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SUBJECT: Uranyl Sulfate-Dowex 21K Anion Exchange: A Literature Survey, Review of Preliminary Data and Outline of a Proposed Experimental Program

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ABSTRACT

The system Dowex 21K and aqueous uranyl sulfate solutions were studied in the solution composition range:

0 - 0.005 mol/liter uranyl sulfate,
0.15 mol/liter total sulfate,
0.02 mol/liter H_2SO_4 (pH 2).

It is shown that UO_2SO_4 and/or $UO_2(SO_4)_2^{2-}$ are sorbed on the resin to form $R_2UO_2(SO_4)_2$. It is surmized that these same species are also involved at higher uranyl concentrations and $pH \leq 2$. Above pH 2 it is suggested that $U_2O_5SO_4$, $U_2O_5(SO_4)_2^{2-}$, and $R_2U_2O_5SO_4$ species may be involved

An IBM 704 calculation and mathematical treatment of the ion equilibria in solution are presented to predict that in solutions of fixed acid and total uranyl sulfate concentration the UO_2SO_4 specie concentration exhibits a maximum as the total sulfate concentration is varied. Based on these observations a method is outlined for determining the solution uranyl ion specie equilibrium constants from equilibrium resin sorption experiments.

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1.0 INTRODUCTION

In the design of equipment for processing uranyl sulfate leach liquors as well as in the interpretation of laboratory data, it is important to know something about the equilibrium and rate processes involved.

Arden and Wood⁽¹⁾ have studied uranyl sulfate anion exchange equilibria with DeAcidite FF and Amberlite IRA 400 resins among others. In one series of tests a 2.4-g sample of the dry resin chloride was contacted in a column with a solution containing 0.098 mol/liter uranyl sulfate with a small excess of sulfate. In another series of tests they employed solutions at pH 1.7-2.0 containing 0.005-.01 mol/liter uranyl sulfate. These tests led to the conclusion that during the early stages of flow through the column more sulfate was removed from solution than uranium, indicating that the chloride sites had to first be converted to sulfate sites before they would sorb uranium. At the end of a given run, analysis of the combined effluent suggested, however, that the net exchange involved one $\text{UO}_2(\text{SO}_4)_3^{4-}$ ion displacing four chloride ions, or that there were three sulfates sorbed per mol of uranium sorbed. This was true for resin samples with a capacity up to about 3.8 milliequivalents per g of dry chloride resin. For resins with a capacity of from 3.8 to 4.8 meq, up to 4.44 chloride ions were removed per mol of uranium. This latter effect the authors attributed to steric hindrance preventing resin saturation with uranium.

In another series of tests with DeAcidite FF solution containing

0.005 mol/liter uranyl sulfate,

0-0.8 mol/liter total sulfate,

1st set of runs pH = 1.8,

2nd set of runs pH = 2.5.

Arden and Wood found that the equilibrium amount of uranium sorbed decreased steadily with increasing sulfate. The pH 2.5 curve lay above that of pH 1.8; this was explained by Longworth's⁽²⁾ work, which indicated that above pH 2.0 there is a measurable degree of hydrolysis of UO_2^{2+} to give the condensed $\text{U}_2\text{O}_5^{2+}$ ion.

In the latter part of any run at pH 1.7-2.0 the authors observed that 1 mol of uranium was removed from solution per mol of SO_4^{2-} removed. This suggested to them that either $\text{UO}_2(\text{SO}_4)_3^{4-}$ could diffuse into the granule as 2 mols of SO_4^{2-} diffused out (i.e., a pure ion exchange takes place) or that UO_2SO_4 simply diffused into the resin, there to complex with SO_4^{2-} -occupied sites and form $\text{UO}_2(\text{SO}_4)_3^{4-}$. The authors seemed to favor the latter explanation and concluded that under the conditions of their tests the resin must always saturate

with $\text{UO}_2(\text{SO}_4)_3^{4-}$ independently of sulfate concentration.

The authors also ran a series of tests to show that as the HSO_4^- concentration increases in solution (i.e., at $\text{pH} < 1.7$) the equilibrium resin loading with uranium decreases. This they attribute to the fact that uranium does not complex with HSO_4^- in the resin.

At the end of all of the foregoing runs the columns were centrifuged to remove the interstitial fluid from the resin. Any remaining adherent fluid was corrected for by the method of Kraus and Moore.⁽³⁾

In a subsequent article Arden and Rowley⁽⁴⁾ described a stock solution of

1.325 mol/liter uranyl sulfate,
1.624 mol/liter total sulfate,
 $\text{pH} = 1.71$.

with various portions diluted to as low as 0.0066 mol/liter of uranium. These solutions were used for various column-type runs. A solution of

0.9 mol/liter NaCl,
0.1 mol/liter HCl.

was used for elution purposes. They found that at the higher solution concentrations the amount of solute dissolved in the water of hydration of the resin was enough to make their resin loadings too high compared with that which could be sorbed on the resin matrix proper. Consequently the authors not only made the Kraus-Moore correction amounting to 0.03 ml of liquor per gram of dry chloride resin but they also measured in separate experiments the water of hydration in the resin and corrected for the solute contained therein, assuming that the solute concentration in this water of hydration was the same as that in the bulk fluid which had surrounded the resin particle. The water of hydration ranged from 0.58 g/g of dry Cl resin at 0.33 mol/liter to 0.56 g/g at 1.2 mol/liter. The specific gravities of the bulk solution varied linearly with uranyl sulfate from 1.00 at zero to 1.414 at 1.21 mol/liter.

The corrected results of Arden and Rowley along with the earlier results suggested that in dilute solutions (0.005 mol/liter of uranyl sulfate and $\text{pH} < 2$) the only ions absorbed to a measureable extent are $\text{UO}_2(\text{SO}_4)_3^{4-}$ and HSO_4^- , the adsorption of the latter decreasing to zero as the pH rises to 2.0. Increase in pH at the same concentration causes adsorption of $\text{U}_2\text{O}_5(\text{SO}_4)_3^{4-}$. Increase in concentration at low pH favors the adsorption of $\text{UO}_2(\text{SO}_4)_2^{2-}$, which displaces all other ions at concentrations greater than 0.3 mol/liter in solution. The authors anticipated that a combination of high pH and high concentration would favor adsorption of $\text{U}_2\text{O}_5(\text{SO}_4)_2^{2-}$, but these conditions cannot be

achieved experimentally.

O'Connor⁽⁵⁾ has also investigated uranyl ion exchange with Amberlite IRA 400. He, too, used the column technique but he introduced an automatic correction into his results by washing the column with anhydrous MeOH prior to eluting with 1N KNO₃ or chloride so that he could analyze the eluate for uranium, hydrogen ion (potentiometric titration with standard base after precipitating the uranium), and total sulfate.

In O'Connor's first series of tests he determined K_a for the reaction

where

$$K_a = \frac{C_{SO_4^{2-}} \cdot C_{RHSO_4}^2}{C_{R_2SO_4} C_{HSO_4^-}^2}. \quad (2)$$

He found that K_a varied from 2 to 42. His efforts to correct for solution activities did not materially improve the situation and he attributed this to the need for also correcting for resin phase activities. In his original calculations of K_a he used

$$0.0118 = \frac{C_H^+ C_{SO_4^{2-}}}{C_{HSO_4^-}}, \quad (3)$$

where the chemical reaction is

The second series of tests included uranyl sulfate. The standard "leach liquors" contain approximately

0.003 mol/liter uranyl sulfate,
0.35 mol/liter total sulfate,
pH = 1 to 2.

and so he made two runs in this range. He measured the H^+ ion concentration in the eluate and consequently the HSO_4^- ion in the resin. Assuming that there were $UO_2(SO_4)_2^{2-}$, $UO_2(SO_4)_3^{4-}$, SO_4^{2-} along with the HSO_4^- ion on the resin, he calculated the percentage of sites occupied by each.

Another run was made at 0.001 mol/liter uranyl sulfate and 5 others ranged from 0.005 mol/liter to 0.1 mol/liter uranyl sulfate. The percentage of resin sites distributed among the four anions was also calculated.

In O'Connor's work there appears to be some question as to whether use of anhydrous MeOH with wet resin really prevents hydrolysis of HSO_4^- and uranyl complexes. Also in view of Bae's work⁽⁶⁾ the activity corrections in solution may not be adequate, as will be discussed later.

In the work of Arden et al. the HSO_4^- concentration on the resin was not measured to serve as a check on some of the theories proposed.

An objection to all of the previous work is that with the exception of three runs by O'Connor there is no extensive work in really dilute solutions, i.e., uranyl sulfate < 0.005 mol/liter.

The foregoing are among the principal reasons for undertaking the investigations leading to the results to be reported herein.

2.0 THE SULFATE-BISULFATE EQUILIBRIUM WITH AMBERLITE IRA 400 RESIN

The chief difference between Dowex 21K (the subject of our subsequent investigations) and IRA 400 resins is that the capacity of the former is claimed to be $4.5 \pm .2$ milliequivalents per gram dry chloride resin whereas the latter is 3.71 to 3.889. The Dowex 21K is somewhat more stable. Both resins are apparently cross-linked polystyrene, containing quaternary groups of the benzyl trimethyl ammonium type.

For lack of any better information it was decided to make the best of the bisulfate-sulfate resin data obtained by O'Connor. In doing this it was recognized that the value of 0.0118 in equation 3 varies with ionic strength, μ , of the solution as discussed by Baes.⁽⁶⁾ Equation 3 may be written

$$K_b = \frac{C_H^+ C_{\text{SO}_4^-}}{C_{\text{HSO}_4^-}}, \quad (5)$$

and then the data of Baes may be plotted as shown in Fig. 1a so as to show the way in which K_b varies with ionic strength. Actually the curve labeled 1 was given by Baes. Additional data in his paper permitted plotting the rest of the curves. Since Fig. 1a involves trial and error in its use, a number of such calculations were made using Fig. 1a and the results were plotted in the form of working charts in Figs. 1b and 1c. Thus, in subsequent work the trial

Fig. 1A. The Effect of Ionic Strength on the Bisulfate-Sulfate Equilibrium Constant.

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Fig. 1b. Working Version of Fig. 1a.

Fig 1c Working Version of Fig 1a

and error effort was materially reduced through the use of the working charts.

Arthurs and Seiler⁽⁷⁾ have also fitted a modified Debye-Huckel Limiting Law equation to Fig. 1a to show that

$$\log \frac{K_b(\mu = 0)}{K_b} = -A \frac{\mu^{1/2}}{1 + B\mu^{1/2}}, \quad (6)$$

where

$$A = -(1.93 + 0.26 S),$$

$$B = +(0.74 - 0.14 S),$$

$$S = \frac{\text{moles sulfuric acid}}{\text{moles total sulfate}}.$$

Above S equal to 0.5 to 0.6 the expressions for A and B are approximate. At

$$S = 1$$

we have

$$A = 0.509 (-4) = -2.036 \text{ (its theoretical value),}$$

$$B = 0.4.$$

Figures 1a through 1c (or equation 6), when used to correct O'Connor's work by substituting the results in equation 2, give a K_a for that equation ranging between 33 and 50, a much more satisfactory consistency. The implications are that resin activity may be somewhat less important than he thought. From the new values of K_a an average value

$$K_a = 43.2$$

was computed and used in deriving the plots in Fig. 2.

The numbered points plotted in Fig. 2 are those resulting from the individual recalculations of O'Connor's data. These points are included on the plot to show the adequacy of an average value of the equilibrium constant in calculating the curves. The total equivalents of anion are: Point 1, 0.532; point 2, 0.1404; point 3, 0.0387; point 4, 0.0728; point 5, 0.01575; point 6, 1.329; point 7, 0.2189; point 8, 0.03907; and point 9, 0.1727.

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Fig. 2. Resin - Solution Equilibrium H_2SO_4 - $\text{SO}_4^{=}$ on IRA-400.

The ionic strength of a solution is defined as

$$\mu = 1/2 \sum C_i Z_i^2 \quad (8)$$

where

C_i = the molal concentration of the i th ion in solution,

Z_i = the valence of the i th ion in solution.

If one knows for example the total acid and total sulfate in solution, determination of the ionic composition of the solution requires a trial and error calculation and this involves Figs. 1a through 1c or equation 6. When the ionic composition is determined, Fig. 2 may be consulted to determine the resin equilibrium ion exchange.

3.0 IONIC COMPOSITION OF AQUEOUS URANYL SULFATE SOLUTIONS

Calculating the ionic composition of an aqueous uranyl sulfate solution from a gross analysis must take into account the uranyl ion species in addition to the sulfate-bisulfate previously discussed.

Ahrland (8) has investigated uranyl sulfate solutions both potentiometrically and spectrophotometrically. He found that uranyl sulfate not only associated according to the equation

where

$$K_1 = \frac{C_{UO_2SO_4}}{C_{UO_2^{++}} C_{SO_4^{=2-}}}, \quad (10)$$

but that it also complexed according to the equation

where

$$K_2 = \frac{C_{UO_2(SO_4)_2^{2-}}}{C_{UO_2^{++}} C_{SO_4^{2-}}^2}, \quad (12)$$

and

where

$$K_3 = \frac{C_{UO_2(SO_4)_3^{4-}}}{C_{UO_2^{++}} C_{SO_4^{2-}}^3}. \quad (14)$$

Here again we would anticipate that the use of molar concentrations in equations 10, 12, and 14 would lead to inconsistencies in the K values due to activity effects. Allen⁽⁹⁾ has investigated this matter and suggested writing

$$K_{a1} = K_1 G_1, \quad (15)$$

$$K_{a2} = K_2 G_2, \quad (16)$$

$$K_{a3} = K_3 G_3, \quad (17)$$

where the G_k are the appropriate activity coefficient ratios. It is customary to assume that such ratios remain constant at a given ionic strength, independent of medium effects. In the aqueous systems at hand, however, both ionic strength and the media change markedly, the latter change being from strong sulfuric acid to a predominantly sodium sulfate solution. This might have some effect on the G_k , but in the absence of quantitative theoretical relations for this estimation they will be ignored.

Ionic strength corrections on the other hand, can be estimated on the basis of the Debye-Huckel Limiting Law,

$$\log K_{ak} = \log K_k - 0.509 \Delta(Z_1^2) \frac{\sqrt{\mu}}{1 + p \sqrt{\mu}} \quad (18)$$

where

K_{ak} = the constant at zero ionic strength, μ , where the activities are assumed to be proportional to concentrations,

K_k = the concentration quotient at a given finite ionic strength,

p = a parameter.

At high ionic strength the Debye-Huckel Limiting Law may be expected to break down. The value of p used by Allen was 2.3 so that

$$\log G_k = -0.509 \Delta(Z_i^2)_k \frac{\sqrt{\mu}}{1 + 2.3 \sqrt{\mu}} . \quad (19)$$

For the monosulfate reaction

$$\Delta(Z_i^2)_1 = 0^2 - 2^2 - 2^2 = -8 , \quad (20)$$

and for the disulfate

$$\Delta(Z_i^2)_2 = 2^2 - (2 \cdot 2^2) - 2^2 = -8 , \quad (21)$$

and for the trisulfate

$$\Delta(Z_i^2)_3 = 4^2 - (3 \cdot 2^2) - 2^2 = 16 - 12 - 4 = 0 , \quad (22)$$

therefore

$$\log G_1 = \log G_2 = 0.509(8) \frac{\sqrt{\mu}}{1 + 2.3 \sqrt{\mu}} , \quad (23)$$

and

$$G_3 = 1. \quad (24)$$

The results of Allen and Ahrland are summarized in Table 1.

Table 1 Some Equilibrium Constants for the Complexes of Uranyl Sulfate in Aqueous Solution

	Allen	Ahrland		Values Used for Calculations on the IBM 704	
		Potentiometric	Spectrophotometric	Allen	Ahrland
	A. At $\mu^{(a)} = 0$ where $G^{(b)} = 1$				
K_{a1}	580(300-2300)	860 ± 170	960 ± 100	580	900
K_{a2}	3450(1900-13,000)	6000 ± 2600	7700 ± 860	3450	7000
K_3	(0 - 125)	2500 ± 1000	$K_3 \ll 2500$	100	2500
K_2/K_1	6.0 ± 1.0	$7(3.3 - 12.5)$	$8(6.5 - 10)$		
	B. At $\mu = 1$ where $G = 17.1$				
K_1	34(17-135)	50 ± 10	56 ± 6		
K_2	200(100-760)	350 ± 150	450 ± 50		
K_3	(0-125)	2500 ± 1000	$K_3 \ll 2500$		
K_2/K_3	6.0 ± 1.0	$7(3.3 - 12.5)$	$8(6.5 - 10)$		

(a) μ (ionic strength) = $1/2 \sum C_i Z_i^2$
 where C = molal concentration of the ith ion in solution,
 and Z_i = valence of the ith ion in solution.

(b) G = activity coefficient ratio.

Note: The numbers in parenthesis are maximum and minimum values of the range of deviation within which calculated values from similar sets of data could be expected to fall nine times out of ten.

O'Connor used Ahrland's potentiometric values at $\mu = 1$ but made no further correction for the changes in ionic strength which actually occurred in his work.

Stoichiometrically we may write for any uranyl sulfate solution

$$C_{UT} = C_{UO_2^{2+}} + C_{UO_2SO_4} + C_{UO_2(SO_4)_2^{2-}} + C_{UO_2(SO_4)_3^{4-}}, \quad (25)$$

$$C_{AT} = 1/2 [C_{H^+} + C_{HSO_4^-}], \quad (26)$$

$$C_{ST} = C_{HSO_4^-} + C_{SO_4^{2-}} + C_{UO_2SO_4} + 2C_{UO_2(SO_4)_2^{2-}} + 3C_{UO_2(SO_4)_3^{4-}}. \quad (27)$$

where

C_{UT} = total molar concentration of uranium in solution,

C_{AT} = total molar sulfuric acid in solution,

C_{ST} = total molar sulfate in solution,

$C_{(ion)}$ = molar concentration in solution of ion (or molecule in question).

If there is no uranium in solution, equations 25 to 27 reduce to those for the simple sulfate-bisulfate system, namely:

$$C_{UT} = 0, \quad (28)$$

$$C_{AT} = 1/2 [C_{H^+} + C_{HSO_4^-}], \quad (29)$$

$$C_{ST} = C_{HSO_4^-} + C_{SO_4^{2-}}. \quad (30)$$

In general the computation of the ionic composition of a uranyl sulfate solution involves simultaneous solution of equations 5, 6, 8, 10, 12, 14, 15-17, 23, 24, and 25-27. This has been done by Arthur et al.⁽⁵⁾ for a wide variety of total uranium, total acid, and total sulfate conditions. An IBM 704 computer was used for this purpose. Two sets of computations were made.

In the first set, Allen's constants were used as indicated in the IBM 704 column of Table 1. The second set was based on Ahrlund's constants similarly shown in Table 1. The results are too voluminous to be included as such in this report and may therefore at some later date become the subject of a separate report. However, an abridged version of some of the results are presented in graphical form in Figs. 3-6.

A sample cross plot is also shown in Fig. 7.

4.0 INVESTIGATION OF EQUILIBRIUM BETWEEN DOWEX 21K RESIN AND URANYL SULFATE AQUEOUS SOLUTIONS

Dowex 21K resin is an improved version of the strong-base anion exchangers used in connection with leach liquor processing among other applications. For this reason it was selected as the subject of this investigation.

In work by W. F. Wagner⁽¹⁰⁾ samples of the dry resin chloride were weighed and contacted with a beaker of solution of prescribed composition. Multiple contacting was also used. Periodically the resin was filtered and contacted with more of the original solution until equilibrium was attained. The contacting in either case lasted 3 days although 2 days gave the same results. At this point the resin sample was given a final filtration and blotted between two blotting papers to remove any adhering liquor.

The dry resin sample was leached by repeated contacting with 5 M chloride solution at pH 0.5. The leach liquor was analyzed to determine total adsorbed uranium and total sulfate. The changes in uranium and total sulfate solution concentrations during contacting were also measured as a double check on the batch contactings only.

The original uranyl solutions used by Wagner in the investigation contained

0.0005 - 0.005 mol/liter uranyl sulfate,
0.02 mol/liter H_2SO_4 (pH 2),
0.15 mol/liter total sulfate,

except for two runs at

0.005 mol/liter uranyl sulfate,
0.0136 mol/liter H_2SO_4 (pH 2),
0.052 mol/liter total sulfate.

Fig. 3. Composition of $\text{UO}_2\text{SO}_4 - \text{H}_2\text{SO}_4 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$ Solutions (Allen Constants).

Fig. 4. Composition of UO_2SO_4 - H_2SO_4 - Na_2SO_4 - H_2O Solutions (Allen Constants).

Fig. 5 Composition of $\text{UO}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ Solutions (Ahrland Constants)

Fig 6 Composition of $\text{UO}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ Solutions (Ahrland Constants)

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Fig. 7. Composition of Aqueous Uranyl Sulfate Solutions.

This range of concentrations was chosen because leach liquors are in this range and little published information is available over this region. Also it is not necessary to correct for the small amounts of solute contained in the water of hydration of the resin. At pH 2 the UO_2^{++} ion is not appreciably hydrolyzed to the $U_2O_5^{+}$ ion.

Figures 3-6 show that under the conditions of the experiment the equivalent fraction of sulfate (compared to sulfate-bisulfate) in solution is about 0.9. From Fig. 2 for IRA 400 it might be surmised that for Dowex 21K resin the fraction of sulfate form resin is about 0.83. This derives from the fact that equation 2 may be written

$$K_a = \frac{C_{RC}}{C_s} \frac{x(1-y)^2}{y(1-x)^2},$$

where

C_{RC} = resin capacity, meq/g dry Cl resin,

C_s = solution total concentration, equivalents/liter,

x = equivalent fraction of $SO_4^{=}$ ion solution,

y = equivalent fraction of SO_4 ion on resin matrix.

In Wagner's work

$$C_{ST} = 0.1566$$

Now if we use subscript e for equivalent concentrations, then

$$x = \frac{C_{eSO_4^{=}}}{C_{eSO_4^{=}} + C_{eHSO_4^{-}}} = \frac{2C_{SO_4^{=}}}{2C_{SO_4^{=}} + C_{HSO_4^{-}}},$$

and

$$C_{ST} = C_{SO_4^{=}} + C_{HSO_4^{-}}.$$

Solving these two equations simultaneously for $C_{SO_4^{=}}$ and $C_{HSO_4^{-}}$ we find

$$C_{SO_4^{=}} = C_{ST} \frac{x}{2-x}; \quad C_{HSO_4^{-}} = 2C_{ST} \frac{1-x}{2-x}$$

Hence

$$C_s = 2C_{SO_4} + C_{HSO_4} = \frac{2C_{ST}}{2-x} = \frac{2 \cdot 0.1566}{1.1} = 0.284$$

It is this value of C_s that is used in the equation for K_a (or in Fig. 2) with $x = .9$ to obtain y equal to 0.83.

Actually y may be computed directly from the data. This can be shown by defining (for example for the case of the monosulfate reaction to be discussed later)

$C_{R_2UO_2(SO_4)_2}$ = total meq of U per g dry Cl resin,

C_{RST} = total meq sulfate per g dry Cl resin,

C_{RC} = resin capacity, meq per g dry Cl resin.

Then

$$y = \frac{2C_{R_2SO_4}}{C_{RC}} \quad (31)$$

and

$$C_{RST} = 2[C_{R_2SO_4} + C_{RHSO_4} + C_{R_2UO_2(SO_4)_2}] \quad (32)$$

and

$$C_{RC} = 2C_{R_2SO_4} + C_{RHSO_4} \quad (33)$$

where

$C_{R_2SO_4}$ = millimols sulfate ion/g dry Cl resin

C_{RHSO_4} = millimols bisulfate ion/g dry Cl resin

Solving equations 31-33 simultaneously we find that

$$y = 2 - \frac{C_{RST} - 2C_{R_2UO_2(SO_4)_2}}{C_{RC}} \quad (34)$$

These computed values of y along with the rest of Wagner's data are shown in Table 2. The results in the "eluate" column were obtained from the analysis of the eluate from the eluted resin. The results in the "difference" column are based on the difference in concentration of the initial and final batch contacting solution.

Except for points 10-13 which were for duplicate runs, it is obvious that the computed values of y do not agree well with what we would anticipate from Fig. 2. The reason seems to be due to early difficulties in obtaining reliable sulfate analysis in the presence of uranium. In some of these cases more sulfate was found than could possibly be held by the resin.

Two sets of C_{RC} values were used in the y calculations because the manufacturer claims $4.5 \pm .2$ whereas in the laboratory we found the value of 4.0 to be more appropriate. These two C_{RC} values lead to y for runs 10-13 which seem to straddle the value of 0.83 determined based on Figs. 3-6.

The first and most obvious place to look for an explanation of the uranium sorption results is in the field of ion exchange chemistry and to do this each possibility will be examined in detail. If the primary reaction between resin and solution is

then the rate equation for this reaction is

$$\frac{\partial C_{R_2UO_2(SO_4)_2}}{\partial t} = k_1 C_{UO_2SO_4} [C_{R_2UO_2(SO_4)_2 Sat} - C_{R_2UO_2(SO_4)_2}] - k_2 C_{R_2UO_2(SO_4)_2}. \quad (36)$$

At equilibrium

$$\frac{k_1}{k_2} = K_C = \frac{C_{R_2UO_2(SO_4)_2}}{[C_{R_2UO_2(SO_4)_2 Sat} - C_{R_2UO_2(SO_4)_2}] C_{UO_2SO_4}} = \frac{C_{R_2UO_2(SO_4)_2}}{C_{R_2SO_4} C_{UO_2SO_4}}. \quad (37)$$

Equation 37 may be rearranged to read

$$C_{R_2UO_2(SO_4)_2} = C_{R_2UO_2(SO_4)_2 Sat} \frac{C_{UO_2SO_4}}{\frac{1}{K_C} + C_{UO_2SO_4}}, \quad (38)$$

Table 2 Equilibrium Data for the System Dowex 21K Resin - Aqueous Uranyl Sulfate Solution at Room Temperature

Run No.		$\frac{C_{UO_2SO_4}}{C_{R_2UO_2(SO_4)_2}} \cdot 10^3$				$C_{UO_2SO_4} \cdot 10^3$		$Y = 2 - \frac{C_{RST} - 2C_{R_2UO_2(SO_4)_2}}{C_{RC}}$	
Batch	Multiple Batch	Eluate		By Difference		Allen	Ahrland	$C_{RC} = 4.5$	$C_{RC} = 4.0$
		Allen	Ahrland	Allen	Ahrland				
1		1.88	1.52	1.95	1.58	1.66	1.35	1.188	1.09
2		2.19	1.77	2.13	1.73	1.85	1.50	1.122	1.012
3		2.25	1.83	2.20	1.79	1.93	1.57	1.123	1.013
4		2.27	1.85	2.24	1.82	1.99	1.62	1.311	1.225
5		2.63	2.14	2.50	2.03	2.06	1.68	0.931	0.797
6		1.84	1.49	1.97	1.59	1.54	1.25	1.041	0.92
7		1.44	1.15	1.57	1.26	1.08	0.87	0.951	0.82
8		1.15	0.908	1.28	1.01	0.785	0.62	1.07	0.95
9		0.918	0.725	1.04	0.821	0.570	0.45	1.51	1.45
	10	2.44	1.99			2.44	1.99	0.84	0.70
	11	2.56	2.09			2.44	1.99	0.89	0.75
	12	2.94	2.45			3.31	2.76	0.82	0.672
	13	3.11	2.59			3.31	2.76	0.80	0.65
14				0.946	0.732	0.323	0.25		
15				0.917	0.679	0.189	0.14		

or

$$C_{R_2UO_2(SO_4)_2} = C_{R_2UO_2(SO_4)_2}^{Sat} \frac{1}{\frac{1}{K_c C_{UO_2SO_4}} + 1} \quad (39)$$

Equation 37 may also be rearranged to read

$$\frac{C_{UO_2SO_4}}{C_{R_2UO_2(SO_4)_2}} = \frac{1}{C_{R_2UO_2(SO_4)_2}^{Sat}} \left[\frac{1}{K_c} + C_{UO_2SO_4} \right], \quad (40)$$

which suggests that a plot of original data in the form

$$\frac{C_{UO_2SO_4}}{C_{R_2UO_2(SO_4)_2}} \text{ vs } C_{UO_2SO_4} \quad (41)$$

should yield a straight line plot of slope

$$\frac{1}{C_{R_2UO_2(SO_4)_2}^{Sat}}$$

and intercept

$$\frac{1}{K_c C_{R_2UO_2(SO_4)_2}^{Sat}}.$$

Next, if the primary reaction is

then the rate equation is

$$\frac{\partial C_{R_2UO_2(SO_4)_2}}{\partial t} = k_3 [C_{R_2UO_2(SO_4)_2}^{Sat} - C_{R_2UO_2(SO_4)_2}] C_{UO_2(SO_4)_2}^{2-} - k_4 C_{SO_4}^{=} \cdot C_{R_2UO_2(SO_4)_2} \quad (43)$$

At equilibrium

$$\frac{k_3}{k_4} = K_d = \frac{C_{SO_4}^{=} C_{R_2UO_2(SO_4)_2}^{Sat}}{[C_{R_2UO_2(SO_4)_2}^{Sat} - C_{R_2UO_2(SO_4)_2}] C_{UO_2(SO_4)_2}^{2-}} = \frac{C_{SO_4}^{=} C_{R_2UO_2(SO_4)_2}}{C_{R_2SO_4} C_{UO_2(SO_4)_2}^{2-}} \quad (44)$$

Equation 44 may be rearranged to read

$$C_{R_2UO_2(SO_4)_2} = C_{R_2UO_2(SO_4)_2}^{Sat} \frac{C_{UO_2(SO_4)_2}^{2-}}{\frac{C_{SO_4}^{=}}{K_d} + C_{UO_2(SO_4)_2}^{2-}} \quad (45)$$

or

$$C_{R_2UO_2(SO_4)_2} = C_{R_2UO_2(SO_4)_2}^{Sat} \frac{1}{\frac{C_{SO_4}^{=}}{K_d C_{UO_2(SO_4)_2}^{2-}} + 1} \quad (46)$$

Equation 44 may also be rearranged to read

$$\frac{C_{UO_2(SO_4)_2}^{2-}}{C_{R_2UO_2(SO_4)_2}} = \frac{1}{C_{R_2UO_2(SO_4)_2}^{Sat}} \left[\frac{C_{SO_4}^{=}}{K_d} + C_{UO_2(SO_4)_2}^{2-} \right], \quad (47)$$

which suggests at constant $C_{SO_4}^{=}$ that a plot of original data in the form

$$\frac{C_{UO_2(SO_4)_2}^{2-}}{C_{R_2UO_2(SO_4)_2}} \quad \text{vs} \quad C_{UO_2(SO_4)_2}^{2-}$$

should yield a straight line plot of slope

$$\frac{1}{C_{R_2UO_2(SO_4)_2Sat}}$$

and intercept

$$\frac{C_{SO_4^{2-}}}{K_d C_{R_2UO_2(SO_4)_2Sat}} .$$

Finally, if the primary reaction is

then the rate equation is

$$\frac{\partial C_{R_4UO_2(SO_4)_3}}{\partial t} = 4k_5 C_{UO_2(SO_4)_3^{4-}} [C_{R_4UO_2(SO_4)_3Sat} - C_{R_4UO_2(SO_4)_3}]^2 - k_6 C_{SO_4^{2-}}^2 \cdot C_{R_4UO_2(SO_4)_3} \quad (49)$$

At equilibrium

$$\frac{k_5}{k_6} = K_e = \frac{C_{SO_4^{2-}}^2 \cdot C_{R_4UO_2(SO_4)_3}}{4[C_{R_4UO_2(SO_4)_3Sat} - C_{R_4UO_2(SO_4)_3}]^2 C_{UO_2(SO_4)_3^{4-}}} = \frac{C_{SO_4^{2-}}^2 \cdot C_{R_4UO_2(SO_4)_3}}{C_{R_2SO_4}^2 C_{UO_2(SO_4)_3^{4-}}} \quad (50)$$

The square terms in equation 50 distinguish it from the equations for the other primary reactions. For purposes of plotting, however, equation 50 may be rearranged to read

$$\left(\frac{C_{R_4UO_2(SO_4)_3}}{C_{UO_2(SO_4)_3^{4-}}} \right)^{1/2} = \frac{2K_e^{1/2}}{C_{SO_4^{2-}}} [C_{R_4UO_2(SO_4)_3Sat} - C_{R_4UO_2(SO_4)_3}] \quad (51)$$

This form suggests plotting

$$\left(\frac{C_{R_4UO_2(SO_4)_3}}{C_{UO_2(SO_4)_3}} \right)^{1/2} \text{ vs } C_{R_4UO_2(SO_4)_3} ,$$

where the slope is

$$\frac{-2K_e^{1/2}}{C_{SO_4}^=}$$

and the intercept is

$$\frac{2K_e^{1/2} C_{R_4UO_2(SO_4)_3}^{Sat}}{C_{SO_4}^=} .$$

A direct comparison of plots for the three primary reactions is obvious if for equation 37 one plots

$$\frac{C_{R_2UO_2(SO_4)_2}}{C_{UO_2SO_4}} \text{ vs } C_{R_2UO_2(SO_4)_2} ,$$

and for equation 44 one plots

$$\frac{C_{R_2UO_2(SO_4)_2}}{C_{UO_2(SO_4)_2}^{2-}} \text{ vs } C_{R_2UO_2(SO_4)_2} .$$

These two plots would also lead to linear plots for appropriate data. This is mentioned here not because it is conventional to plot this way but simply to show that there exists a definite distinction between data that would fulfill the plotting requirements for the first two primary reactions as compared to that that would fulfill the plotting requirements for the third primary reaction.

In Fig. 8 the data of Table 2 using Allen's constants are plotted in accord with equation 40. The reasons for this preference are twofold. First, pre-

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Fig. 8. Test of Data for the Reaction $R_2SO_4 + UO_2SO_4 = R_2UO_2(SO_4)_2$.

liminary plots showed that the primary reaction could not involve the $\text{UO}_2(\text{SO}_4)_3^{4-}$ ion. Second, equations 40 and 47 are actually identical because of the reaction

for which

$$K_4 = \frac{K_2}{K_1} = \frac{C_{\text{UO}_2(\text{SO}_4)_2^{2-}}}{C_{\text{UO}_2\text{SO}_4} C_{\text{SO}_4^{2-}}},$$

where K_4 is a constant because (ΔZ_1^2) is zero for the reaction. The equation for K_4 may be substituted into equation 47 to show that by comparison with equation 40

$$K_c = \frac{K_2}{K_1} K_d.$$

Thus, the monosulfate and disulfate primary reactions are indistinguishable by this means. As a matter of convenience in the remainder of the report, the data will be treated as though the monosulfate reaction were the primary one, keeping in mind of course that it could be either.

Two different interpretations of the data are shown in Fig. 8. The first is a least squares line of the type

$$Y = a + bX \quad (52)$$

where

$$a = \frac{\sum Y \sum (X^2) - \sum X \sum (XY)}{n \sum (X^2) - (\sum X)^2} \quad (53)$$

$$b = \frac{n \sum (XY) - \sum X \sum Y}{n \sum (X^2) - (\sum X)^2} \quad (54)$$

n = number of datum points.

The least squares line is based on all the datum points with no regard for weighting datum points according to reliability. In this case

$$a = 0.69899 \cdot 10^{-3}, \quad (55)$$

$$b = 0.75919, \quad (56)$$

and from equation 40

$$K_c = 1086.12. \quad (57)$$

Also in view of the fact that

$$y = \frac{2C_{R_2UO_2(SO_4)_2Sat}}{C_{RC}}, \quad (58)$$

we find

$$y = 0.58 \text{ if } C_{RC} = 4.5, \quad (59)$$

$$y = 0.66 \text{ if } C_{RC} = 4.0, \quad (60)$$

$$y = 0.83 \text{ if } C_{RC} = 3.17. \quad (61)$$

The second interpretation involves a straight line drawn to give weight to points 10-13 in particular because those were points for which 10 and 11 were duplicates and 12 and 13 were duplicates. Thus greater confidence could be placed in these points. For this case

$$a = 1.09 \cdot 10^{-3}, \quad (62)$$

$$b = 0.58333. \quad (63)$$

Here

$$K_c = 535.16, \quad (64)$$

and

$$y = 0.761 \quad \text{if } C_{RC} = 4.5, \quad (65)$$

$$y = 0.86 \quad \text{if } C_{RC} = 4.0, \quad (66)$$

$$y = 0.83 \quad \text{if } C_{RC} = 4.13. \quad (67)$$

It is quite evident that the second interpretation and particularly equation 67 gives the better agreement with what is known about the system, i.e. $y = 0.83$ agrees with the value surmised earlier in the report and $C_{RC} = 4.13$ is more nearly consistent with the value actually measured in a separate experiment on our lot of resin than it is with the manufacturer's claim of 4.5 ± 0.2 which was probably based on an average of several lots.

Thus, it is concluded that equations 36-40 are suitable for representing the sorption equilibrium.

Use of Ahrland's constants in Fig. 8 change the intercept value but not the conclusion. It is not, however, necessarily concluded that the sorption is of a chemical nature as implied by equation 35 because equations 36-40 are also derivable from the Langmuir adsorption theory.

The nature of the binding between the UO_2SO_4 molecule at the sulfate-occupied sites of the resin is a subject for future study. Such studies might involve the temperature dependence of K_c to determine the value of the activation energy E involved in the Arrhenius equation,

$$K_c = A e^{-E/RT},$$

if the reaction is of a chemical nature.

Although equilibrium of more concentrated solutions was not studied, an important implication of these conclusions is that at or below pH 2 the $R_2UO_2(SO_4)_2$ is always formed in the resin. This is in contrast to the conclusion of Arden et al. that $R_2UO_2(SO_4)_2$ forms only from the more concentrated solutions. For $pH > 2$ we suspect one would find a similar conclusion for $R_2U_2O_5(SO_4)_2$.

From Figs. 3-6 we find that

$$x = 0.9$$

throughout Wagner's work. Had this not been the case and y changed from one run to the next, then in fitting the equation which is

$$y \frac{C_{UO_2SO_4}}{C_{R_2UO_2(SO_4)_2}} = \frac{2}{C_{RC}} \left(\frac{1}{K_c} + C_{UO_2SO_4} \right) \quad (68)$$

one would plot

$$y \frac{C_{UO_2SO_4}}{C_{R_2UO_2(SO_4)_2}} \quad \text{vs} \quad C_{UO_2SO_4}$$

5.0 AREAS FOR FURTHER RESEARCH WITH THE SYSTEM DOWEX 21K - AQUEOUS URANYL SULFATE SOLUTIONS

Figure 7 should have a profound bearing on future research because of the rather sharp maximum in UO_2SO_4 at a total sulfate concentration of about 0.05 mol/liter. This fact was apparently overlooked in the research of Arden et al and O'Connor. We also failed to recognize this fact during Wagner's experimental work and consequently the IBM calculations were stopped at 0.05 mol/liter total sulfate. Had they been carried out at values below .05, the two maxima (one for Ahrlund's constants and one for Allen's) would have come to light as is illustrated by extrapolation in Fig. 7.

The important point about the maxima is that the correct one should be reflected in the resin equilibrium sorption at the same value of total sulfate in solution and thus reveal the correct set of constants. Also if the resin sorption showed this maximum value, there would be no doubt that UO_2SO_4 or $UO_2(SO_4)_2^{2-}$ is being sorbed.

The maximum in the UO_2SO_4 curve can be demonstrated mathematically. For this purpose we will assume

$$\mu \rightarrow 0$$

due to the dilute solutions involved in this region. Also $C_{UO_2(SO_4)_3^{4-}}$ is essentially zero in this region. We start by defining the total molar uranium concentration as

$$C_{UT} = C_{UO_2^{++}} + C_{UO_2SO_4} + C_{UO_2(SO_4)_2^{2-}}, \quad (69)$$

and the total molar sulfate concentration as

$$C_{ST} = C_{HSO_4^-} + C_{SO_4^{2-}} + C_{UO_2SO_4} + 2C_{UO_2(SO_4)_2^{2-}} = C_{AT} + C_{UT} + C_{Na_2SO_4}, \quad (70)$$

and finally the total molar acid concentration as

$$C_{AT} = 1/2(C_{H^+} - C_{HSO_4^-}) + C_{HSO_4^-} = 1/2(C_H + C_{HSO_4^-}). \quad (71)$$

Also

$$K_1 = \frac{C_{UO_2SO_4}}{C_{UO_2^{++}} C_{SO_4^{2-}}}, \quad (72)$$

and

$$K_2 = \frac{C_{UO_2(SO_4)_2^{2-}}}{C_{UO_2^{++}} C_{SO_4^{2-}}^2}, \quad (73)$$

and

$$K_b = \frac{C_{H^+} C_{SO_4^{2-}}}{C_{HSO_4^-}} = 0.0118 \text{ at } \mu = 0. \quad (74)$$

From equations 71, 73, and 74,

$$C_{HSO_4^-} = \frac{2C_{AT} C_{SO_4^{2-}}}{K_b + C_{SO_4^{2-}}}. \quad (75)$$

This with 70 gives

$$C_{ST} = \frac{2C_{AT} C_{SO_4^-}}{K_b + C_{SO_4^-}} + C_{SO_4^-} + C_{UO_2SO_4} + 2K_2 C_{UO_2^{++}} C_{SO_4^-}^2 . \quad (76)$$

From 69 and 73,

$$C_{UT} = C_{UO_2^{++}} + C_{UO_2SO_4} + K_2 C_{UO_2^{++}} C_{SO_4^-}^2 . \quad (77)$$

This with 72 gives

$$C_{UT} = \frac{C_{UO_2SO_4}}{K_1 C_{SO_4^-}} + C_{UO_2SO_4} + \frac{K_2}{K_1} C_{UO_2SO_4} C_{SO_4^-} . \quad (78)$$

From 72 and 76,

$$C_{ST} = \frac{2C_{AT} C_{SO_4^-}}{K_b + C_{SO_4^-}} + C_{SO_4^-} + C_{UO_2SO_4} + 2 \frac{K_2}{K_1} C_{UO_2SO_4} C_{SO_4^-} . \quad (79)$$

From 78,

$$C_{SO_4^-}^2 = - \frac{K_1}{K_2} \left(\frac{C_{UT}}{C_{UO_2SO_4}} - 1 \right) C_{SO_4^-} + \frac{1}{K_2} = 0 , \quad (80)$$

and this has the derivative

$$\frac{dC_{UO_2SO_4}}{dC_{SO_4^-}} = \frac{C_{UO_2SO_4}^2}{C_{UT} C_{SO_4^-}} \left[\left(\frac{C_{UT}}{C_{UO_2SO_4}} - 1 \right) - 2 \frac{K_2}{K_1} C_{SO_4^-} \right] . \quad (81)$$

At the maximum the derivative is zero and so

$$\left[C_{SO_4^{2-}} = 1/2 \frac{K_1}{K_2} \left(\frac{C_{UT}}{C_{UO_2SO_4}} - 1 \right) \right]_{Max} . \quad (82)$$

We may substitute this in 80 to show that at the maximum

$$C_{SO_4^{2-}}_{Max} = \left(\frac{1}{K_2} \right)^{1/2} . \quad (83)$$

From 82 and 83,

$$C_{UO_2SO_4}_{Max} = \frac{C_{UT}}{1 + 2 \left(\frac{K_2}{K_1} \right)^{1/2}} . \quad (84)$$

From 79, 83, and 84,

$$C_{ST}_{Max} = \frac{2C_{AT}}{K_b \sqrt{K_2} + 1} + \frac{1}{\sqrt{K_2}} + C_{UT} . \quad (85)$$

We can also show that

$$C_{UO_2(SO_4)_2^{2-}}_{Max} = 1/2 [C_{UT} - C_{UO_2SO_4}] , \quad (86)$$

and

$$x_{Max} = \frac{1}{\frac{C_{AT}}{K_b + \frac{1}{\sqrt{K_2}} + 1}} . \quad (87)$$

Also with this information $C_{UO_2^{++}}_{Max}$ may be computed from equation 69.

The important point is that the position of the maximum is, according to equation 83, determined only by K_2 . On the other hand, the value or height of

the maximum is, according to equation 84, determined by $\sqrt{K_2/K_1}$.

Based on Ahrland's constants and our equations,

$$C_{ST \text{ Max}} = 0.037 \text{ mol/liter}; C_{UO_2SO_4 \text{ Max}} = 0.00422 \text{ mol/liter},$$

where

$$C_{AT} = .02 \text{ mol/liter (pH 2)}; C_{UT} = 0.005 \text{ mol/liter}.$$

If we make up a solution of C_{AT} and C_{UT} only with no Na_2SO_4 , the minimum value of C_{ST} is

$$C_{ST \text{ Min}} = 0.025 \text{ mol/liter}.$$

Thus, one should be able to observe the maximum in the resin equilibrium sorption by making up two solutions that could be mixed in various proportions for the equilibrium studies. The one solution would contain

0.005 mol/liter uranyl sulfate,

0.02 mol/liter H_2SO_4 ,

and the other would contain

0.005 mol/liter uranyl sulfate,

0.02 mol/liter H_2SO_4 ,

0.075 mol/liter Na_2SO_4 .

The range from 0.025 to 0.1 mol/liter total sulfate could be studied in detail to discern the validity of the values of K_2 whether they be from Allen or Ahrland or some new set of values.

There is also a point of inflection to the left of the maximum that can be calculated by setting the second derivative of the dilute solution theory equal to zero. It occurs at

$$\left[C_{SO_4} \left(\frac{3}{K_1} - \frac{K_2}{K_1} C_{SO_4}^2 \right) + \frac{1}{K_2} = 0 \right] \text{ infl.}, \quad (88)$$

or for Ahrlund's case at

$$C_{SO_4} \text{ infl.} = 0.0316 \text{ mol/liter} \quad (89)$$

(This fact is not as useful as it might appear due to the difficulty of identifying points of inflection in experimental data.)

The $C_{UO_2SO_4} - C_{ST}$ curve must not only be positioned on the plot according to the experimental value of K_2 , but also the curvature of the plot must conform to the ratio of equations 37, i.e.,

$$\frac{1 C_{UO_2SO_4}}{2 C_{UO_2SO_4}} = \frac{1 C_{R_2UO_2(SO_4)_2} \left[2 C_{R_2UO_2(SO_4)_2} \text{Sat} - 2 C_{R_2UO_2(SO_4)_2} \right]}{2 C_{R_2UO_2(SO_4)_2} \left[1 C_{R_2UO_2(SO_4)_2} \text{Sat} - 1 C_{R_2UO_2(SO_4)_2} \right]}, \quad (90)$$

This must be so on both sides of the maximum. Among other things the position of the tail of the curve at larger values of C_{ST} will depend experimentally on equation 90. In theory it depends on K_3 .

In summary, the position of the maximum determines K_2 ; the curvature to the left of the maximum determines K_1 , and the high sulfate tail position or curvature determines K_3 .

It is quite obvious that the precise determination of K_1 , K_2 , and K_3 from resin sorption data taking ionic strength into account would be expedited by use of a computer such as an analog computer. The K_1 , K_2 , and K_3 would be determined by the setting of potentiometers, the setting of which could be adjusted to produce conformity with experimental data.

It should be quite obvious from the discussion of Wagner's work that in the range $pH \leq 2$ it would be desirable to further corroborate the proposed sorption theory by

- (a) actually determining the y - x diagram for the pure $SO_4^{2-} - HSO_4^-$ system and Dowex 21 K;
- (b) measuring y for various x in uranyl sulfate solutions so that these results may be compared on the y - x diagram. The y should be calculated both from gross analysis and bisulfate H^+ ion titration in

the eluate so that they might be compared;

- (c) repeating Wagner's work at other total sulfate concentrations. This work should also be extended over a wider range of uranyl concentrations using appropriate methods for correcting for solute in the resin water of hydration;
- (d) repeating Wagner's work at other temperatures to investigate K_c and its associated activation energy. The linear plots should all be parallel, i.e., the plots of $y \frac{C_{UO_2SO_4}}{C_{R_2UO_2(SO_4)_2}}$ vs $C_{UO_2SO_4}$ for various temperatures should be parallel. Whether K_c varied as $e^{-E/RT}$, $T^{2/3}$, or some other function would depend on the nature of the equilibrium sorption. This work might be laborious because Figs. 3-6, among others, are also functions of temperature;
- (e) the Dowex 21K resin capacity should also be measured by direct titration.

Determining y in (b) involves eluting the resin and measuring the hydrogen concentration in the presence of uranyl in the eluate. O'Connor has investigated this problem and recommends adding a 100-ml aliquot of the eluate to a 200-ml centrifuge flask along with 10 ml of saturated potassium ferrocyanide solution and 25 g of solid KNO_3 , and agitating the mixture for one hr. This amount of KNO_3 is sufficient to saturate the solution. The solution containing a very fine precipitate of $K_2UO_2Fe(CN)_6$, is then centrifuged and the solution decanted. The precipitate is washed twice with 5-ml portions of saturated KNO_3 , and the washings are added to the original solution. The H^+ ion is determined potentiometrically by titration with standard base. This procedure, it is claimed⁽⁵⁾, gives excellent results, whereas other presumably competitive procedures failed.

As a matter of practical experience, it might also be remarked that in future work the total effort is reduced if

- (a) multiple contact runs are made,
- (b) standard solutions are made up beforehand. The standard solution for each run can be synthesized from two stock solutions by mixing in the proportions necessary to produce a desired total uranium concentration. The first stock solution should be made up to the maximum uranyl sulfate concentration that will be required in a given set of runs. Enough Na_2SO_4 and H_2SO_4 should be added to produce the desired total sulfate and pH. The second stock solution should be made up only from Na_2SO_4 and H_2SO_4 produce the same total sulfate concentration and pH as for the first stock solution.

Above pH 2 investigations would be principally of academic interest. For this purpose, however, one would certainly want to investigate

(a) the reaction

(b) $\text{U}_2\text{O}_5\text{SO}_4$ and the same factors previously discussed in the case of UO_2SO_4 .

Ultimately, of course, one would also hope to study the actual kinetic mechanism of uranyl sorption. Because of the mathematical simplifications inherent in the method, one should employ a single stage stirred or fluidized contactor with continuous flow of standard solution through it.

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6. F. R. Bruce
7. F. L. Culler
8. W. K. Eister
9. D. E. Ferguson
10. E. R. Gilliland (MIT consultant)
11. H. E. Goeller
12. A. T. Gresky
13. P. A. Haas
14. R. W. Horton
15. E. Lamb
16. R. B. Lindauer
17. J. T. Long
- 18-23. S. H. Jury
24. M. J. Skinner
25. P. E. Stein (Y-12)
26. C. D. Watson
27. J. S. Watson
28. M. E. Whatley
29. Central Research Library
30. Document Reference Section
- 31-32. Laboratory Records
33. Laboratory Records (RC)
- 34-48. TISE, AEC