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SUBJECT: Uranium Anion Exchange Equilibria on Dowex 21K

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ABSTRACT

Equilibrium loading of uranium on Dowex 21K has been studied in a sulfate system for uranium concentrations from 0.0005 M to 0.005 M, total sulfate concentrations of 0.045 M to 0.6 M, and sulfuric acid concentration of 0.020 M. Loading data have been fitted to Langmuir adsorption isotherms and Langmuir constants have been evaluated. Resin was equilibrated with uranium feed solutions by flowing the feed through a shallow fixed bed of resin.

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1.0 INTRODUCTION

An important application of ion exchange is the concentration of uranium from its ores. Concentration consists in separation of uranium from the main bulk of diluents which accompany it in nature.

Because of the unsuitability of specific gravity and floatation-concentration methods, the extraction of uranium from ores is now effected almost exclusively by leaching. When acid solutions are used for the leaching step, solvent extraction or ion exchange is the preferred method of recovering uranium because either of these permits reuse of some or all of the leaching solution with the next batch of ore. Uranium can be recovered selectively from acidic leach solutions by conventional anion-exchange resins.(1)

A series of experiments have been carried out to determine the uranium loading on Dowex 21K* in equilibrium with solutions of various uranium and sulfate concentrations.

In the system containing the uranyl ion, sulfate ion, and hydrogen ion the following equilibria are involved:

$$UO_2^{++} + SO_4^{=} \rightleftarrows UO_2SO_4 \qquad (1)$$

$$UO_2SO_4 + SO_4^{=} \rightleftarrows UO_2(SO_4)_2^{=} \qquad (2)$$

$$UO_2(SO_4)_2^{=} + SO_4^{=} \rightleftarrows UO_2(SO_4)_3^{\equiv} \qquad (3)$$

$$H^+ + SO_4^{=} \rightleftarrows HSO_4^- \qquad (4)$$

Equilibrium constants for reactions 1, 2, and 3 have been determined by Ahrland(2) and Allen(3).

Sulfuric acid is added to the system to maintain the pH ≤ 2. At higher pH's the uranyl ion hydrolyzes to the $U_2O_5^{++}$ species.

S. H. Jury and J. B. Adams have reported that the UO_2SO_4 and/or $UO_2(SO_4)_2^{=}$ species are involved in the exchange mechanism.(4) Assuming this hypothesis, the reaction could be thought of as:

$$UO_2SO_4 + R_2SO_4 \rightleftarrows R_2UO_2(SO_4)_2 \qquad (5)$$

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* Dowex 21K is an anion exchanger which contains quaternary benzyl-trimethyl-ammonium groups on a cross-linked polystyrene-divinyl benzyne matrix.

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or

$$UO_2(SO_4)_2^{=} + R_2SO_4 \rightleftarrows R_2UO_2(SO_4)_2 + SO_4^{=} \qquad (6)$$

where R represents the resin.

Arden and Wood, however, report that uranium is adsorbed from sulfate solution by strong-base anion-exchanges as the complex $UO_2(SO_4)_3^{\equiv}$ at pH's < 2.5.(5) If this were the case, then the exchange could be represented by:

$$UO_2(SO_4)_3^{\equiv} + R_2SO_4 \rightleftarrows R_2UO_2(SO_4)_2 + 2SO_4^{=} \qquad (7)$$

From equilibrium data it is hoped that eventually a consistent model for the exchange mechanism can be formulated.

2.0 ANALYSIS OF RESULTS

Equilibrium sorption of uranium onto resin can be treated mathematically by a formal analogy to the Langmuir adsorption isotherm. The semi-emperical Langmuir isotherm was derived for the adsorption of a monomolecular layer of gas onto a solid.(6)

By extension of this relation to the case of uranium sorption onto resin, the loading expression for a constant sulfate concentration becomes:

$$q = \frac{aC_U}{1 + bC_U} \qquad (8)$$

with

q = equilibrium resin loading $\left(\frac{\text{millimoles U adsorbed}}{\text{g dry resin}}\right)$

C_U = uranium concentration in feed solution $\left(\frac{\text{millimoles U}}{\text{liter of solution}}\right)$

a, b = Langmuir constants.

Equation (8) can also be written as:

$$\frac{C_U}{q} = \frac{1}{a} + \left(\frac{b}{a}\right) C_U \qquad (9)$$

Figure 1 is a plot of $\frac{C_U}{q}$ vs. C_U using experimental data at six

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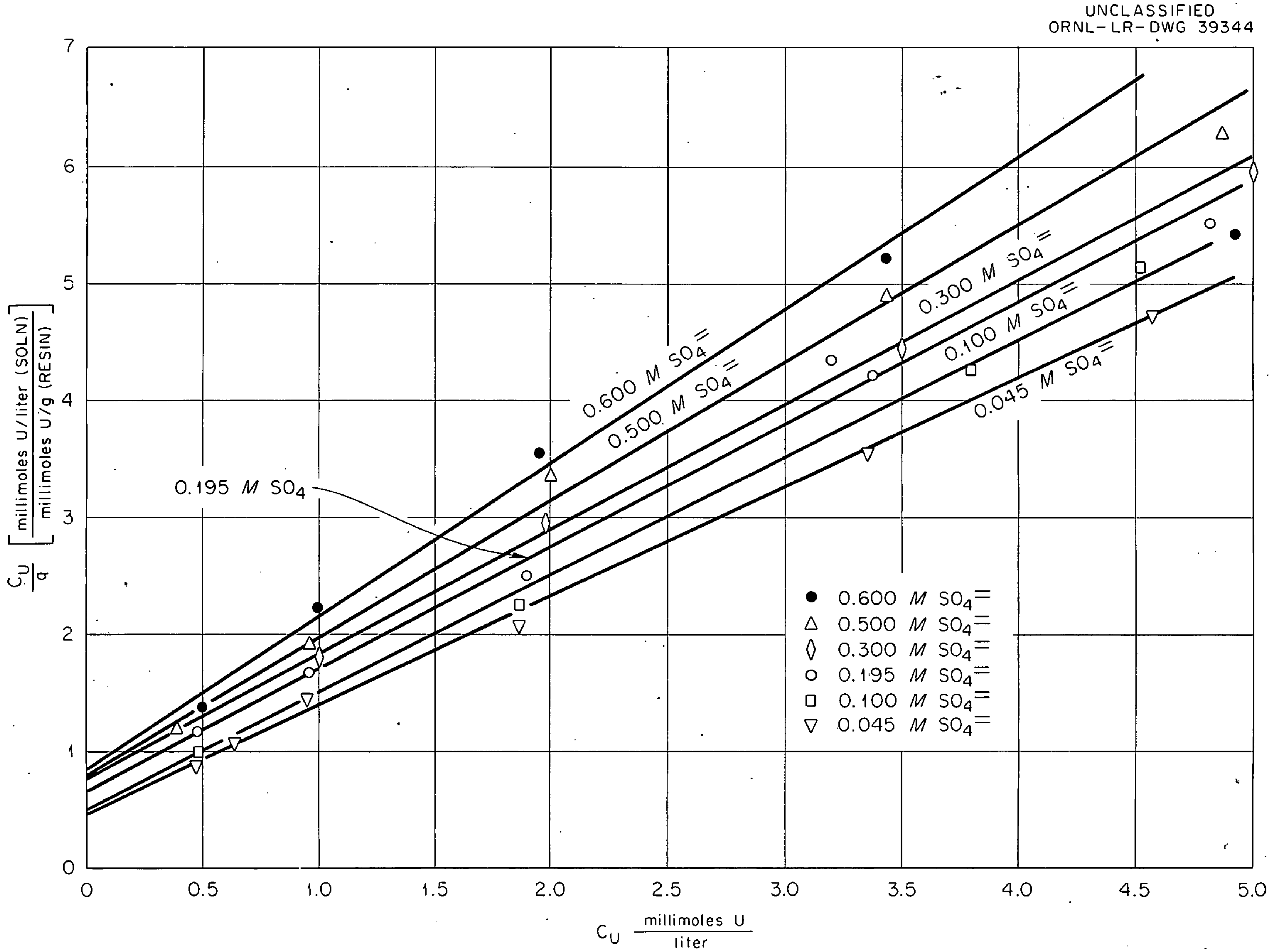

Fig. 1. Resin Loading Data Fitted to Langmuir Adsorption Isotherms.

different sulfate concentrations. This plot shows that the loading decreases with increasing sulfate concentrations over the range of sulfate concentrations studied. From Equation (9) the slope of this line is b/a and the intercept 1/a. Constants a and b are tabulated in Table 1 for each isotherm in Fig. 1. Also included in Table 1 are maximum resin loading values. Maximum resin loading occurs when $C_U \rightarrow \infty$. Equation (8) predicts this value of q to be a/b.

3.0 EXPERIMENTAL

Dowex 21K, available commercially in the chloride form, was converted to the sulfate form by elution with 1 M Na_2SO_4 at a pH of 2. This sulfate resin was converted back to the chloride form by elution with 1 M NaCl. Resin was cycled from chloride to sulfate twice to insure that the final sulfate resin was free from extraneous ionic and organic contaminants.

Uranium feed solutions were prepared by pipetting stock solutions of uranium and sulfuric acid into volumetric flasks. All solutions were made up to be 0.020 M H_2SO_4. Na_2SO_4 was carefully weighed out to adjust the total sulfate concentration to the desired value. A total of 8 liters of solution was prepared for the dilute feed solutions and 4 liters for the more concentrated solutions. Homogeneity of solution was achieved by agitation for a period of 1 hr. Samples of these solutions were analyzed potentiometrically for uranium and gravimetrically for sulfate. PH's were measured on a Beckman pH meter.

Approximately 1 gm of resin was placed in a 3.5 cm sintered glass filtering funnel, and feed solutions were flowed through the bed at a rate of 1 cc/min (Fig. 2). After all the feed solution had passed through the bed, the resin was centrifuged for thirty minutes to remove any entrained solution. The resin was then eluted with two 1 liter passes of 1 M NaCl and the effluent was analyzed for uranium. After elution, the resin was washed with 250 ml of demineralized water, dried in an oven at 55°C for a period greater than three days, and weighed on an analytical balance.

Resin loadings are reported as millimoles of uranium adsorbed (as determined from the total uranium in the effluent) per gram of dry chloride resin.

4.0 ACKNOWLEDGMENT

The author wishes to acknowledge J. S. Newman and J. S. Watson who carried out a great deal of the experimental work and again to J. S. Watson for developing the procedures and correlations used.

5.0 REFERENCES

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Table 1 Langmuir Constants and Maximum Loading

Sulfate Concentration M	$\frac{1}{a}$ gm resin	a $\frac{1}{\text{gm resin}}$	$\frac{b}{a}$ $\frac{\text{gm resin}}{\text{millimoles of U}}$	b $\frac{1}{\text{millimoles of U}}$	$\frac{a}{b}$ $\frac{\text{millimoles of U}}{\text{g resin}}$
0.045	0.46	2.18	0.89	1.94	1.12
0.100	0.50	2.00	1.01	2.02	0.99
0.195	0.64	1.56	1.05	1.64	0.95
0.300	0.75	1.33	1.07	1.42	0.93
0.500	0.78	1.28	1.18	1.51	0.85
0.600	0.84	1.19	1.32	1.57	0.76

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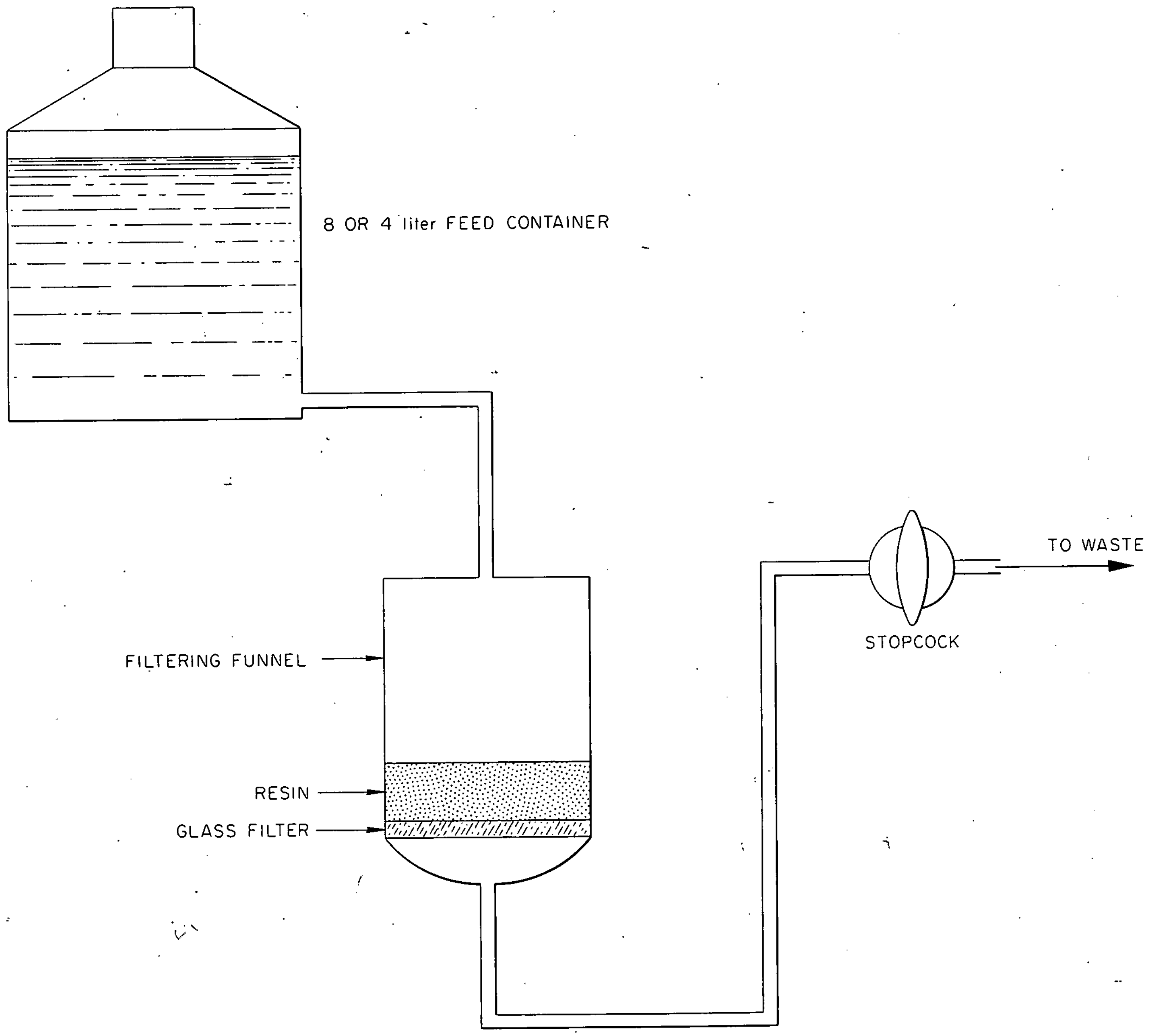

Fig. 2. Schematic Diagram of Apparatus.

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