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ELUTION OF URANIUM SORBED ON ANION EXCHANGE RESINS FROM LOW-GRADE ORE LEACH LIQUIDS

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CHEMICAL TECHNOLOGY DIVISION

CHEMICAL DEVELOPMENT SECTION

ELUTION OF URANIUM SORBED ON ANION EXCHANGE RESINS FROM LOW-GRADE ORE LEACH LIQUORS

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ABSTRACT

It is shown that uranium which has been sorbed by an anion exchange resin from synthetic sulfate and carbonate ore leach liquors can be obtained in a relatively concentrated form and free of excess salts by treating the resin with hydrochloric acid and eluting with water.

ACKNOWLEDGMENT

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1.0 INTRODUCTION

The use of anion exchange resins to recover uranium from acidic and basic ore leaches and from phosphoric acid has been studied at several installations.[1-7] Uranium is sorbed by the resin in the form of anionic complexes of the uranyl ion with sulfate, carbonate, and phosphate ions. One of the major problems associated with this work is the reclamation of the uranium from the resin in a desirable form with low losses. Elution of the resin, with the various salt and acidified salt solutions which have been tried, has been characterized by recovery of the uranium in low-to-moderate concentrations in the presence of relatively large amounts of sodium or ammonium salts (such as chlorides, nitrates, sulfates, of carbonates), and by the difficulty of obtaining complete removal of the uranium from the resin.

In connection with another problem, the separation of uranium from thorium by ion exchange, it was observed that uranium which had been sorbed by an anion exchange resin from concentrated chloride solutions could be eluted completely at fairly high concentrations merely with water. It was decided to try water elution of uranium sorbed from ore leach liquors by treating the loaded resin with HCl before eluting.

2.0 SUMMARY

Uranium was sorbed on an anion exchange resin bed from a synthetic sulfate ore leach liquor; the bed was washed with concentrated hydrochloric acid to remove the sulfate, and the uranium was then eluted with water. For a loading of 58 mg of uranium per milliliter of Dowex-1 resin and with one volume of 10 N HCl used per volume of resin, the uranium elution curve had a peak concentration of 115 g/liter and 97% of the uranium was recovered in 4 bed volumes of water. For the same loading, elution with a conventional 0.1 N HNO_3-0.9 N $NaNO_3$ solution gave a peak concentration of 20 g/liter with 80% recovery in 8 bed volumes of elutant.

Uranium was sorbed on an anion exchange resin bed from a synthetic carbonate ore leach liquor; the resin was reacted, with agitation, with enough hydrochloric acid to decompose the carbonate, and the uranium was then eluted with water. Eighty-five percent of the uranium was recovered in 2 bed volumes of water, with a peak concentration of about 19 g/liter. For the same loading, elution with a conventional 4 M $(NH_4)_2SO_4$ solution gave a recovery of 66% of the uranium in two bed volumes, with a peak concentration of about 17 g/liter.

In both cases studied, the conversion of the resin to the chloride form and elution with water gave results with advantages over the conventional salt elutions in that the uranium was obtained at relatively

high concentrations and in the absence of high salt concentrations. The procedure might give even better results with more development work since optimum conditions have not been determined. The excess HCl used in the sulfate system might be recovered by evaporation, and less HCl could be used, apparently, in the carbonate system.

It is recommended that further studies be undertaken to optimize the variables, to investigate the application of this method to recovery of uranium from phosphate solutions, and to determine the applicability of the continuous ion exchange contactor described by Higgins[8] to the recovery of uranium from leach liquors.

3.0 EXPERIMENTAL

3.1 Sulfate Liquors

A bed of 150 ml volume, measured in the backwashed and settled chloride form, of 60-100 mesh Dowex-1 anion exchange resin was prepared in a 3/4-in.-i.d. glass pipe column. This resin bed, in the chloride form, was loaded with 8.65 g of uranium (approximately 58 mg of uranium per milliliter of resin) by passing through it 5 liters of a synthetic sulfate leach liquor of the following composition:

U (as UO_2SO_4)	1.73 g/liter
H_2SO_4 (Conc.)	1 g/liter
$Al_2(SO_4)_3 \cdot 18H_2O$	16.5 g/liter (0.15 N)
$MgSO_4 \cdot 7H_2O$	25 g/liter (0.20 N)
H_3PO_4 (85%)	0.65 g/liter

The loading flow rate was 37.5 ml/min (equivalent to about 2 gal/ft^3/min or 13.5 ml/cm^2/min). Under these conditions the uranium breakthrough was negligible, approximately 0.001 g/liter, and examination of the column under ultraviolet light indicated a uranium loading of about 90% of the column length. These loading conditions were similar to those used by Kirk[5a]. The bed was next washed with 150 ml of distilled water at 18.75 ml/min (approximately 1 gal/ft^3/min) and then with 150 ml of 10 N HCl (20° Bé) at the same flow rate. Effluent collection was staggered with respect to change of influent to allow for a 50-ml voids volume. The effluent from the hydrochloric acid elution contained almost all the sulfate on the bed plus 0.098 g (1.1%) of the uranium. The hydrochloric acid "metathesis" step was followed by elution with 600 ml of distilled water, also at a flow rate of 18.75 ml/min. The uranium broke through sharply within 10 ml after the first voids volume, rising to a peak of 115 g/liter at approximately 60 ml, after which the concentration dropped

to 10% of this value at approximately 140 ml and to 1% at approximately 375 ml. This water elution step recovered 8.39 g (97%) of the uranium. The elution curve is shown in Fig. 1. The free acid concentration during the elution is also shown in this figure, a total of 312 milliequivalents coming off after the uranium breakthrough. A small amount of sulfate was eluted with the uranium. Finally, the resin was eluted with 0.9 N $NaNO_3$-0.1 N HNO_3 until negative tests for uranium (ferrocyanide) and chloride (silver nitrate) were given by the effluent. This yielded an additional 0.33 g (3.9%) of uranium to give a calculated total recovery of 102% (the discrepancy being within the analytical accuracy).

The same resin bed, this time in the washed nitrate form, was loaded with uranium and washed with 150 ml water in the manner described in the preceding paragraph for the chloride resin. Again, the uranium breakthrough was negligible and a column loading of about 90% was indicated under ultraviolet light. The uranium was eluted, after the manner of Kirk[5a], with a "conventional" 0.9 N $NaNO_3$-0.1 N HNO_3 solution at a flow rate of 18.75 ml/min. The uranium broke through at about 50 ml after the first voids volume, the concentration rising to a peak concentration of 20 g/liter at approximately 160 ml and then dropping to 10% of the peak value at approximately 1125 ml. The elution was stopped after 1200 ml (8 volumes elutant per volume of resin) with a recovery of 6.89 g (80%) of the uranium. Treating the resin with concentrated hydrochloric acid and eluting with water, as described above, recovered an additional 1.55 g (18%) of uranium, for a calculated total yield of 98%.

Other experiments with the chloride metathesis--water elution procedure indicated that lower uranium loadings of the resin reduced the amount of uranium which was eluted with the sulfate by the hydrochloric acid, while higher loadings increased it. Qualitatively similar results were obtained with commercial grade Amberlite IRA-400 resin and with the synthetic Belgian Congo liquor used by Kirk[5a] which contained iron, cobalt, copper, and nickel in addition to aluminum and magnesium. This liquor was not used in the experiments reported above since the additional ions interfered with analyses and led to poor material balances. They also interfered with ultraviolet light examination of the column.

3.2 Carbonate Liquors

A 75-ml, measured in the backwashed and settled chloride form, bed of 50-100 mesh Dowex-1 anion exchange resin was prepared in a 1-in. glass pipe column. The bed, in the chloride form, was loaded with 1.5 g of uranium by passing through it 500 ml of a synthetic carbonate liquor,

U (as UO_2SO_4)	3.3 g/liter
Na_2CO_3	0.9 M
$NaHCO_3$	0.1 M

which was similar to that used by Kirk[5b] except that the vanadium was left out. The loading flow rate was 18.75 ml/min (equivalent to 2 gal/ft^3/min). A total of 0.039 g (2.6%) of the uranium broke through during the loading. The bed was washed with 75 ml of distilled water at 9.375 ml/min (approximately 1 gal/ft^3/min). At this point the water level was at the surface of the bed and there was 100% freeboard above the bed. Twenty-five milliliters of 6 N HCl was poured in, and the bed was agitated with a stirrer until gas evolution ceased; then the bed was resettled, the excess solution was drained out, and 100 ml of distilled water was passed through at 9.375 ml/min. The uranium came off as shown in Fig. 2, with a total recovery of 1.27 g (85%), along with 70 meq of HCl. The bed was then eluted with 4 M $(NH_4)_2SO_4$, to convert it to the sulfate form for the run described below, and an additional 0.15 g (10%) of uranium was recovered, for a material balance of 98%.

The same resin bed, in the washed sulfate form, was loaded with uranium and washed with 75 ml of water as described above, with a breakthrough of 0.030 g (2%) of the uranium. Then the bed was eluted with 150 ml of 4 M $(NH_4)_2SO_4$ solution, as used by Abrams[6], at a flow rate of 9.375 ml/min. This step recovered 0.99 g (66%) of uranium; the elution curve is shown in Fig. 2. On standing, a yellow precipitate formed in the four most concentrated fractions (25 ml each). Finally, the bed was eluted with concentrated hydrochloric acid and water, as described in section 3.1, and an additional 0.475 g (32%) of uranium was recovered, giving a material balance of 98%.

It was found that nitric acid could be used instead of hydrochloric to decompose the carbonate with similar results on elution with water. This system seems less promising, however, since when the resin was initially in the nitrate form the uranium broke through on loading much earlier than when the resin was initially in the chloride or sulfate form.

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Figure 1

ELUTION OF URANIUM SORBED FROM SYNTHETIC SULFATE LEACH LIQUOR

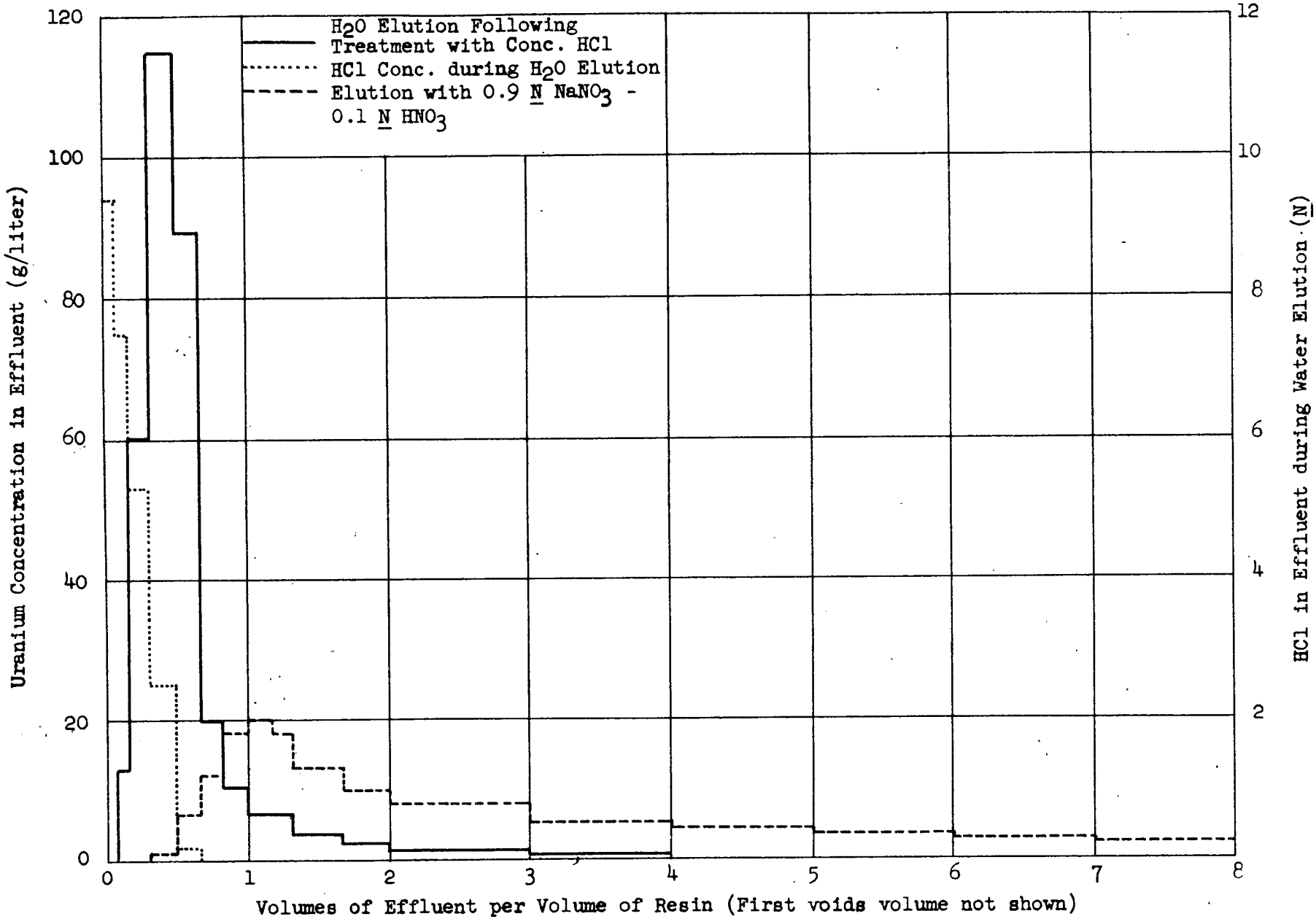
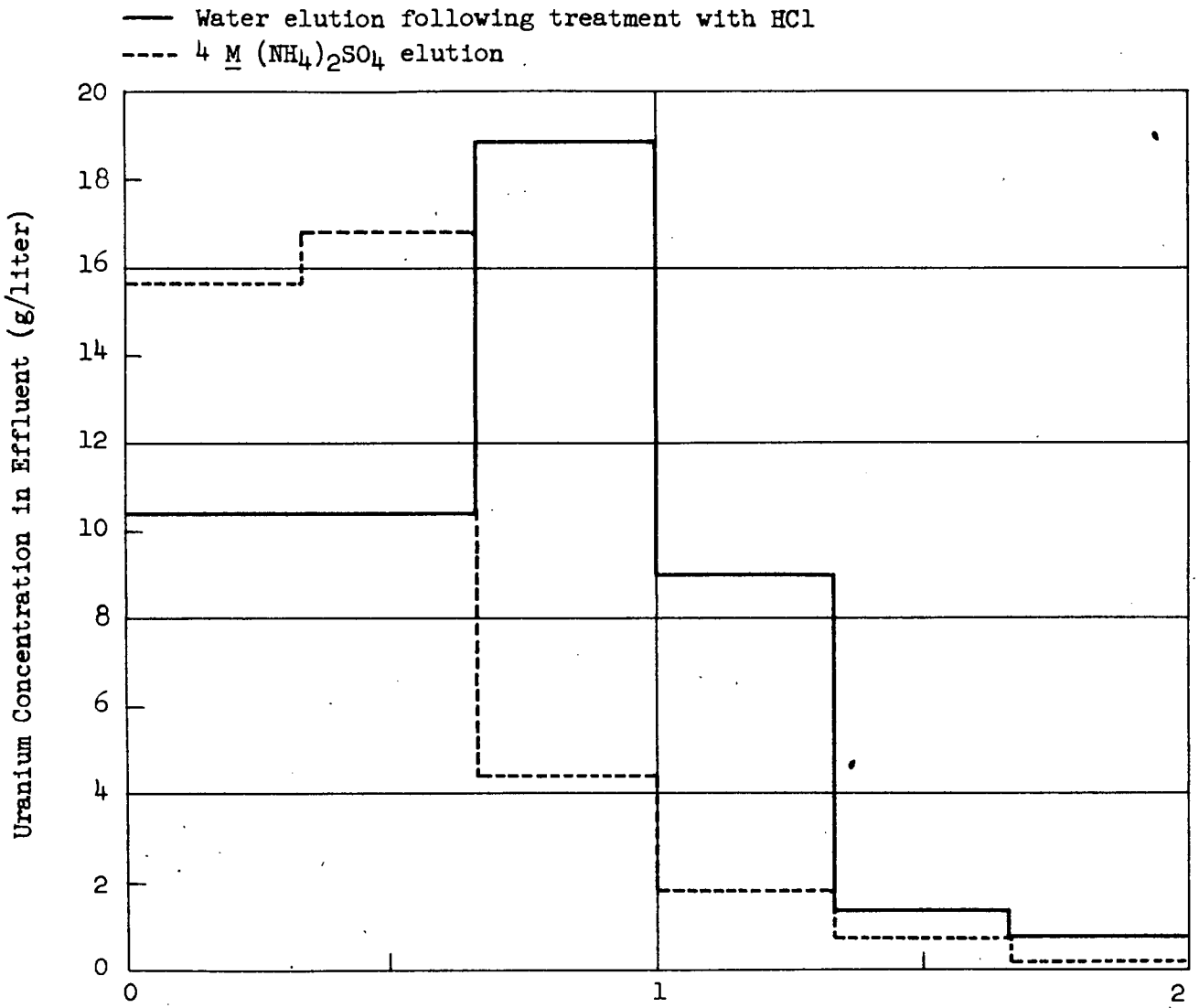


Figure 2

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