillex™-HPQ between pH 2 and 12 in 1.00 M NaNO_3 has been examined and the results are reported here.
- Results of the measurements of the K_d values for ReO_4^- on Reillex™-HPQ as a function of nitrate and hydroxide ion concentrations are presented.
- Results of the measurements of the K_d values for ReO_4^- on Reillex™-HP as a function of nitrate and hydroxide ion concentrations are presented.
- The sorption behavior of ReO_4^- on Reillex™-HPQ resin in base with time as a variable has been investigated. The results are presented.
- The results of the early attempts at determining the K_d values for $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ on Reillex™-HPQ resin are reported.
- The breakthrough of $\text{UO}_2(\text{NO}_3)_2$ in varying nitric acid solutions on Reillex™-HPQ columns has been examined and the results are reported here.
- The paper *"SORPTION BEHAVIOR OF PERRHENATE AND OXOCHROMIUM(VI) ON REILLEX™-HPQ ANION EXCHANGE RESIN FROM NITRIC ACID SOLUTION"* was accepted for publication in the journal "Ion Exchange and Solvent Extraction."
- A copy of a paper entitled *"SORPTION BEHAVIOR OF URANIUM ONTO REILLEX™-HPQ ANION EXCHANGE RESIN FROM NITRIC AND HYDROCHLORIC ACID SOLUTIONS"* which was presented at The 207th National Meeting of the American Chemical Society, 1994, was submitted for publication in the Proceedings of that meeting.

The Sorption Behavior of ReO_4^- on the Reillex™-HPQ between pH 2 and 12 in 1.00 M NaNO_3

Abstract

The results of the investigation of the sorption behavior of ReO_4^- on the Reillex™-HPQ in 1.00 M sodium nitrate and variable pH between 2 and 12 are reported. The system for determining K_d is the same as previous milestones.² The definition and the determination of K_d' is represented by Eq. 1.

$$K_d' = \frac{\text{mmol of } \text{ReO}_4^-/\text{g dry resin}}{\text{mmol of Re(VII)/mL of solution}} = \frac{\frac{[\text{ReO}_4^-]_{\text{tot}} - [\text{ReO}_4^-]_{\text{sol tot}} \times V_{\text{sol}}}{\text{mass dry resin}}}{\frac{[\text{ReO}_4^-]_{\text{sol tot}} \times V_{\text{sol}}}{V_{\text{sol}}}} \quad (1)$$

From Eq. 1 the value of K_d' at pH 2.83 is 99.00 and the value at pH 11.56 is 78.61.

Introduction

The Reillex™-HPQ resin is an anion exchange resin possessing a co-polymer of divinylbenzene and 4-vinylpyridine which has been subsequently methylated (75%) at the pyridine nitrogen to give pyridinium strong base sites. The ionic interaction of ReO_4^- and Reillex™-HPQ in NaOH can be represented by Eq. 2. The symbol R^+ represents the

strong base sites of the Reillex™-HPQ resin. The equilibrium for Eq. 2 can be represented by Eq. 3. The ionic interaction of ReO_4^- with the Reillex™-HPQ in HNO_3 can be represented by Eq. 4.

$$K_{\text{OH}^-}^{\text{ReO}_4^-} = \frac{(\text{R}^+\text{ReO}_4^-)[\text{OH}^-]}{[\text{ReO}_4^-]} = K_{\text{OH}^-}^{\text{ReO}_4^-}(\text{R}^+\text{OH}^-) \quad (3)$$

The equilibrium for Eq. 4 can be represented by Eq. 5.

$$\frac{\text{ReO}_4^-}{\text{NO}_3^-} K = \frac{(\text{R}^+ \text{ReO}_4^-) [\text{NO}_3^-]}{[\text{ReO}_4^-]} = \frac{\text{ReO}_4^-}{\text{NO}_3^-} K' (\text{R}^+ \text{NO}_3^-) \quad (5)$$

The remaining $\approx 25\%$ of the Reillex™-HPQ contains the unmethylated pyridine sites which in acid solution ($< \approx \text{pH } 3.5$) are protonated. As the pH increases, these sites lose the proton and are no longer anion sorbers. This is represented by Eq. 6.

Hence, the value of K'_d is expected to decrease by $\approx 25\%$ from pH 2 to pH ≈ 6 and then to remain constant, if all other parameters are maintained constant. This is a report of the investigation and determination of the values of K'_d below pH 2 at 1.00 M NaNO_3 .

Experimental

The KReO_4 was acquired from Cleveland Refractory Metals and is assumed to be 100.0% pure. The other reagents used in the assay were the same as previously reported.¹ The Reillex™-HPQ resin (Lot # 90928AC) was acquired from Reilly Industries as a 30-60 mesh resin in the chloride form. It was washed with at least 20 volumes of 18 M Ω deionized water (all water used in this study was of this type) by decantation in order to remove the beads that floated. It was converted to the nitrate form by passing 20 bed volumes of 2 M HNO_3 through the resin. This has the effect of protonating the weak base sites of the unmethylated pyridine. The resin was washed with 20 bed volumes of water and stored in water until used. The resin was dried at 60°C for a minimum of 24 hours and then stored in a desiccator over silica gel.

The K'_d and pH determinations were performed in the following manner.² Each sample was prepared by accurately massing 2.0 g of the dried resin in a 30 mL centrifuge tube. To the tube was added 20 mL of 9.00 mM ReO_4^- , the desired concentration of the NaOH or HNO_3 , and the NaNO_3 concentration remained constant at 1.00 M. The solution and resin were then shaken for thirty minutes. The resin was then removed from the solution by gravity filtration using Whatman #41 filter paper, pH readings were recorded,

and the rhenium concentrations were determined using AA methods.

Results and Discussion

For these experiments, 2.00 g of Reillex™-HPQ and 20 mL of 9.00 mmol ReO_4^- were used. The volume to mass ratio and the analytical data for the concentration of ReO_4^- gave the values of K_d under the same conditions as the previous milestones.²

The results of the measurement of K_d for the Reillex™-HPQ in a constant 1.00 M sodium nitrate and variable sodium hydroxide or nitric acid are consistent with previous results. With increasing pH, ReO_4^- sorption initially increases. Between pH 2.00 and 4.00, K_d values reach a plateau due to the sorption behavior of ReO_4^- onto the Reillex™-HPQ resin. Beyond a pH of 6.00, ReO_4^- sorption decreases. This is consistent with the results in the march and June milestones under the same conditions. The results of ReO_4^- sorption on the Reillex™-HPQ in 1.00 M sodium nitrate and variable sodium hydroxide do not fit the described model of K_d' that has been used in the previous milestones. There is no good explanation at this time. The results are listed in Table 1 and the plot of the data is in Figure I.

Table 1. The values of K_d' for ReO_4^- on the Reillex™-HPQ as a function of pH.

pH	K_d' , mL/g	pH	K_d' , mL/g
2.83	99.00	3.95	116.4
3.21	102.8	4.05	109.0
3.41	102.0	4.14	109.3
3.47	107.6	4.23	115.5
3.49	84.13	4.33	111.9
3.52	97.56	4.41	110.1
3.54	95.03	4.50	106.9
3.57	108.0	4.81	104.0
3.60	120.9	5.16	102.1
3.64	121.3	5.95	97.19
3.65	121.3	6.75	91.83
3.71	112.9	8.21	89.76
3.76	113.1	10.20	81.82
3.83	107.4	11.21	80.12
3.86	107.3	11.56	78.61

Figure I. The plot of K'_d for ReO_4^- on the Reillex™-HPQ in 1.00 M sodium nitrate and variable HNO_3 or NaOH .

References

- 1) Reilly Industries, Inc., 1510 Market Square Center, 151 Delaware St., Indianapolis, IN 46204
- 2) "An Investigation of the Applicability of the New Reillex™-HPQ Anion Exchange Resin System for Technetium/Rhenium and Uranium in the Hanford Waste Tanks", Milestone II, March 7, 1994, submitted to LANL for Contract 670HH0013-9Z, Kenneth R. Ashley, Jason R. Ball, Stephen L. Cobb, Michael Adams, and Daniel A. Young.
- 3) "An Investigation of the Applicability of the New Reillex™-HPQ Anion Exchange Resin System for Technetium/Rhenium and Uranium in the Hanford Waste Tanks", Milestone III, June 6, 1994, submitted to LANL for Contract 670HH0013-9Z, Kenneth R. Ashley, Jason R. Ball, Stephen L. Cobb, Michael Adams, and Daniel A. Young.

The Sorption Behavior of ReO_4^- on the Reillex™-HPQ and Reillex™-HP in Variable Base Solutions

Abstract

The results of the investigation of the sorption behavior of ReO_4^- on the Reillex™-HPQ and Reillex™-HP resins in 1.00 M sodium hydroxide and variable sodium nitrate concentrations are reported. The system for determining K_d is the same as reported in previous milestones. The data can be fit to Eq. 1. The non-linear least squares fit of the

$$K'_d = \frac{\frac{\text{ReO}_4^- \text{K}}{\text{NO}_3^-}}{[\text{NO}_3^-] + \frac{\text{OH}^-}{\text{NO}_3^-} \text{K}[\text{OH}^-]} \quad (1)$$

data result in values of $\frac{\text{ReO}_4^- \text{K}^{\text{HPQ}}}{\text{NO}_3^-} = 155 \pm 66 \text{ mL/g}$ and $\frac{\text{OH}^-}{\text{NO}_3^-} \text{K}^{\text{HPQ}} = -0.026 \pm 0.19$ on the Reillex™-HPQ. Results from the Reillex™-HP resin indicate values of $\frac{\text{ReO}_4^- \text{K}^{\text{HP}}}{\text{NO}_3^-} = 111 \pm 10 \text{ mL/g}$ and $\frac{\text{OH}^-}{\text{NO}_3^-} \text{K}^{\text{HP}} = 3.73 \pm 0.41$.

A similar approach using Reillex™-HPQ and Reillex™-HP resins in 1.00 M sodium nitrate and variable sodium hydroxide concentrations were performed. The data was fit by least squares methods to Eq. 2.

$$K'_d = \frac{\frac{\text{ReO}_4^- \text{K}}{\text{NO}_3^-}}{1 + \frac{\text{OH}^-}{\text{NO}_3^-} \text{K}[\text{OH}^-]} \quad (2)$$

The sorption characteristics of ReO_4^- on the Reillex™-HP resin at a constant 1.00 M sodium nitrate and sodium hydroxide concentration varying from 0.100 to 5.00 M can be described from the previous equation. This is assuming that both NO_3^- and OH^- are sorbed by the resin. The results from this experiment indicate values of $\frac{\text{ReO}_4^- \text{K}^{\text{HP}}}{\text{NO}_3^-} = 148 \pm 73 \text{ mL/g}$ and $\frac{\text{OH}^-}{\text{NO}_3^-} \text{K}^{\text{HP}} = 6.63 \pm 5.37$.

The sorption behavior of ReO_4^- on the Reillex™-HPQ resin at a constant 1.00 M sodium nitrate and sodium hydroxide concentration varying from 0.100 to 5.00 M can not be described by assuming that both NO_3^- and OH^- anions are sorbed by the resin. With increasing sodium hydroxide concentration, the values of K'_d increase. The results are consistent with the data in the March Milestone.

Introduction

The Reillex™-HPQ resin is an anion exchange resin possessing a co-polymer of divinylbenzene and 4-vinylpyridine that has been subsequently methylated (75%) at the pyridine nitrogen to give pyridinium strong base sites. Reillex™-HP is the same resin without methylation of the pyridine nitrogen. Hence, there are no strong base sites.

The ionic interaction of ReO_4^- with the Reillex™-HPQ and Reillex™-HP resin in NaOH can be represented by Eq. 3. The symbol R^+ represents the strong base sites of

the Reillex™-HPQ resin and the protonated weak base sites of the Reillex™-HP resin. As with the March Milestone we are assuming no weak base capacity for the Reillex™-HP resin.

The equilibrium for Eq. 3 can be represented by Eq. 4.

$$K = \frac{(\text{R}^+\text{ReO}_4^-)[\text{OH}^-]}{[\text{ReO}_4^-]} = K'(\text{R}^+\text{OH}^-) \quad (4)$$

The evaluation of the distribution coefficients for ReO_4^- with the Reillex™-HPQ and Reillex™-HP resins as a function of sodium hydroxide and sodium nitrate concentrations has been reported in the March Milestone. This September milestone compiles the results of the measurements of the distribution coefficients, K_d' , for the ReO_4^- ion on the Reillex™-HPQ and Reillex™-HP resins.

Experimental

The KReO_4 was acquired from Cleveland Refractory Metals and is assumed to be 100.0% pure. The other reagents used in the assay were the same as previously reported.¹ The Reillex™-HPQ resin (Lot # 90928AC) and Reillex™-HP resin (Lot # 21227AA) were acquired from Reilly Industries as a 30-60 mesh resin in the chloride form. It was washed with at least 20 volumes of 18 MΩ deionized water (all water used in this study was of this type) by decantation in order to remove the beads that floated. It was

converted to the nitrate form by passing 20 bed volumes of 2 M HNO₃ through the resin. This has the effect of protonating the weak base sites of the unmethylated pyridine. The resin was washed with 20 bed volumes of water and stored in water until used. The resin was dried at 60°C for a minimum of 24 hours and then stored in a desiccator over silica gel.

The K_d determinations were performed in the following manner.² Each sample was prepared by accurately massing 1.0 g of the dried resin in a 30 mL centrifuge tube. To the tube was added 10 mL of 9.00 mM ReO₄⁻ and the desired NaNO₃ and NaOH concentration. The solution and resin were then shaken for one hour. The resin was then removed from the solution by gravity filtration using Whatman #41 filter paper and analyzed using AA methods.

Results and Discussion

For these experiments, 1.00 g of Reillex™-HPQ or Reillex™-HP and 10 mL of 9.00 mmol ReO₄⁻ were used. The volume to mass ratio and the analytical data for the concentration of ReO₄⁻ gave the values of K_d' under the same conditions as the March Milestone.

The results of the measurement of K_d' for the Reillex™-HPQ in a constant 1.00 M sodium hydroxide and variable sodium nitrate concentration are consistent with the previous results. With increasing nitrate concentration, ReO₄⁻ sorption decreases indicating the competition for the strong base sites. The compiled results are listed in Table 1 and the plots of the data are in Figure I, II and III. The solid line in Figure I and II is the fit of the data to a model which assumes that ReO₄⁻, NO₃⁻, and OH⁻ all compete for the anion exchange site on Reillex™-HPQ. Figure III is the fit of the combined data.

The equation for the least squares fit of the data is defined by Eq. 5. The numerator

$$K_d' = \frac{\frac{\text{ReO}_4^- \text{K}}{\text{NO}_3^-}}{[\text{NO}_3^-] + \frac{\text{OH}^-}{\text{NO}_3^-} \text{K}[\text{OH}^-]} \quad (5)$$

is derived from equilibrium of Eq. 6. The equilibrium coefficient is defined in Eq. 7.

Table 1. The values of K_d' for ReO_4^- on the Reillex™-HPQ in variable NaNO_3 and constant 1.00 M NaOH .

$[\text{NaNO}_3], \text{M}$	$K_d', \text{mL/g}^1$	$K_d', \text{mL/g}^2$
5.00	38.2	37.3
4.00	47.4	44.2
3.00	54.6	53.9
2.00	74.9	79.1
1.00	139.2	117.4
0.900	111.6	164.6
0.800	112.4	223.6
0.700	130.4	244.3
0.600	228.8	301.7
0.500	158.9	363.9
0.400	199.7	392.0
0.300	272.4	553.0
0.200	422.6	926.9
0.100	452.1	132921.5

¹March data. ²September data.

$$K = \frac{(R^+ \text{ReO}_4^-) [\text{NO}_3^-]}{[\text{ReO}_4^-]} = K' (R^+ \text{NO}_3^-) \quad (7)$$

The constant in the denominator of Eq. 5 represents the competition equilibrium constant for the hydroxide form of the resin over the nitrate form of the resin. The value of $\text{ReO}_4^-/\text{NO}_3^- K^{\text{HPQ}}$ is $155 \pm 66 \text{ mL/g}$ and the value of $\text{OH}^-/\text{NO}_3^- K^{\text{HPQ}}$ is -0.026 ± 0.19 . The results from the March Milestone indicate a value of $\text{ReO}_4^-/\text{NO}_3^- K^{\text{HPQ}}$ at $162 \pm 95 \text{ mL/g}$ and the value of $\text{OH}^-/\text{NO}_3^- K^{\text{HPQ}}$ being 0.33 ± 0.022 . The results from the combined data give the value of $\text{ReO}_4^-/\text{NO}_3^- K^{\text{HPQ}}$ at $200 \pm 46 \text{ mL/g}$ and the value of $\text{OH}^-/\text{NO}_3^- K^{\text{HPQ}}$ at 0.21 ± 0.11 .

Table 2 lists the results of the measurement of K_d' for the Reillex™-HPQ in constant 1.00 M sodium nitrate and variable sodium hydroxide solutions.

Figure I. The plot of K_d' for ReO_4^- on the ReillexTM-HPQ in 1.00 M NaOH and variable NaNO_3 . The solid line is the non-linear least squares fit of the data to the equation:

$$K_d' = (155 \pm 66.) / \{(-0.026 \pm 0.19) + [\text{NaNO}_3]\}$$

Figure II. The plot of K'_d for ReO_4^- on the Reillex™-HPQ in 1.00 M NaOH and variable NaNO_3 from the March milestone. The solid line is the non-linear least squares fit of the data to the equation:

$$K'_d = (162 \pm 95) / \{(0.33 \pm 0.52) + [\text{NaNO}_3]\}$$

Figure III. The plot of K'_d for ReO_4^- on the Reillex™-HPQ in 1.00 M NaOH and variable NaNO_3 from the two milestones. The solid line is the non-linear least squares fit of the data to the equation:

$$K'_d = (200 \pm 46) / \{(0.21 \pm 0.11) + [\text{NaNO}_3]\}$$

Table 2. The values of K_d' for ReO_4^- on the Reillex™-HPQ in variable NaOH and 1.00 M NaNO_3 .

[NaOH], M	K_d' , mL/g ¹	K_d' , mL/g ²
5.00	212.6	3487.8
4.00	207.7	239.7
3.00	194.7	156.6
2.00	138.5	138.6
1.00	142.6	131.2
0.900	119.7	116.7
0.800	125.7	115.9
0.700	125.6	113.4
0.600	119.7	114.2
0.500	114.4	113.8
0.400	109.3	113.5
0.300	100.5	101.8
0.200	104.8	111.2
0.100	104.8	111.9

¹March data. ²September data.

The plots of the data are in Figure IV and V. The two runs indicate good consistency when compared to each other and to the similar results obtained with TcO_4^- under the same conditions.

Figure IV. The plot of K'_d for ReO_4^- on the Reillex™-HPQ in 1.00 M NaNO_3 and variable NaOH .

Figure V. The plot of K'_d for ReO_4^- on the Reillex™-HPQ in 1.00 M NaNO_3 and variable NaOH from the March Milestone.

Startling results were observed in the previous milestone from the observation that the Reillex™-HP sorbs ReO_4^- in basic solution. The results from this experiment indicate the same trend. This is illustrated in Table 3 and 4. The data is plotted in Figures VI, VII, VIII, IX, X, and XI. The data has been treated with the same model as the Reillex™-HPQ

was treated above (Eq. 3). In the solutions of constant sodium hydroxide and variable sodium nitrate concentrations (Fig. VI, VII and VIII), the fit of the data yield values of $\text{ReO}_4^- \text{K}^{\text{HP}}$ and $\text{OH}^- \text{K}^{\text{HP}}$ of 111 ± 10 mL/g and 3.73 ± 0.41 . The previous data indicate values of $\text{ReO}_4^- \text{K}^{\text{HP}}$ and $\text{OH}^- \text{K}^{\text{HP}}$ of 133 ± 181 mL/g and 4.54 ± 0.54 , respectively. The combined data gives values of $\text{ReO}_4^- \text{K}^{\text{HP}}$ and $\text{OH}^- \text{K}^{\text{HP}}$ of 127 ± 11 mL/g and 4.30 ± 0.42 . In the solutions using constant sodium nitrate and variable sodium hydroxide concentrations (Fig. IX, X and XI), the fit of the data gives values for $\text{ReO}_4^- \text{K}^{\text{HP}}$ at 148 ± 73 mL/g and $\text{OH}^- \text{K}^{\text{HP}}$ at 6.63 ± 5.37 . The previous data yields values of 423 ± 296 mL/g for $\text{ReO}_4^- \text{K}^{\text{HP}}$ and 12.4 ± 8.2 for $\text{OH}^- \text{K}^{\text{HP}}$. The combined data gives values of $\text{ReO}_4^- \text{K}^{\text{HP}}$ and $\text{OH}^- \text{K}^{\text{HP}}$ at 277 ± 119 mL/g and 9.94 ± 6.4 respectively.

Table 3. The values of K_d' for ReO_4^- on the ReillexTM-HP in variable NaNO_3 .

$[\text{NaNO}_3]$, M	K_d' , mL/g ¹	K_d' , mL/g ²
5.00	13.7	12.5
4.00	14.8	15.7
3.00	20.7	17.6
2.00	19.5	20.5
1.00	24.4	22.0
0.900	25.1	22.6
0.800	24.8	23.8
0.700	27.8	24.1
0.600	29.6	24.5
0.500	28.4	26.3
0.400	26.5	26.7
0.300	26.9	27.3
0.200	28.1	29.9
0.100	27.2	31.1

¹March data. ²September data.

Table 4. The values of K'_d for ReO_4^- on the Reillex™-HP in variable NaOH.

[NaOH], M	K'_d , mL/g ¹	K'_d , mL/g ²
5.00	32.7	38.7
4.00	47.3	36.5
3.00	25.7	31.0
2.00	28.7	28.3
1.00	39.9	24.2
0.900	38.1	15.9
0.800	35.9	17.8
0.700	35.9	16.6
0.600	33.8	13.9
0.500	35.8	13.9
0.400	33.2	32.8
0.300	100.5	60.8
0.200	165.6	83.0
0.100	176.7	83.1

¹March data. ²September data.

Figure VI. The plot of K'_d for ReO_4^- on the ReillexTM-HP in 1.00 M NaOH and variable NaNO_3 . The solid line is the non-linear least squares fit of the data to the equation:

$$K'_d = (111 \pm 10) / \{(3.73 \pm 0.41) + [\text{NaNO}_3]\}$$

Figure VII. The plot of K'_d for ReO_4^- on the Reillex™-HP in 1.00 M NaOH and variable $NaNO_3$ from the March Milestone. The solid line is the non-linear least squares fit of the data to the equation:

$$K'_d = (133 \pm 181) / \{(4.54 \pm 0.0535) + [NaNO_3]\}$$

Figure VIII. The plot of K_d' for ReO_4^- on the Reillex™-HP in 1.00 M NaOH and variable NaNO_3 from the two milestones. The solid line is the non-linear least squares fit of the data to the equation:

$$K_d' = (127 \pm 11) / \{(4.30 \pm 0.42) + [\text{NaNO}_3]\}$$

Figure IX. The plot of K'_d for ReO_4^- on the ReillexTM-HP in 1.00 M NaNO_3 and variable NaOH. The solid line is the non-linear least squares fit of the data to the equation:

$$K'_d = (148 \pm 73) / \{1 + (6.63 \pm 5.37)[\text{NaNO}_3]\}$$

Figure X. The plot of K'_d for ReO_4^- on the ReillexTM-HP in 1.00 M NaNO_3 and variable NaOH from the March Milestone. The solid line is the non-linear least squares fit of the data to the equation:

$$K'_d = (422 \pm 195) / \{1 + (12.4 \pm 8.21)[\text{NaNO}_3]\}$$

Figure XI. The plot of K_d' for ReO_4^- on the Reillex™-HP in 1.00 M NaNO_3 and variable NaOH from the two milestones. The solid line is the non-linear least squares fit of the data to the equation:

$$K_d' = (277 \pm 119) / \{1 + (9.94 \pm 6.44)[\text{NaNO}_3]\}$$

References

- 1) Reilly Industries, Inc., 1510 Market Square Center, 151 Delaware St., Indianapolis, IN 46204
- 2) "An Investigation of the Applicability of the New Reillex™-HPQ Anion Exchange Resin System for Technetium/Rhenium and Uranium in the Hanford Waste Tanks", Milestone II, March 7, 1994, submitted to LANL for Contract 670HH0013-9Z, Kenneth R. Ashley, Jason R. Ball, Stephen L. Cobb, Michael Adams, and Daniel A. Young.

The Sorption Behavior of ReO_4^- on Reillex™-HPQ Resin in Base with Time as a Variable

Abstract

The K_d values for ReO_4^- on Reillex™-HPQ resin have been determined in 1.00 M NaOH after resin has been in contact with 5.00 M NaOH at 60 °C for up to 120 hours. The average value for 17 samples is 152 ± 23 mL/g. The uncertainties are the estimated one standard deviation of the mean. The value of K_d reported in the previous section is 165 ± 91 mL/g. After the first 0.50 hours, the K_d value is 105 ± 14 mL/g with no apparent trend with time. The uncertainty in the data due to the error in measuring the rhenium concentrations in the solutions using Atomic Absorption spectrophotometry precludes a definite conclusion. But, the tentative conclusion is that there is no degradation of the resin in 120 hours at 60 °C, as indicated by a change in K_d values.

Introduction

Whenever Reillex™-HPQ anion exchange resin is kept in 1.0 M, or greater, sodium hydroxide solution, a yellowish-red color develops and the odor of pyridine is evident. This implies that there might be degradation of the resin or that some of the lower molecular weight polymers are being leached out of the resin. If this is degradation of the resin, one concern is that this might decrease the values of the distribution coefficients of ReO_4^- and the resin. This is a report of the experiments designed to ascertain the values of K_d as a function of time of Reillex™-HPQ in 5.00 M NaOH at 60 °C. The K_d values were measured in 1.0 M NaOH.

Experimental

Reillex™-HPQ chloride form resin was converted to the nitrate form by eluting twenty bed volumes of 2 M HNO_3 through a column of the resin. Then the resin was rinsed with another 20 bed volumes of water and dried at 60 °C. for more than 24 hours.

Evergreen Scientific chromatography tubes (≈ 8 mL total volume)) were used as the containers for the determination of the K_d values. Into the columns were placed 0.500 g of dry resin. Next, 5 mL of 5 M NaOH was added to each of the resin samples and the samples were placed in a 60 °C water bath-shaker and allowed to shake for the allotted amount of time. After the prescribed amount of time, the NaOH was removed by suction. The resin was then rinsed, in the container, with 25 mL of water. The suction filtration was continued until the resin was as dry as possible to avoid any potential dilutions. Then, 5 mL of a solution which was 1 M NaOH, 1 M NaNO₃, and 0.009 M ReO₄⁻ was added to the resin. This ReO₄⁻ concentration is such that no more than 2% loading of the resin occurred. The solutions were allowed to set for two hours at room temperature. After the 2 hours, the solution was drained from the resin and the effluent analyzed for rhenium by Atomic Absorption spectrophotometer as previously described.

AA standards were made by the following procedure. In separate 100 mL volumetric flasks, 0.0289, 0.0145, 0.0084, and 0.0042 g of KReO₄ were placed. In each of the flasks, 8.50 g NaNO₃ and 9.91 mL of a 10.09 M standardized solution of NaOH were added and diluted to the mark to result in 0.001, 0.0005, 0.0003, and 0.00015 M ReO₄⁻ standard solutions, 1.00 M in both NaNO₃ and NaOH. This gives the same matrix as used for the treatment of the resin. All of the standards and samples were measured using an AA instrument as previously described. The absorbances varied from 0.002 to 0.018. Because of the low absorbances, the error was quite large.

Results and Conclusions

In Table 1 are reported the values of K_d at the various times. The values of the first four entries are not very certain since the absorbance of these samples in the rhenium analyses was about 0.003. In Figure 1 is plotted the values of K_d as a function of time. The error bars are set at $\pm 20\%$.

The results are somewhat inconclusive. There appears to be a decrease in the values of K_d as time progresses. However, the errors in the determination of the rhenium concentration prohibits a firm conclusion about this. It is clear that the work needs to be repeated with more attention directed to the analyses of the rhenium samples.

Table 1. Parameters for the individual solutions.

Sample number	Time, hours, in 5.00 M NaOH	K _d , mL/g
Std. 1	0.50	320
Std. 2	0.50	320
Std. 3	0.50	255
Std. 4	0.50	320
1	6.0	86
2	12	80
3	18	112
4	24	77
5	30	74
6	36	86
7	42	139
8	48	255
9	65	102
10	72	124
11	84	86
12	96	59
13	120	86

Figure 1. Plot of the K_d values vs. the time of degradation for the resin in a strong base.

Early Attempts for Determining the K_d Values for $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ on Reillex™-HPQ Resin

Abstract

The K_d value found for uranyl carbonate in 0.103 M NaNO_3 was 21.9 ± 1.4 mL/g. Atomic Absorption spectrophotometry was used to determine the concentration of the uranium carbonate solutions. However, the method proved to be very inaccurate and imprecise. Hence, the values reported for K_d are only estimates.

Introduction

The sorption of $\text{UO}_2(\text{NO}_3)_3^-$ and/or other nitrato complexes of UO_2^{2+} onto Reillex™-HPQ form concentrated nitric acid solutions has been investigated. It is also of interest to see if other anionic complexes of UO_2^{2+} can be sorbed onto Reillex™-HPQ. This is an initial attempt to measure the K_d values for $\text{UO}_2(\text{CO}_3)_3^{4-}$.

The distribution coefficient for $\text{UO}_2(\text{CO}_3)_3^{4-}$ can be described by the Eq. 1.

$$K'_d = \frac{\text{mmol of } \text{UO}_2(\text{CO}_3)_3^{4-} / \text{g dry resin}}{\text{mmol of } \text{UO}_2(\text{CO}_3)_3^{4-} / \text{mL of solution}} = \frac{\frac{[\text{UO}_2(\text{CO}_3)_3^{4-}]_{\text{tot}} - [\text{UO}_2(\text{CO}_3)_3^{4-}]_{\text{sol tot}} \times V_{\text{sol}}}{\text{mass dry resin}}}{\frac{[\text{UO}_2(\text{CO}_3)_3^{4-}]_{\text{sol tot}} \times V_{\text{sol}}}{V_{\text{sol}}}} \quad (1)$$

The uranium concentration in solution was measured by AA spectrophotometry.

Experimental

The uranyl carbonate solution was prepared by dissolving 12.553 g of $\text{UO}_2(\text{NO}_3)_2$ and 10.599 g of sodium carbonate in a 250 mL volumetric flask. This resulted in a 0.100 M solution of uranyl carbonate and 0.200 M solution of sodium nitrate. Next, into another 250 mL flask, 2.125 g of NaNO_3 and 4.175 mL of the original solution were dissolved and diluted to the mark. This resulted in a 0.00167 M $\text{UO}_2(\text{CO}_3)_3$ and a final concentration of 0.103 M of sodium nitrate in the solution. Thirty mL of this solution was pipetted onto 3 g of dry HPQ resin and the mixture was shaken for two hours. The resin was removed by

gravity filtration and the liquid analyzed. A set of three samples was run. AA standards were made by dissolving 0.85 g samples of sodium nitrate in four separate 100 mL volumetric flasks and then adding 59.88, 29.94, 5.988, and 2.994 mL of the second solution made. This gave 0.001, 0.0005, 0.0001, and 0.00005 M molar solutions of $\text{UO}_2(\text{CO}_3)_3$. The absorbances of the solutions were measured on AA at a wavelength of 356.7 nm. The absorbances ranged from 0.001 to 0.006.

Results

It was found that the absorbance values of the uranium samples were very unstable. The absorbance measurements were made for very long times and averaged. The entire 30 mL samples were used in the measurements. This method would not be possible (or as accurate) if the sample size had been any smaller. The results for the three samples are as follows. The absorbances of the three samples were 0.004, 0.00375, and 0.0038. This resulted in values of K_d of 20.4, 23.0, and 22.4 mL/g.

Conclusion

The value of K_d is very tentative. And, the dependence of K_d on $[\text{NO}_3^-]$ is not addressed at all. We are continuing to investigate this system. We are currently developing a spectrophotometric method for uranium.

The Breakthrough of $\text{UO}_2(\text{NO}_3)_2$ in Varying Nitric Acid Solutions on Reillex™-HPQ Columns

Abstract

Breakthrough experiments have been performed with 0.020 M $\text{UO}_2(\text{NO}_3)_2$ in varying nitric acid solutions. Reillex™-HPQ columns in the nitrate form were prepared using a 1.00 cm diameter column with heights of 20.5 cm and 50.9 cm. The flow rate was kept between 0.50 cm/min and 1.00 cm/min for all experiments. The uranium content was analyzed by UV/Vis absorption spectra. Furthermore, for the 50.9 cm columns, the amount of deionized water necessary to remove the UO_2^{+2} was determined. Elution and K'_d studies have shown that maximum sorption occurs at a nitric acid concentration of about 7 M. For the breakthrough studies, this trend holds true. A plot of 50 % breakthrough vs. bed volume produces a bell shaped curve with maxima at 4.36 BV at 8 M for the 20.5 cm column and 4.49 BV at 7 M HNO_3 for the 50.9 cm column.

Introduction

Uranyl ion, UO_2^{+2} , complexes with varying numbers of NO_3^- ligands to form species of the form $\text{UO}_2(\text{NO}_3)_n^{(2-n)}$. Since evidence from the K'_d studies has shown that there are species of $n \geq 3$, further experimentation using Reillex™-HPQ anion exchange resin as a means to isolate the uranyl species was initiated. Elution behavior was studied and results indicated that sorption occurred to some extent at nitric acid concentrations of ~7 M. In order to fully characterize sorption of the UO_2^{+2} species, breakthrough studies were made. The purpose of these breakthrough studies was threefold: 1) to further illustrate the relationship between sorption and acid concentration, 2) to quantify the amount of UO_2^{+2} that sorbs onto the resin, and 3) to measure the breakthrough volume at useful percentages.

Experimental

The appropriate amount of resin (5.51 g and 12.5 g) was massed in a beaker and soaked in 18 MΩ deionized water for at least an hour. The resin was then poured into a 1.00 cm diameter Kontes column. The resin bed was washed with 8 M HNO₃ and water. The UO₂(NO₃)₂ solutions were made by massing 5.0465 g of 99.5 % UO₂(NO₃)₂ and adding the appropriate amount of standardized concentrated nitric acid and water. Nitric acid solutions of 2, 4, 6, 8, and 10 M were used with the 20.5 cm column, while the 50.9 cm column used 1, 2, 3, 4, 6, 7, 8, and 10 M solutions. The UO₂(NO₃)₂ solutions were eluted through the columns using a Masterflex peristaltic pump to obtain a constant flow rate. The effluent was collected using a fraction collector. Fraction collection time was 7 minutes for each solution. For the 50.9 cm column, once 100 % breakthrough had been achieved, 18 MΩ deionized water was added. Fraction collection continued until all of the uranyl eluted through the column. Analysis for uranium was conducted using a UV/Vis Spectrophotometer at a wavelength setting of 420 nm.

Results and Discussion

The initial method for uranium analyses was by Atomic Absorption (AA) spectrophotometry at 357 nm; however, reproducible results could not be obtained. Therefore, the analyses were performed using visible absorption spectrophotometry. The absorbance of each fraction was measured at 420 nm. This absorbance was ratioed against the absorbance of the uranium feed solution to yield the percent breakthrough. Sequentially are reported the conditions for each set of breakthrough experiments, the data for each experiment, and then the plots of the percent breakthrough vs. the effluent volume in units of Bed Volume (BV). Finally, correlation between the data is made by examining the number of bed volumes required to reach 50 percent breakthrough.

For these breakthrough studies, it is important to notice the difference in column length and flow rate that occurs in the 20 and 50 cm columns. Much of this is due to the difficulty in repeatability in controlling the pump controller. The working flow rate was at the minimum setting for the pump and slight variations in the setting created definite differences in the volume being pumped. The differences in the column length, particularly in the 20 cm column is, to some effect, due to the differing amount of resin in

the column. Also, problems were incurred in properly laying the column bed due to expansion of the resin inside the column. This problem does affect the 20 cm column, but was to most extents overcome in the 50 cm column work.

A second problem was the elution of some species at or before the void volume. This peak was found in most of the column breakthroughs. This could be the result of something on the column which absorbs at the same wavelength as uranium; however, the same resin bed was used for all of the breakthroughs in the 50 cm column. Yet, even the last breakthrough with that column showed this. AA spectrophotometry could be used to determine whether this species is uranium or not, but as previously noted, there are inherent errors in this process as well.

Table 1. The conditions for each column for the experimental runs with a 20.5 cm column.

HNO ₃ , M	2.00	4.00	6.00	8.00	10.0
Amount of Resin, g	5.50	5.50	5.50	5.52	5.51
Column Height, cm	20.5	20.5	22.2	21.5	23.1
Bed Volume, mL	16.3	16.3	16.3	16.4	16.3
Collection Time, min	7.00	7.00	7.00	7.00	7.00
Fraction Volume, mL	4.20	3.85	5.60	3.80	4.60
Flow Rate, mL/min	0.600	0.550	0.800	0.543	0.657
Linear Flow Rate, cm/min	0.764	0.700	1.02	0.691	0.837
Standard Absorbance	0.172	0.239	0.233	0.282- 0.251	0.291*

* More than one standard absorbance was used for the run made at 8.00 M.

Table 2. Data for the breakthrough study in 2.00 M HNO₃ using 5.50 g of dry resin in a 20.5 x 1.00 cm column.

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
1	4.20	0.26	0.0131	7.63
2	8.40	0.52	0.0078	4.54
3	12.6	0.77	0.0318	18.5
4	16.8	1.03	0.0775	45.1
5	21.0	1.29	0.1276	74.3
6	25.2	1.55	0.1541	89.6
7	29.4	1.80	0.1613	93.9
8	33.6	2.06	0.1629	94.9
9	37.8	2.32	0.1648	96.0
10	42.0	2.58	0.1634	95.2

Figure 1. Plot of Percent Breakthrough versus Effluent volume, BV for UO_2^{+2} in 2.00 M HNO_3 using 5.50 g of dry resin in a 20.5 cm x 1.00 cm column.

Table 3. Data for the breakthrough study in 4.00 M HNO₃ using 5.50 g of dry resin in a 20.5 x 1.00 cm column.

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
1	3.85	0.236	0.0140	5.86
2	7.70	0.472	0.0114	4.77
3	11.6	0.709	0.0225	9.41
4	15.4	0.950	0.0336	14.1
5	19.3	1.18	0.0310	13.0
6	23.1	1.42	0.0716	30.0
7	27.0	1.65	0.1335	55.9
8	30.8	1.89	0.1694	70.9
9	34.7	2.13	0.1803	75.5
10	38.5	2.362	0.1836	76.8
11	42.4	2.60	0.1900	79.5
12	46.20	2.83	0.1873	78.4
13	50.1	3.07	0.1864	78.0
14	53.9	3.31	0.1872	78.3
15	57.8	3.54	0.1858	77.7

Figure 2. Plot of Percent Breakthrough versus Effluent volume, BV for UO_2^{+2} in 4.00 M HNO_3 using 5.50 g of dry resin in a 20.5 x 1.00 cm column.

Table 4 . Data for the breakthrough study in 6.00 M HNO₃ using 5.50 g of resin in a 20.5 x 1.00 cm column.

Fraction	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
1	5.6	0.344	0.0110	4.72
2	11.2	0.687	0.0050	2.15
3	16.8	1.03	0.0305	13.10
4	22.4	1.37	0.0202	8.67
5	28.0	1.72	0.0093	3.99
6	33.6	2.06	0.0048	2.06
7	39.2	2.41	0.0071	3.05
8	44.8	2.75	0.0161	6.91
9	50.4	3.09	0.0359	15.4
10	56.0	3.44	0.0682	29.3
11	61.6	3.78	0.1022	43.9
12	67.2	4.12	0.1375	59.0
13	72.8	4.47	0.1691	72.6
14	78.4	4.81	0.1926	82.7
15	84.0	5.15	0.2096	90.0
16	89.6	5.50	0.2205	94.7
17	95.2	5.84	0.2276	97.7

Figure 3. Plot of Percent Breakthrough versus Effluent volume, BV for UO_2^{+2} in 6.00 M HNO_3 using 5.50 g of resin in a 20.5 x 1.00 cm column.

Table 5. Data for the breakthrough study in 8.00 M HNO₃ using 5.52 g of dry resin in a 20.5 x 1.00 cm column.

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
1	3.8	0.232	0.0293	10.388
2	7.6	0.465	0.0338	11.984
3	11.4	0.697	0.0288	10.211
4	15.2	0.929	0.0464	16.451
5	19.0	1.162	0.0797	28.257
6	22.8	1.394	0.0621	22.017
7	26.6	1.626	0.0495	17.550
8	30.4	1.858	0.0494	17.515
9	34.2	2.091	0.0451	15.990
10	38.0	2.323	0.0431	15.281
11	41.8	2.555	0.0468	16.392
12	45.6	2.788	0.0533	18.669
13	49.4	3.020	0.0465	16.287
14	53.2	3.252	0.0537	18.809
15	57.0	3.485	0.0652	22.837
16	60.8	3.717	0.0819	28.687
17	64.6	3.949	0.1012	35.447
18	68.4	4.181	0.1283	44.939
19	72.2	4.414	0.1476	51.699
20	76.0	4.646	0.172	60.245
21	79.8	4.878	0.193	66.323
22	83.6	5.111	0.2149	73.849
23	87.4	5.343	0.2314	79.519
24	91.2	5.575	0.2456	84.399
25	95.0	5.808	0.2583	88.763
26	98.8	6.040	0.2679	92.062

Figure 4. Plot of Percent Breakthrough versus Effluent volume, BV for UO_2^{+2} in 8.00 M HNO_3 using 5.50 g of resin in a 20.5 x 1.00 cm column.

Table 6. Data for the breakthrough study in 10.0 M HNO₃ for 5.51 g of dry resin in a 20.5 x 1.00 cm column.

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
1	4.600	0.282	0.0101	4.018
2	9.200	0.563	0.0082	3.262
3	13.800	0.845	0.0238	9.469
4	18.400	1.127	0.0886	35.250
5	23.000	1.409	0.0567	22.558
6	27.600	1.690	0.035	13.925
7	32.200	1.972	0.0282	11.219
8	36.800	2.254	0.0236	9.389
9	41.400	2.535	0.0242	9.628
10	46.000	2.817	0.0315	12.532
11	50.600	3.099	0.0476	18.938
12	55.200	3.380	0.068	27.054
13	59.800	3.662	0.0966	38.432
14	64.400	3.944	0.124	49.334
15	69.000	4.226	0.1492	59.359
16	73.600	4.507	0.1763	70.141
17	78.200	4.789	0.1958	77.899
18	82.800	5.071	0.2115	84.146
19	87.400	5.352	0.2223	88.442
20	92.000	5.634	0.2308	91.824
21	96.600	5.916	0.2369	94.251

Figure 5. Plot of Percent Breakthrough versus Effluent volume, BV for UO_2^{+2} in 10.0 M HNO_3 using 5.51 g of resin in a 20.5 x 1.00 cm column.

Table 7. The conditions for the breakthrough studies conducted using the 50.9 cm x 1.00 cm columns.

HNO ₃	1 M	2 M	3 M	4 M	6 M	7 M	8 M	10 M
Amount of resin, g	12.50	12.50	12.50	12.50	12.50	12.50	12.50	12.50
Column height, cm	50.9	50.9	50.9	50.9	49.7	50.9	49.7	50.9
Bed Volume, mL	37.05	37.05	37.05	37.05	37.05	37.05	37.05	37.05
Collect. time, min	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00
Fraction, volume, mL	5.20	5.50	5.30	5.00	4.00	4.80	5.05	4.70
Flow Rate, mL/min	0.743	0.786	0.757	0.714	0.571	0.686	0.721	0.671
Linear Flow Rate, cm/min	0.946	1.00	0.964	0.909	0.728	0.873	0.919	0.855
Stan. Abs.	0.1415	0.1665	0.1833	0.2219	0.2427	0.2543	0.2607	0.2430
Water Added at Tube	29	26	26	25	54	49	41	30

Table 8 Data for the breakthrough study in 1.00 M HNO₃ using 12.5028 g of dry resin in a 50.9 x 1.00 cm column.

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
1	5.20	0.140	0.0275	19.435
2	10.4	0.281	0.0232	16.396
3	15.6	0.421	0.0205	14.488
4	20.8	0.561	0.0080	5.654
5	26.0	0.702	0.0154	10.883

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Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
6	31.2	0.842	0.0540	38.163
7	36.4	0.982	0.0783	55.336
8	41.6	1.12	0.1055	74.558
9	46.8	1.26	0.1335	94.346
10	52.0	1.40	0.1379	97.456
11	57.2	1.54	0.1380	97.527
12	62.4	1.68	0.1388	98.092
13	67.6	1.82	0.1379	97.456
14	72.8	1.97	0.1416	100.071
15	78.0	2.11	0.1403	99.152
16	83.2	2.25	0.1371	96.890
17	88.4	2.39	0.1372	96.961
18	93.6	2.53	0.1400	98.940
19	98.8	2.67	0.1363	96.325
20	104	2.81	0.1426	100.777
21	109	2.95	0.1373	97.032
22	114	3.09	0.1376	97.244
23	120	3.23	0.1397	98.728
24	125	3.37	0.1423	100.565
25	130	3.51	0.1380	97.527
26	135	3.65	0.1431	101.131
27	140	3.79	0.1403	99.152
28	146	3.93	0.1427	100.848
29	151	4.07	0.1426	100.777
30	156	4.21	0.1399	98.869
31	161	4.35	0.1429	100.989
32	166	4.49	0.1385	97.9
33	172	4.63	0.1397	98.8
34	177	4.77	0.1423	101
35	182	4.91	0.1407	99.4
36	187	5.05	0.1275	90.1
37	192	5.19	0.0560	39.6
38	198	5.33	0.0295	20.8

Figure 6. Plot of Percent Breakthrough versus Effluent volume, BV for UO_2^{+2} in 1.00 M HNO_3 using 12.5028 g of dry resin in a 50.9 x 1.00 cm column.

Table 9. Data for the breakthrough study in 2.00 M HNO₃ using 12.50 g of dry resin in a 50.9 x 1.00 cm column.

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
1	5.50	0.148	0.0367	22.04
2	11.0	0.297	0.0822	49.4
3	16.5	0.445	0.0897	53.9
4	22.0	0.594	0.0270	16.2
5	27.5	0.742	0.0283	17.0
6	33.0	0.891	0.0365	21.9
7	38.5	1.039	0.0445	26.7
8	44.0	1.19	0.0726	43.6
9	49.5	1.34	0.1263	75.9
10	55.0	1.48	0.1561	93.8
11	60.5	1.63	0.1644	98.7
12	66.0	1.78	0.1643	98.7
13	71.5	1.93	0.1632	98.0
14	77.0	2.08	0.1666	100
15	82.5	2.23	0.1647	98.9
16	88.0	2.38	0.1646	98.9
17	93.5	2.52	0.1644	98.7
18	99.0	2.67	0.1641	98.6
19	105	2.82	0.1643	98.7
20	110	2.97	0.1641	98.6
21	116	3.12	0.1654	99.3
22	121	3.27	0.1658	99.6
23	127	3.41	0.1708	103
24	132	3.56	0.1633	98.1
25	138	3.71	0.1651	99.2
26	143	3.86	0.1615	97.0
27	149	4.01	0.1618	97.2
28	154	4.16	0.1640	98.5
29	160	4.31	0.1640	98.5
30	165	4.45	0.1622	97.4

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
31	171	4.60	*	!*
32	176	4.75	0.1671	100.
33	182	4.99	0.2032	122.
34	187	5.05	0.2677	161
35	193	5.20	0.0145	8.71
36	198	5.34	0.0039	2.34
37	204	5.49	0.0022	1.32
38	209	5.64	0.0021	1.26
39	215	5.79	0.0020	1.20

* The data for fraction 31 was not obtained due to a malfunction with the fraction collector.

Figure 7 Plot of Percent Breakthrough versus Effluent volume, BV for UO_2^{+2} in 2.00 M HNO_3 using 12.50 g of dry resin in a 50.9 x 1.00 cm column.

Table 10. Data for the breakthrough study in 3.00 M HNO₃ using 12.50 g of dry resin in a 50.9 x 1.00 cm column.

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
1	5.30	0.143	0.0182	9.93
2	10.6	0.286	0.0064	3.49
3	15.9	0.429	0.0185	10.1
4	21.2	0.572	0.0197	10.8
5	26.5	0.715	0.0051	2.78
6	31.8	0.858	0.0074	4.04
7	37.1	1.00	0.0025	1.36
8	42.4	1.14	0.0014	0.76
9	47.7	1.29	0.0013	0.71
10	53.0	1.43	0.0068	3.71
11	58.3	1.57	0.0228	12.4
12	63.6	1.72	0.0523	28.5
13	68.9	1.86	0.0878	47.9
14	74.2	2.00	0.1267	69.1
15	79.5	2.15	0.1531	83.5
16	84.8	2.29	0.1607	87.7
17	90.1	2.43	0.1652	90.1
18	95.4	2.58	0.1709	93.2
19	101	2.72	0.177	96.6
20	106	2.86	0.1714	93.5
21	111	3.00	0.1703	92.9
22	117	3.15	0.1723	94.0
23	122	3.29	0.173	94.4
24	127	3.43	0.172	93.8
25	133	3.58	0.1715	93.5
26	138	3.72	0.1732	94.5
27	143	3.86	0.1754	95.7
28	148	4.01	0.1741	95.01
29	154	4.15	0.1738	94.8
30	159	4.29	0.1738	94.8

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
31	164	4.43	0.1761	96.1
32	170	4.58	0.1734	94.6
33	175	4.72	0.1758	95.9
34	180	4.86	0.2507	137
35	186	5.01	0.6934	378
36	191	5.15	0.0425	23.2
37	196	5.29	0.0006	0.327

Figure 8 Plot of Percent Breakthrough versus Effluent volume, BV for UO_2^{+2} in 3.00 M HNO_3 using 12.50 g of dry resin in a 50.9 x 1.00 cm column.

Table 11. Data for the breakthrough study in 4.00 M HNO₃ using 12.50 g of dry resin in a 50.9 x 1.00 cm column.

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
1	5.00	0.135	0.0033	1.49
2	10.0	0.270	0.0037	1.67
3	15.0	0.405	0.0164	7.39
4	20.0	0.540	0.0237	10.7
5	25.0	0.675	0.0073	3.29
6	30.0	0.810	0.0047	2.12
7	35.0	0.945	0.0063	2.84
8	40.0	1.08	0.0065	2.93
9	45.0	1.22	0.0073	3.29
10	50.0	1.35	0.0081	3.65
11	55.0	1.48	0.0110	4.96
12	60.0	1.62	0.0172	7.75
13	65.0	1.75	0.0301	13.56
14	70.0	1.89	0.0475	21.4
15	75.0	2.02	0.0714	32.2
16	80.0	2.16	0.0990	44.6
17	85.0	2.29	0.1255	56.6
18	90.0	2.43	0.1477	66.5
19	95.0	2.56	0.1668	75.2
20	100.	2.70	0.1813	81.7
21	105	2.83	0.1927	86.8
22	110	2.97	0.1997	90.0
23	115	3.10	0.2014	90.8
24	120	3.24	0.2035	91.7
25	125	3.37	0.2049	92.3
26	130	3.51	0.2051	92.4
27	135	3.64	0.2063	92.8
28	140	3.78	0.2072	93.4
29	145	3.91	0.2082	93.8
30	150	4.05	0.2022	91.1

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
31	155	4.18	0.2032	91.6
32	160	4.32	0.2049	92.3
33	165	4.45	0.2464	111
34	170	4.59	0.6804	307
35	175	4.72	1.0449	471
36	180	4.86	0.0396	17.8
37	185	5.00	0.0072	3.25
38	190	5.13	0.0054	2.43
39	195	5.26	0.0052	2.34

Figure 9 Plot of Percent Breakthrough versus Effluent volume, BV for UO_2^{+2} in 4.00 M HNO_3 using 12.50 g of dry resin in a 50.9 x 1.00 cm column.

Table 12. Data for the breakthrough study in 6.00 M HNO₃ using 12.50 g of dry resin in a 50.9 x 1.00 cm column.

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
1	4.00	0.108	0.0186	7.66
2	8.00	0.216	0.0275	11.3
3	12.0	0.324	0.0092	3.79
4	16.0	0.432	0.0128	5.27
5	20.0	0.540	0.0290	11.9
6	24.0	0.648	0.1051	43.3
7	28.0	0.756	0.1039	42.8
8	32.0	0.864	0.0687	28.3
9	36.0	0.974	0.0608	25.1
10	40.0	1.08	0.0585	24.1
11	44.0	1.19	0.0426	17.6
12	48.0	1.30	0.0432	17.8
13	52.0	1.40	0.0260	10.7
14	56.0	1.51	0.0292	12.0
15	60.0	1.62	0.0218	8.98
16	64.0	1.73	0.0250	10.3
17	68.0	1.84	0.0217	8.94
18	72.0	1.94	0.0207	8.53
19	76.0	2.05	0.0197	8.12
20	80.0	2.16	0.0170	7.00
21	84.0	2.27	0.0176	7.25
22	88.0	2.38	0.0162	6.68
23	92.0	2.48	0.0190	7.83
24	96.0	2.59	0.0196	8.08
25	100	2.70	0.0227	9.35
26	104	2.81	0.0338	13.93
27	108	2.92	0.0489	20.1
28	112	3.02	0.0663	27.3
29	116	3.13	0.0920	37.9
30	120	3.24	0.1169	48.2

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
31	124	3.35	0.1444	59.5
32	128	3.46	0.1663	68.5
33	132	3.56	0.1840	75.8
34	136	3.67	0.2017	83.1
35	140	3.78	0.2112	87.0
36	144	3.89	0.2214	91.2
37	148	3.99	0.2195	90.4
38	152	4.10	0.2287	94.2
39	156	4.21	0.2279	93.9
40	160	4.32	0.2299	94.7
41	164	4.43	0.2401	98.9
42	16	4.53	0.2329	96.0
43	172	4.64	0.2328	95.9
44	176	4.75	0.2407	99.2
45	180	4.86	0.2349	96.8
46	184	4.97	0.2363	97.4
47	188	5.07	0.2409	99.3
48	192	5.18	0.2383	98.2
49	196	5.29	0.2378	98.0
50	200	5.40	0.2398	98.8
51	204	5.51	0.2408	99.2
52	208	5.61	0.2440	101
53	212	5.72	0.2402	99.0
54	216	5.83	0.2425	99.9
55	220	5.94	0.2422	99.8
56	224	6.05	0.2409	99.3
57	228	6.15	0.2327	95.9
58	232	6.26	0.2356	97.1
59	236	6.37	0.2378	98.0
60	240	6.48	0.2355	97.0
61	244	6.59	0.2361	97.2
62	248	6.69	0.2353	97.0

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
63	252	6.80	0.2674	110
64	256	6.91	0.9019	371.
65	260	7.02	2.0684	852
66	264	7.13	0.1217	50.1
67	268	7.23	0.1592	65.6
68	272	7.34	0.0359	14.8
69	276	7.45	0.0201	8.28
70	280	7.56	0.0180	7.42
71	284	7.67	0.0167	6.88
72	288	7.77	0.0167	6.88

Figure 10 Plot of Percent Breakthrough versus Effluent volume, BV for UO_2^{+2} in 6.00 M HNO_3 using 12.50 g of dry resin in a 50.9 x 1.00 cm column.

Table 13. Data for the breakthrough study in 7 M HNO₃ using 12.50 g of dry resin in a 50.9 x 1.00 cm column.

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
1	4.80	0.130	0.0340	13.4
2	9.60	0.259	0.0506	19.9
3	14.4	0.389	0.0553	21.8
4	19.2	0.518	0.0450	17.7
5	24.0	0.648	0.0200	7.87
6	28.8	0.777	0.0121	4.76
7	33.6	0.907	0.0128	5.03
8	38.4	1.036	0.0235	9.24
9	43.2	1.166	0.0304	12.0
10	48.0	1.295	0.0314	12.4
11	52.8	1.425	0.0222	8.73
12	57.6	1.555	0.0146	5.74
13	62.4	1.684	0.0107	4.21
14	67.2	1.814	0.0086	3.38
15	72.0	1.943	0.0083	3.26
16	76.8	2.07	0.0088	3.46
17	81.6	2.20	0.0077	3.03
18	86.4	2.33	0.0078	3.07
19	91.2	2.46	0.0095	3.77
20	96.0	2.59	0.0112	4.40
21	101	2.72	0.0114	4.48
22	106	2.85	0.0136	5.35
23	110	2.98	0.0177	6.96
24	115	3.11	0.018	7.08
25	120	3.24	0.0221	8.69
26	125	3.37	0.0253	9.95
27	130	3.50	0.0341	13.4
28	134	3.63	0.0437	17.2
29	139	3.76	0.0496	19.5
30	145	3.89	0.059	23.2

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
31	149	4.02	0.0744	29.3
32	153	4.15	0.0854	33.58
33	158	4.28	0.1011	39.76
34	163	4.41	0.1155	45.4
35	168	4.53	0.1342	52.8
36	173	4.66	0.1492	58.7
37	178	4.79	0.1685	66.3
38	182	4.92	0.1875	73.7
39	187	5.05	0.2049	80.6
40	192	5.18	0.2196	86.4
41	197	5.31	0.226	88.9
42	202	5.44	0.237	93.2
43	206	5.57	0.2449	96.3
44	211	5.70	0.2411	94.8
45	216	5.83	0.2435	95.8
46	221	5.96	0.2469	97.1
47	226	6.09	0.2473	97.2
48	230	6.22	0.2531	99.5
49	235	6.35	0.2515	98.9
50	240	6.48	0.2383	93.7
51	245	6.61	0.2466	96.1
52	245	6.74	0.2468	97.1
53	254	6.89	0.2456	96.6
54	259	7.00	0.2478	97.4
55	264	7.13	0.2488	97.8
56	269	7.26	0.2507	98.6
57	274	7.38	0.3634	143
58	278	7.51	2.2534	886.
59	283	7.64	2.3082	907
60	288	7.77	0.0272	10.7
61	293	7.90	0.0096	3.78
62	298	8.03	0.0096	3.78
63	302	8.16	0.0086	3.38

Figure 11 Plot of Percent Breakthrough versus Effluent volume, BV for UO_2^{+2} in 7 M HNO_3 using 12.50 g of dry resin in a 50.9 x 1.00 cm column.

Table 14. Data for the breakthrough study in 8.00 M HNO₃ using 12.5028 g of dry resin in a 50.9 x 1.00 cm column.

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
1	5.05	0.136	0.0250	9.59
2	10.1	0.273	0.0236	9.05
3	15.2	0.409	0.0206	7.90
4	20.2	0.545	0.0251	9.63
5	25.3	0.681	0.0116	4.45
6	30.3	0.818	0.0094	3.61
7	35.4	0.954	0.0239	9.17
8	40.4	1.09	0.0466	17.9
9	45.5	1.23	0.0496	19.0
10	50.5	1.36	0.0262	10.0
11	55.6	1.50	0.0197	7.56
12	60.6	1.64	0.0141	5.41
13	65.7	1.77	0.0123	4.71
14	70.7	1.91	0.0108	4.14
15	75.8	2.04	0.0082	3.15
16	80.8	2.18	0.0087	3.34
17	85.9	2.32	0.0100	3.84
18	90.9	2.45	0.0072	2.76
19	96.0	2.59	0.0083	3.18
20	101	2.73	0.0076	2.92
21	106	2.862	0.0067	2.57
22	111	3.00	0.0072	2.76
23	116	3.14	0.0064	2.46
24	121	3.27	0.0096	3.68
25	126	3.41	0.0117	4.49
26	131	3.54	0.0131	5.03
27	136.	3.68	0.0244	9.36
28	141	3.82	0.0355	13.6
29	146	3.95	0.0504	19.3
30	1512	4.09	0.0728	27.9

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
31	157	4.23	0.0923	35.4
32	161	4.36	0.1171	44.9
33	167	4.50	0.1407	54.0
34	171	4.63	0.1615	61.9
35	177	4.77	0.1852	71.0
36	181	4.91	0.2017	77.4
37	187	5.04	0.2145	82.3
38	192	5.18	0.2253	86.4
39	197	5.32	0.2315	88.8
40	202	5.45	0.2389	91.6
41	207	5.59	0.2475	94.9
42	212	5.72	0.2460	94.3
43	217	5.86	0.2520	96.7
44	222	6.00	0.2416	92.7
45	227	6.13	0.2458	94.3
46	232	6.27	0.2394	91.8
47	237	6.40	0.2522	96.7
48	242	6.54	0.4444	170
49	247	6.68	3.1006	1190
50	253	6.82	0.8536	327
51	258	6.95	0.0239	9.17
52	263	7.09	0.0191	7.33
53	268	7.22	0.0108	4.14
54	273	7.36	0.0133	5.10
55	278	7.50	0.0128	4.91

Figure 12. Plot of Percent Breakthrough versus Effluent volume, BV for UO_2^{+2} in 8.00 M HNO_3 using 12.5028 g of dry resin in a 50.9 x 1.00 cm column.

Table 15. Data for the breakthrough study in 10.0 M HNO₃ using 12.50 g of dry resin in a 50.9 x 1.00 cm column.

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
1	4.70	0.127	0.0300	12.3
2	9.40	0.254	0.0272	11.2
3	14.1	0.381	0.0598	24.6
4	18.8	0.507	0.0683	28.1
5	23.5	0.634	0.0429	17.7
6	28.2	0.761	0.0207	8.52
7	32.9	0.888	0.0219	9.01
8	37.6	1.015	0.0680	28.0
9	42.3	1.14	0.1016	41.8
10	47.0	1.27	0.0747	30.7
11	51.7	1.40	0.0560	23.0
12	56.4	1.52	0.0466	19.2
13	61.1	1.65	0.0385	15.8
14	65.8	1.78	0.0344	14.2
15	70.5	1.90	0.0257	10.6
16	75.2	2.03	0.033	13.6
17	79.9	2.16	0.0291	12.0
18	84.6	2.28	0.0346	14.2
19	89.3	2.41	0.036	14.8
20	94.0	2.54	0.0400	16.5
21	98.7	2.66	0.0539	22.2
22	103	2.79	0.0733	30.2
23	108	2.92	0.0883	36.3
24	113	3.04	0.1017	41.9
25	118	3.17	0.1132	46.6
26	122	3.30	0.1317	54.2
27	127	3.43	0.1582	65.1
28	132	3.55	0.1654	68.1
29	136.	3.68	0.1821	74.9
30	141	3.80	0.1993	82.0

Fraction #	Volume Through Column, mL	Volume, Bed Volumes	Fraction Absorbance	Percent Breakthrough
31	146	3.93	0.1911	78.6
32	150	4.06	0.2016	83.0
33	155	4.19	0.2086	85.8
34	160	4.31	0.2092	86.1
35	169	4.44	0.2177	89.6
36	169	4.57	0.2212	91.0
37	179	4.69	0.2271	93.5
38	179	4.82	0.1924	79.2
39	183	4.95	0.6984	287
40	188	5.07	1.7592	724
41	198	5.20	0.8525	350
42	197	5.33	0.1743	71.7
43	202	5.45	0.0622	25.6
44	207	5.58	0.0237	9.75
45	212	5.71	0.02817	11.6
46	210	5.84	0.0053	2.18

Figure 13. Plot of Percent Breakthrough versus Effluent volume, BV for UO_2^{+2} in 10.0 M HNO_3 using 12.50 g of dry resin in a 50.9 x 1.00 cm column.

The summary of the 50 % breakthrough volumes for all of the data collected is presented in Table 16. Notice that there is a difference in column lengths and linear flow

Table 16. Summary of the 50 % Breakthrough Volume data.

20.5 cm Column

HNO ₃ , M	2.00	4.00	6.00	8.00	10.0
Column Height, cm	20.5	20.5	22.2	21.5	23.1
Linear Flow Rate, cm/min	0.764	0.700	1.02	0.691	0.837
50 % Breakthrough, BV	1.07	1.59	3.91	4.36	3.94

50.9 cm column

HNO ₃	1 M	2 M	3 M	4 M	6 M	7 M	8 M	10 M
Column height, cm	50.9	50.9	50.9	50.9	49.7	50.9	49.7	50.9
Linear Flow Rate, cm/min	0.946	1.00	0.964	0.909	0.728	0.873	0.919	0.855
50 %	0.94	1.22	1.878	2.21	3.25	4.49	4.45	3.22

rates among the columns of each set of 20 and 50 cm column lengths. The plot of this data is presented as Figure 14.

As expected, the 50 % Breakthrough vs. [HNO₃] plot produces a bell shaped curve with a maximum in the region of 7-8 M. This is the general region for maximum sorption of the uranyl nitrate anionic species as predicted by K_d' determinations and elution studies. For the studies in the 20 cm column, the ordering of the 50 percent breakthrough volumes was 8.00 > 10.0 ≈ 6.00 >> 4.00 > 2.00 M HNO₃. The ordering of the 50 percent breakthrough volumes for the 50 cm column was 7.00 ≈ 8.00 > 10.0 ≈ 6.00 > 4.00 > 2.00 > 1.00 M HNO₃.

As can be seen from the 50 percent breakthrough data, the breakthrough volume is independent of the column height. This is a useful, if unexpected result, It can therefore be implied that an equilibrium state exists in the loading of the UO₂⁺²-HNO₃ solutions.

Figure 14. Plot of 50 Percent Breakthrough, BV versus Nitric acid concentration for UO_2^{+2} with the 20.5 x 1.00 and 50.9 x 1.00 cm columns used in these experiments..

Further experimentation with different column lengths is expected to ascertain the nature of this result. Should this trend continue to hold, it could prove very useful.

In order to quantify the amount of the UO_2^{+2} - HNO_3 species that sorbs onto the resin, the sorbed species was eluted with 18 MΩ water. The absorbance as measured at 420 nm was then ratioed against the feed solution to obtain its percentage. First, it should be noted that water will elute the UO_2^{+2} - HNO_3 species. No uranyl species sorbed at 1 M while a maximum sorption occurred at 8 M. Again this data shows a bell shaped distribution. From this elution, the ordering of the amount sorbed was $8.00 > 7.00 > 6.00 > 10.0 > 4.00 > 3.00 > 2.00 > 1.00$ M HNO_3 . This data is presented in Table 17 and is plotted in Figure 15.

Table 17. The tabulation of the amount of the UO_2^{+2} sorbed on the 50.9 cm columns at various nitric acid concentration as indicated by the amount eluted with water. The amount is reported as percent of the feed solution concentration.

[HNO_3], M	UO_2^{+2} sorbed on column as % of feed concentration
2.00	161
3.00	378
4.00	471
6.00	852
7.00	907
8.00	1190
10.0	724

Figure 15. Plot of the amount of the UO_2^{+2} sorbed on the 50.9 cm columns at various nitric acid concentration as indicated by the amount eluted with water. The amount is plotted as percent of the feed solution concentration.

STATEMENT OF PROPOSED WORK

An Investigation of the Applicability of the New Reillex™-HPQ Anion Exchange Resin System for Technetium/Rhenium and Uranium in the Hanford Waste Tanks

Introduction

The separation and isolation of pertechnetate ion in various waste streams is an important technology that still has not attained the level necessary to be universally applicable.¹ This is very evident with regard to the problems associated with the Hanford Waste Tanks Remediation. The use of ion exchange resins to separate various ions from solutions is well documented.²⁻⁵ In fact, the resin Dowex™-1 has proven to be very useful for the isolation of pertechnetate ion.²

Recently a new ion exchange resin made from polystyrene and vinylpyridine to give a strong base resin with $\text{RC}_5\text{H}_4\text{NCH}_3^+$ as the exchange site has been introduced.⁶ This resin is called Reillex™-HPQ and has been found to be very resistant to radiation damage.⁴ The behavior of plutonium(IV) on the Reillex™-HPQ has been reported to be very favorable for the isolation of the ion.³ However, no general data with other ions were reported.

Because of the very good radiolytic stability, there is a need to explore the utility of this resin for the isolation of TcO_4^- . The characterization of the interaction of this resin with ReO_4^- and TcO_4^- has been investigated and reported.⁶⁻⁹ We have found that the behavior of the resin Reillex™-HPQ with ReO_4^- is very close to that with TcO_4^- . Hence, the characterization of the behavior of a different resin with ReO_4^- should closely approximate that with TcO_4^- . This is the intent of the investigation of the behavior of the resin Reillex™-HP with ReO_4^- .

Requested Research

The Chemistry Department at East Texas State University will investigate the stability of the anion exchange resin Reillex™-HPQ and Reillex™-HP in basic solution and in acid solution. The exact nature of these results can not be anticipated. Hence, the expectations will be nothing more than the results of the experiments. The abilities and judgments of the investigators will be depended upon to pursue the most fruitful lines of development in the research. It should be explicitly noted that the investigators and Kent Abney, Norman Schroeder, and other LANL staff will be in weekly communication. This will ensure that the evolving interest of the Hanford Waste Tank Remediation project will be communicated to the investigators and that the investigations will drift in the direction of programmatic needs.

- 1) The measure of the stability will be indicated by the value of K_d (distribution coefficient for ReO_4^- and hydroxide exchange capacity of the resin. The base concentration will be varied from 0.10 to 2.0 M. The acid concentration will be varied from 5 M to pH 6.0. The temperature will be varied from 25 to 60°C.
- 2) The values of K_d for ReO_4^- between a nitric acid/nitrate ion concentration of 10.0 M and pH 6 and in sodium hydroxide solutions will be determined on Reillex™-HP anion exchange resin.
- 3) The values of K_d for UO_2^{2+} in nitric acid with both high nitrate and carbonate ion concentration will be determined as a function of anion concentration. The breakthrough volumes for uranyl ion in nitric acid on various size anion exchange columns will also be determined.
- 4) The breakthrough volumes for perrhenate in nitric acid with high nitrate ion concentration on various size anion exchange columns will also be determined.

Experimental

The general techniques that will be used in this investigation are ones that have been developed during the past 15 months.⁶⁻⁹ However, there are some new techniques

that will have to be developed. These will be based on our previous experience with ion exchange resins. The necessity to characterize the uranyl species in high nitrate and carbonate media will utilize our 30 years experience in aqueous chemistry and UV-visible spectroscopy.

Results

Expectations

The requested research serves as an outline for the course of the investigation to be taken. Contained in the list of Milestones below is the outline of the anticipated research. As with all research, the anticipated results may not be what is found. We will be prepared to exploit any developments that appear to be in the interest of the Hanford Waste Tank Remediation project. Additionally, any changes in the needs of the project will be addressed to the best of our capabilities.

Deliverables

The expected deliverable is a final report. This report will contain a detailed description of all experimental work performed, the results of those experiments, and the interpretation of those results. Three interim reports, a final report, and a two page summary will be presented. These will constitute the Milestones.

Milestones

There will be three quarterly reports and a final report submitted. The dates for these quarterly reports to be received are December 6, 1993, March 7, and June 6, 1994. The final report will be due by September 23, 1994. A two page summary report will be submitted by September 30, 1994 containing all research and development activities performed for the project. The expected progress is outlined below.

December 7, 1993

The general analytical techniques for determination of the hydroxide ion exchange capacity of the resin will be developed. Results of the measurements of the exchange

capacity and K_d values for ReO_4^- on Reillex™-HPQ as a function of nitric acid and hydroxide concentration, temperature, and one month time will be reported.

Initial results of the measurements of the K_d values for ReO_4^- on Reillex™-HP as a function of nitric acid concentration will be reported.

The general analytical techniques for determination of the uranyl ion in acid and basic solutions will be developed. Initial results of the determination of the K_d values for UO_2^{2+} on Reillex™-HPQ as a function of nitric acid concentration will be reported.

March 7, 1994

Results of the measurements of the exchange capacity and K_d values for ReO_4^- on Reillex™-HPQ as a function of nitric acid and hydroxide concentration, temperature, and four months time will be reported.

Results of the measurements of the K_d values for ReO_4^- on Reillex™-HP as a function of nitric acid concentration will be reported.

Results of the determination of the K_d values for UO_2^{2+} on Reillex™-HPQ as a function of nitric acid and nitrate ion concentration will be reported. The initial results of the measurements in carbonate medium will be reported.

Initial results of the breakthrough volumes for ReO_4^- on Reillex™-HPQ chromatography columns as a function of nitric acid concentration in high nitrate ion concentrations and various column sizes will be reported..

June 7, 1994

Results of the measurements of the exchange capacity and K_d values for ReO_4^- on Reillex™-HPQ as a function of nitric acid and hydroxide concentration, temperature, and seven months time will be reported.

Results of the measurements of the K_d values for ReO_4^- on Reillex™-HP as a function of sodium hydroxide concentration will be reported.

Results of the determination of the K_d values for UO_2^{2+} on Reillex™-HPQ as a

function of carbonate ion concentration will be reported.

Results of the breakthrough volumes for ReO_4^- on Reillex™-HPQ chromatography columns as a function of nitric acid concentration in high nitrate ion concentrations and various column sizes will be reported.

Initial results of the breakthrough volumes for UO_2^{2+} on Reillex™-HPQ chromatography columns as a function of nitric acid concentration and various column sizes will be reported.

September 7, 1994

Results of the measurements of the exchange capacity and K_d values for ReO_4^- on Reillex™-HPQ as a function of nitric acid and hydroxide concentration, temperature, and ten months time will be reported.

Results of the breakthrough volumes for UO_2^{2+} on Reillex™-HPQ chromatography columns as a function of carbonate ion concentration in high nitrate ion concentrations and various column sizes will be reported.

September 30, 1994

A two page summary report containing all research and development activities performed for the contract will be submitted.

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8. "The Sorption Behavior of TcO_4^- on Reillex™-HPQ Anion Exchange Resin from Nitric Acid Solution", Submitted to "Solvent Extr. Ion Exch"., Kenneth R. Ashley, Jason Ball, Anthony Pinkerton, Kent D. Abney, and Norman C. Schroeder.
- 9) "An Investigation of the Applicability of the New Ion Exchange Resin Reillex™-HPQ in ATW Separations" Milestone III June 7, 1993, submitted to LANL for Contract 9-XZ2-7998E-1, Kenneth R. Ashley.