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SUBJECT: The Rate of Uranium Sorption by a Strong-Base Anion-Exchange Resin

TO: J. C. Bresee

FROM: J. S. Newman

ABSTRACT

The rate of uranium sorption by a strong-base anion-exchange resin (Dowex 21K) from a uranyl sulfate solution (U 0.005 M, H_2SO_4 0.02 M, SO_4 0.2 M) was studied using a stirred vessel technique and measuring the U^{235} gamma radiation on each bead. Resin initially in the chloride form and the sulfate form was studied.

The data fit, reasonably well, the equation of Boyd, Adamson, and Myers for "particle diffusion". Values of the apparent diffusion coefficient obtained are 10.2×10^{-8} and 7.2×10^{-8} cm²/sec for the chloride and sulfate forms respectively. For any one run, the value was observed to increase as the exchange proceeded.

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1.0 INTRODUCTION

A system consisting of uranyl sulfate solution and a strong-base anion-exchange resin has been the subject of a basic study in the Unit Operations Section. This system is of interest because it is widely used for concentrating and separating uranium, especially from ore leaches. The objects of the current program are to elucidate the mechanism of the sorption and to obtain information which will enable one to predict the behavior of deep beds and thereby to design operating columns.

The object of this paper is to apply the results of previous rate studies on other ion exchange systems to rate data which have been obtained. Thus, the equilibria involved are only of minor interest in this paper.

Some work has been done elsewhere on systems of uranyl sulfate solution and anion resins. (2,3,12) Most of this has concerned itself with equilibrium relationships. The conclusion was that uranium is present on the resin in the form of a uranyl trisulfate anion, $\text{UO}_2(\text{SO}_4)_3^{4-}$, at a pH of 2, but that higher pH favors the presence of $\text{U}_2\text{O}_5(\text{SO}_4)_3^{4-}$. One paper (2) presents rate studies investigating the effect of pH. The diffusion rate decreased with increasing pH, presumably because $\text{U}_2\text{O}_5(\text{SO}_4)_3^{4-}$ became the principal diffusing species.

The method used to obtain the rate data herein reported was the suggestion of C. V. Chester.

2.0 RESULTS

Ion exchange resins are available commercially in the form of spherical particles. Resin beads of uniform diameter with no cracks were selected for each run. The amount of uranium on each bead and its diameter were measured after it had been in contact with the uranyl sulfate solution for a known length of time. Three runs are reported, all of which utilized the same uranium solution (initially 0.00428 M U, 0.0198 M H_2SO_4 , and 0.2 M SO_4^{2-}). However, evaporation caused some concentration of the solution which was compensated for by periodic dilutions. The conditions prevailing for the runs were:

Table 1

Run	U conc. M	Average bead diameter mm	Initial resin form	Notes
KCX	0.00428	1.161	SO_4^{2-}	---
KCX-2	0.005	0.7954	SO_4^{2-}	---
KCL	0.00434	0.989	Cl^-	Clear beads selected

The results are plotted in Figs. 2.1, 2.2, and 2.3 as the uranium loading per unit volume of the bead against the term $(t/a^2)^{1/2}$ where a is the radius of the bead. The equilibrium loading was obtained from beads of long contact time (more than 46 hours). These data, which are somewhat erratic, are summarized below.

Table 2

Run	U conc. <u>M</u>	Average Loading <u>Mg U</u> cm ³ resin	Standard deviation	Notes
KCX	0.00428	96.88	11.5%	Equilibrium
KCX-2	0.005	114.29	9.4%	Contact times between 100 and 1800 min.
KCX-2	0.008	109.83	12.3%	Equilibrium
KCL	0.00434	87.49	8.5%	Equilibrium

The ionic sites in an ion exchange resin are introduced after polymerization in the form of spherical beads. In a commercial resin one would not expect perfectly homogeneous resin. The scatter in Fig. 2.2 and in the values for equilibrium loading (standard deviation, above) show that the resin is not homogeneous since the experimental error for the equilibrium samples should be less than 3%.

The data in Table 2 suggest that the specific capacity of the larger beads may be less than that of the smaller beads and that the clear beads have a definitely smaller specific capacity.

Clear beads (uniform in appearance) were selected for run KCL in an attempt to obtain more nearly uniform resin. Some improvement is shown in the decreased scatter in Fig. 2.3 and in the lower standard deviation in Table 2.

The loading values for run KCX-2 (Table 2) do not appear to be in order. One would expect the uranium loading to increase as the uranium solution concentration increases, although the increased sulfate concentration would tend to suppress the equilibrium value. As a compromise, a value of 105 mg U/cm³ resin was chosen for that run.

3.0 DISCUSSION

Three possible processes could affect the rate of reaction in this system.

Fig. 2.1. Loading of Uranium on Dowex 21K Resin Initially in the Sulfate Form. (Run KCX)

Fig. 2.2. Loading of Uranium on Dowex 21K Resin Initially in the Sulfate Form. (Run KCX-2)

Fig. 2.3. Loading of Uranium on Dowex 24K Resin Initially in the Chloride Form. (Run KCL)

These are:

1. A chemical reaction.
2. Diffusion of a species through the resin ("particle diffusion").
3. Diffusion of a species through the stagnant layer (Nernst film) surrounding the bead ("film diffusion").

These possibilities have been investigated in other ion exchange systems. The result is that both of the diffusion mechanisms affect the rate. Generally, the conditions can be adjusted so that either alone is controlling. An introduction to the important literature of ion exchange kinetics and an excellent treatment of the results are given by Kitchener.^(8,9)

Rate studies using a shallow bed technique, a uranyl sulfate solution, and an anion resin⁽¹⁾ have shown that particle diffusion is likely to be controlling.

If the rate of sorption were controlled entirely by particle diffusion, the process would be described by the equation:⁽⁴⁾

$$F = \frac{Q_t}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(- \frac{D\pi^2 n^2 t}{a^2} \right), \quad (1)$$

where t = contact time.

Q_t = quantity sorbed in the interval $(0, t)$.

D = apparent diffusion coefficient.

a = radius of bead.

This equation is most conveniently used in the form of a table⁽¹³⁾ of Dt/a^2 as a function of F . Where the equation applies to the coupled diffusion of two different ions, the value of D observed will represent a compromise between the two. The equation applies to sorption from an infinite bath. This condition was approximated closely in the experiment.

Plots of F versus $(t/a^2)^{1/2}$ are given for the three runs in Figs. 3.1, 3.2, and 3.3. The best theoretical curve from the particle diffusion model is included along with one curve of greater D and one of lesser D . For run KCX, the best value of D was obtained by calculating the average of the values of D for the seven points shown. For run KCX-2, values of D for points between $F = 0.4$ and 0.6 and for run KCL, those between $F = 0.4$ and 0.7 were averaged in order to obtain the best values of D . In this region the effect of the errors of the experiment and the method of calculation of D should be minimized. The scatter in the second two runs indicates that the few points obtained in the first run are not very reliable.

Fig. 3.1. Fractional Attainment of Equilibrium Loading for Run KCX.

Fig. 3.2. Fractional Attainment of Equilibrium Loading for Run KCX-2.

Fig. 3.3. Fractional Attainment of Equilibrium Loading for Run KCL.

It should be pointed out that the values of the apparent diffusion coefficient obtained contain an error. The beads were measured in a medium of demineralized water rather than in the solution used in the experiment. Therefore, the values of D obtained should be multiplied by the ratio of the squares of the radius in the solution and in water. Since the beads contract in an ionic medium⁽¹⁰⁾, the values given are high.

Figures 3.1, 3.2, and 3.3 show that D increases as the sorption takes place. This could be due to one or more of the following factors:

1. The effect of the Nerst film.
2. Non-homogeneity of the resin.
3. Gross changes in the form of the resin as the reaction proceeds.
4. Use of an erroneous equilibrium value, especially in run KCX-2.

Only for a self-diffusion experiment should one expect D to remain strictly constant (although Boyd and Soldano⁽⁵⁾, measuring self-diffusion coefficients of cations, found that for resins of high crosslinking, i.e., 16 and 24% divinyl-benzene, " D became progressively smaller as equilibrium was approached, while with the 1% DVB exchanger, D increased initially and then became quite constant.").

In addition to the satisfactory agreement of the data with the particle-diffusion model, Fig. 3.4 provides evidence of the type of mechanism. On a plot of $\log (1 - F)$ against t , both a film-diffusion controlled process and a chemically controlled process would yield straight lines. (This curve indicates that the value for the equilibrium loading used for run KCX-2 was too low).

The value of the apparent diffusion coefficient obtained with the sulfate resin (7.2×10^{-8} cm²/sec) suggests that the uranium sulfate anions are not attached to the resin with covalent bonds. Conway, Green, and Reichenberg⁽⁶⁾ obtained a value of 3.92×10^{-9} for the exchange of sodium and hydrogen on a weak acid exchanger (containing carboxylic acid groups). The exchange of two alkali-metal cations on the weak-acid resin gave a value comparable to the alkali exchange on a strong-acid resin, i.e., 10^{-6} . The explanation given, which is not perfectly clear, seemed to be that, if covalent bonds (-COOH) do not manifest themselves in determining the mechanism of the exchange, they may still influence the rate of exchange by limiting the magnitude of the concentration gradient of one or more of the diffusing ions. Further pursuit of this line of reasoning would require measurement of the exchange rates of other anions in Dowex 21K since values are not given in the literature.

The results of run KCL and the sulfate runs considered together suggest that the uranium sorption process is essentially the same in both systems. Since uranium does not form anionic complexes with chloride ions (to an appreciable extent) the diffusing uranium species would have to be an anionic uranium sulfate complex (possibly $\text{UO}_2(\text{SO}_4)_3^{4-}$). If the sorption process is a normal ion exchange process, then the apparent diffusion coefficient applies

Fig. 3.4. Uranium Sorption in Runs KCX-2 and KCL.

to the coupled diffusion of the two exchanging ions. The higher value of D obtained for the chloride run would indicate that the chloride ion is more mobile than the sulfate ion. This would be expected, based primarily upon the dependence of diffusion rate upon ionic charge. (The effect of the lower capacity of the resin in the chloride run would be expected to decrease the diffusion rate⁽¹⁴⁾).

It has been suggested that the mechanism of uranium sorption on resin in the sulfate form and in the chloride form might be quite different. It is conceivable that uncharged uranyl sulfate (UO_2SO_4) could diffuse into the resin in the sulfate form, forming an anionic complex within the resin. If UO_2SO_4 remained the diffusin species, then diffusion of uranium into a chloride saturated resin would require the prior conversion of the resin to the sulfate form. No hint of such a delay is seen; the sorption of uranium into chloride resin is, in fact, faster than sorption into sulfate resin.

4.0 RECOMMENDATIONS

Data for diffusion rates of anions in Dowex 21K resin were not found⁽⁷⁾ in the literature. Furthermore, crosslinking in Dowex 21K is "undefined". This does not allow reliable comparison of measured values of diffusion coefficients with those of other strong-base anion-exchange resins. Consequently, it is felt that the rate of exchange of sulfate and chloride ions on Dowex 21K should be measured.

It has been pointed out⁽⁵⁾ that particle-self-diffusion coefficients are more meaningful in terms of processes within the resin and are therefore more important for a basic study of ion exchange mechanisms. Therefore, self-diffusion coefficients for the uranium system and the sulfate and chloride ions should be measured.

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6.0 APPENDIX EXPERIMENTAL DETAILS

6.1 Resin

The resin used was commercial Dowex 21K, nominally 16 to 20 standard mesh wet. Resin size fractions were obtained by combinations of wet and air-dry screening in the chloride form (as received). The sizing method given by Kunin⁽¹¹⁾ is recommended.

For the sulfate runs, the resin was then converted to the sulfate form, back to the chloride form, and finally to the sulfate form again. For the chloride run, the resin was converted to the sulfate form and then back to the chloride form.

6.2 Equipment

6.21 Mixer. The mixing vessel was a 1200 ml stainless steel beaker. The stirrer was a 1/2-in. six-blade, flat-blade turbine impeller (blade height 1/4-in.) operated at about 1650 rpm. For run KCX-2 a 1-1/2 in. two blade propeller with a variable speed motor was used. This latter method was unsatisfactory.

6.22 Gamma Counter. The gamma counter utilized a "deep-well" sodium-iodide crystal and a photomultiplier tube. The sample to be analyzed was placed in a small test tube (10 x 75 mm) which was placed in the well of the crystal, thus giving essentially a 4π geometry. Gamma radiation from the sample causes the crystal to scintillate. This light is detected by the photomultiplier tube whose output is analyzed with pulse circuitry.

6.3 Procedure

About 900 ml of the enriched uranium solution (92.55% U^{235}) were placed in the stainless steel beaker. Between 50 and 150 resin beads were sorted from the prepared resin. The selected beads were spherical, unbroken, and uncracked; for the chloride run they were also clear.

The beads so chosen were placed on a spatula in contact with demineralized water. Just before zero time, the beads were dried with tissue and at zero time they were plunged into the agitated tank.

Samples were obtained at recorded intervals with a small (about 1 in. across) wire-screen basket manipulated with tongs. The resin was washed immediately with demineralized water and placed in 10 x 75 mm test tubes (one bead per tube). The contacting was carried out at room temperature, ca, 24°C.

The individual beads were counted for U^{235} gamma radiation for periods ranging from 32 minutes to 64 hours, most of the samples being counted for 64 minutes. Counting statistics may be expected to be accurate to about 3 per cent.

After counting gamma radiation, the beads were immersed in demineralized water. After at least two hours of contact, the beads were measured with a calibrated microscope. The beads were measured as loaded, in contact with demineralized water. The beads were placed on a microscope slide in a well formed by a slice of tygon tubing. Optical effects of the water meniscus were eliminated by placing a cover plate over the well. Diameters so measured may be expected to be accurate to better than 0.5 per cent.

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