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RECOVERY OF URANIUM FROM 30 VOL % TRIBUTYL PHOSPHATE SOLVENTS

CONTAINING DIBUTYL PHOSPHATE

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RECOVERY OF URANIUM FROM 30 VOL % TRIBUTYL PHOSPHATE SOLVENTS  
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A number of solid sorbents were tested for the removal of uranium and dibutyl phosphate (DBP) from 30% tributyl phosphate (TBP) solvent. The desired clean uranium product can be obtained either by removing the DBP, leaving the uranium in the solvent for subsequent stripping, or by removing the uranium, leaving the DBP in the solvent for subsequent treatment.

Solid sorbents were tested in shake-outs, and promising candidates were examined in small packed columns. The variables examined included temperature and residence time of the solvent in contact with the solid sorbent. No method for removing DBP while leaving the uranium in the solvent was found. Both cation resins and diethylenetriamine pentaacetic acid (DTPA) deposited on glass beads preferentially removed the uranium, leaving the DBP in the solvent. The DBP could then be readily removed by a number of simple treatments, and the uranium could be recovered by elution with acidified TBP. Both hydroxide-form anion exchange resins and activated alumina (used with dry solvent) removed both uranium and DBP. It is possible that the DBP and uranium could be separately eluted from these sorbents, but it was not successfully tested. These results suggest a number of possible applications in solvent extraction systems.

Solvent cleanup practice in Purex plants is to scrub the contaminated tributyl phosphate (TBP) solvent with a sodium carbonate solution before recycle to the solvent extraction system. This procedure removes the acidic solvent degradation products, including dibutyl phosphoric acid (HDBP) and monobutyl phosphoric acid, and transfers the metallic contaminants to the aqueous phase as carbonate complexes.

Transfer of the metals that are complexed with DBP to the carbonate scrub solution makes their recovery difficult. If the value of the metals is sufficiently high, as for enriched uranium or plutonium, a process for removing the metals prior to such scrubbing may be useful. The desired treatment method would (1) use a solid sorbent to preferentially remove the DBP, leaving the uranium or plutonium in the solvent (this would allow direct recycle of the solvent); or (2) use a procedure which would separately remove both the DBP and uranium or plutonium, yielding a clean product. We prepared a series of solid sorbents which have potential for this separation, performed scouting tests with uranium solutions to determine which sorbents provided separations, and conducted tests in small packed columns using the promising sorbents.

## EXPERIMENTAL

### Expected Reactions

It is expected that, before reaction with a damp solid, the components of the organic phase will first have to distribute to the aqueous layer on the solid sorbent. Thereafter, the reactions with the sorbent will be the ones expected for the same components in the aqueous phase. In addition, if a component such as uranyl nitrate should react to form an inextractable

compound, the uranium would be trapped in the aqueous layer of the sorbent. An example would be reactions that replace the nitrates of uranyl nitrate with other anions such as hydroxide or carbonate; the resulting compounds would likely not be extractable. Sorbents that are active in the dry state (the principal example is activated alumina) may remove components directly from the solvent.

### Scouting Tests

The ability of a number of solid sorbents to remove uranium and DBP from 30% TBP in normal paraffin hydrocarbon (NPH) was investigated in small-batch equilibrations. A  $\sim 0.01$  M DBP solution was prepared by adding HDBP containing about 3.3 mol % monobutyl phosphoric acid to 30% TBP-NPH. This solution was then contacted with a uranyl nitrate solution containing 5 g of uranium per L ( $0.02$  M uranium) in water (pH = 3) to prepare a uranium-DBP test solution containing  $\sim 0.01$  M DBP and  $\sim 0.01$  M uranium. One-half of the uranium-DBP solution was dried by sparging with 1 volume of dry air per min per volume of solution for about 5 h at  $\sim 60^\circ\text{C}$ . This procedure has been shown to result in quite dry solvent (removal of  $>97\%$  of the water from water-saturated solvent) (1). It is expected that some solid sorbents, especially activated alumina, will have higher capacities if water is excluded. Most of the solid sorbents were tested by two methods: dried with dry solvent and damp with wet solvent. The dry sorbents were dried at  $\sim 100^\circ\text{C}$ , except for activated alumina that was dried at  $\sim 200^\circ\text{C}$ . The damp sorbents were stored in a "desiccator" with a layer of water in the bottom for several days before use. Complete saturation of sorbents with a high capacity for water may not have been

achieved; later tests with activated alumina exposed for longer periods gave poorer results than those from these scouting tests. Some sorbents required preparation; these procedures were as follows:

Preparation of solid sorbents - Literature information (1) indicates that DBP can be removed from nitric acid solutions containing uranium by extracting the DBP with 2-ethylhexanol and that the extraction occurs by hydrogen bonding of the HDBP to the hydroxyl of the alcohol. The extraction is most effective when the nitric acid concentration is greater than 3.5 M. Sucrose and cellulose, compounds with numerous hydroxyl groups, were tested for their ability to remove DBP. Sucrose was deposited on 12-28 mesh silica gel by dissolving 100 mg of sucrose in 3 mL of H<sub>2</sub>O, soaking the silica gel in the solution, draining the solution, and drying the solid. The sucrose-coated silica gel was tested with a solvent of low acidity and with a solvent equilibrated with 1 or 4 M HNO<sub>3</sub>. Cellulose (adjustable pipette filters) was tested with a solvent of low acidity and a solvent equilibrated with 4 M HNO<sub>3</sub>.

It is known that iron forms a relatively strong DBP complex. A cation exchange resin (BIO-RAD AG MP-50) was loaded with ferric iron, the resin was treated with ammonium hydroxide to precipitate the iron, and the resin was washed with H<sub>2</sub>O to remove the excess ammonia.

Diethylenetriamine pentaacetic acid (DTPA) (0.216 g) was dissolved in 10 mL of H<sub>2</sub>O by increasing the pH to ~7 to increase the solubility; 1 mL of dried Dowex 21K anion resin in the hydroxyl form was then added, soaked overnight, and then drained. The pH of the solution increased to 7.70 after contact with the resin.

Zirconium oxynitrate (0.5 g) dissolved in 5 mL of H<sub>2</sub>O was contacted with 2 g of Norton Z-900 molecular sieve over the weekend; the sieve was drained, and rinsed with 5 mL of H<sub>2</sub>O.

The anion exchange resins, which were obtained in the chloride form, were converted to hydroxide form by passing 1 M NaOH through a packed column of the resin until a negative chloride result was obtained by a silver nitrate test. The resin was then rinsed with water until the effluent water was near neutral. The nitrate form was produced by passing 1 M NaNO<sub>3</sub> through a bed of hydroxide-form resin, followed by rinsing with water. Dowex 21K anion-exchange resin in the carbonate/bicarbonate form was prepared by suspending the hydroxide-form resin in water and sparging with CO<sub>2</sub> for about 1 h. The pH of the water was decreased from an initial reading of 8 to 9 to about 7 at the end of the sparging.

The cation exchange resins were received in the H<sup>+</sup> form and were used as-received in most tests.

Scouting test procedure - Either 1 g (most solids) or 1 mL (ion exchange resins) of solid was contacted with 10 mL of the appropriate solvent (dry solvent with dry sorbent, wet solvent with damp sorbent) by shaking for 1 min three times over a 10-min period. The transfer of uranium color from the organic phase was noted. A portion of the organic phase was stripped with water; if the DBP had been removed leaving the uranium in the organic phase, the uranium would strip with water. In those cases where the uranium was quantitatively removed by contact with the solid sorbent, the colorless solvent was contacted with a uranyl nitrate solution in water. The presence of HDBP in the solvent causes extraction of uranium.

Solid sorbents tested - The solid sorbents examined were Dowex 50W-X4 [50-100 mesh,  $H^+$  form (Bio-Rad Laboratories, Richmond, Calif.)], Duolite CS-100 [20-50 mesh,  $H^+$  form (Diamond Shamrock Chemical Co., Cleveland, Ohio)], Dowex 21K anion exchange resin [50-100 mesh,  $OH^-$  form (Bio-Rad Laboratories, Richmond, Calif.)], BIORAD AG MP-1 anion exchange resin [20-50 mesh  $OH^-$  form (Bio-Rad Laboratories, Richmond, Calif.)], Amberlyst A-26 anion exchange resin [14-50 mesh,  $OH^-$  form (Rohm and Haas Co., Philadelphia, Penn.)], Dowex 1-X4 anion exchange resin [50-100 mesh,  $Cl^-$  form (Bio-Rad Laboratories, Richmond, Calif.)], Amberlyst A-26 anion exchange resin in the  $Cl^-$  form, Dowex 21K anion exchange resin in the  $Cl^-$  form, BioRad AG MP-1 anion exchange resin in the  $NO_3^-$  form, Dowex 21K coated with DTPA (Prepared by and obtained from D. O. Campbell and S. R. Buxton, Oak Ridge National Laboratory), Norton Z-900 zeolite in the  $Na^+$  form [0.16-cm-diam. by ~0.6-cm-long cylinders; pore size, ~7 Å (Norton Co., Worcester, Mass.)], zirconium loaded on Norton Z-900 molecular sieve, silica gel [12-28 mesh, grade 408 (Fisher Scientific Co., Fairlawn, N.J.)], sucrose on the same silica gel, Florex attapulgite clay [Florex AA-LVM, 45-60 mesh (Floridin Co., Pittsburgh, Penn.)], hydrous zirconium oxide [100-200 mesh (formerly available from Bio-Rad Laboratories, Richmond, Calif.)], activated alumina [Alcoa F-1 type, 60-120 mesh (Aluminum Co. of America, Pittsburgh, Penn.)], and cellulose from automatic pipette filters.

Results of scouting tests - The only solids that showed promise for the removal of uranium and/or DBP were the Dowex cation exchange resins in the  $H^+$  form or loaded with iron, anion exchange resins in the hydroxyl or carbonate/bicarbonate forms, and activated alumina. The ion exchange

resins must be used damp. The anion exchange resins removed both uranium and DBP, while the cation exchange resin removed only the uranium. The cation resin loaded with iron had less capacity than the as-received resin; it appears that the iron was not effective, but occupied some of the sorption sites. Note that the removal of the DBP after the removal of the uranium and the recovery of the uranium from the cation resin should be relatively easy. The scouting tests indicated that activated alumina could be used either dry or damp, but later column tests showed that the capacity for both uranium and DBP are reduced by the presence of water.

The promising solid sorbents were then tested in small packed columns.

#### Analysis of Solvents for Uranium and DBP

Uranium in the solvent was analyzed by stripping the uranium (plus any DBP and nitric acid) from the solvent with an equal or greater volume of 0.5 M ammonium carbonate. This stripping produced the uranyl carbonate complex in the aqueous phase, which is determined spectrophotometrically using the absorbance at 450.4 nm. The absorbance was found to be linear, with concentrations up to 0.01 M uranium. The molar concentration in the aqueous phase is given by the absorbance (1-cm path length) divided by 25.1. The molar absorptivity is determined from uranium standards in the same spectrophotometer used for the analyses (Model 200, Hitachi Co., Tokyo, Japan). Under most conditions, uranium forms a 1:1 complex with DBP in TBP solutions (3). The fact that a 0.01 M HDBP solution extracted only about 0.01 M uranium in the current tests is in agreement with this. Extraction of uranium by TBP and DBP-TBP solutions



was investigated to develop a simple method for analyzing solvents for DBP. A 0.02 M aqueous uranyl nitrate solution with a pH of ~3 was contacted with an equal volume of clean 30% TBP. The uranium distribution coefficient was 0.0526. Uranium distribution coefficients were then determined for organic phases containing 0.001, 0.0025, 0.005 and 0.01 M DBP. Assuming the uranium-DBP complex was 1:1, the free DBP was calculated for each case. Figure 1 shows a plot of the distribution of uranium to the DBP complex (extracted uranium corrected for extraction by TBP; distribution coefficient of 0.0526) vs the free DBP concentration. The plot is approximately linear, with a slope of 314. An unknown solvent can be contacted with a standard uranyl nitrate solution, and the extracted uranium can be determined; the correlation given in Fig. 1, plus the extraction of uranium by TBP, allows the calculation of the DBP content. When the organic phase itself initially contains uranium, its concentration must be determined to know the total uranium in the system. To determine both the uranium and DBP in a 30% TBP sample, the solution is divided into two parts. The uranium in one portion is determined by stripping with ammonium carbonate solution and determining the absorbance. The other portion is contacted with an equal volume of the standard 0.02 M uranyl nitrate solution. This solution is stripped with ammonium carbonate, and the uranium is determined by absorbance. The DBP concentration is then determined by the following BASIC program:

```

10 INPUT "WHAT IS THE ABSORBANCE OF THE FIRST CARBONATE
    STRIP";A1
20 INPUT "WHAT IS THE ABSORBANCE OF THE CARBONATE STRIP
    AFTER URANIUM EQUILIBRATION";A2
30 UT=0.0526*(0.02+A1/25.1)

```

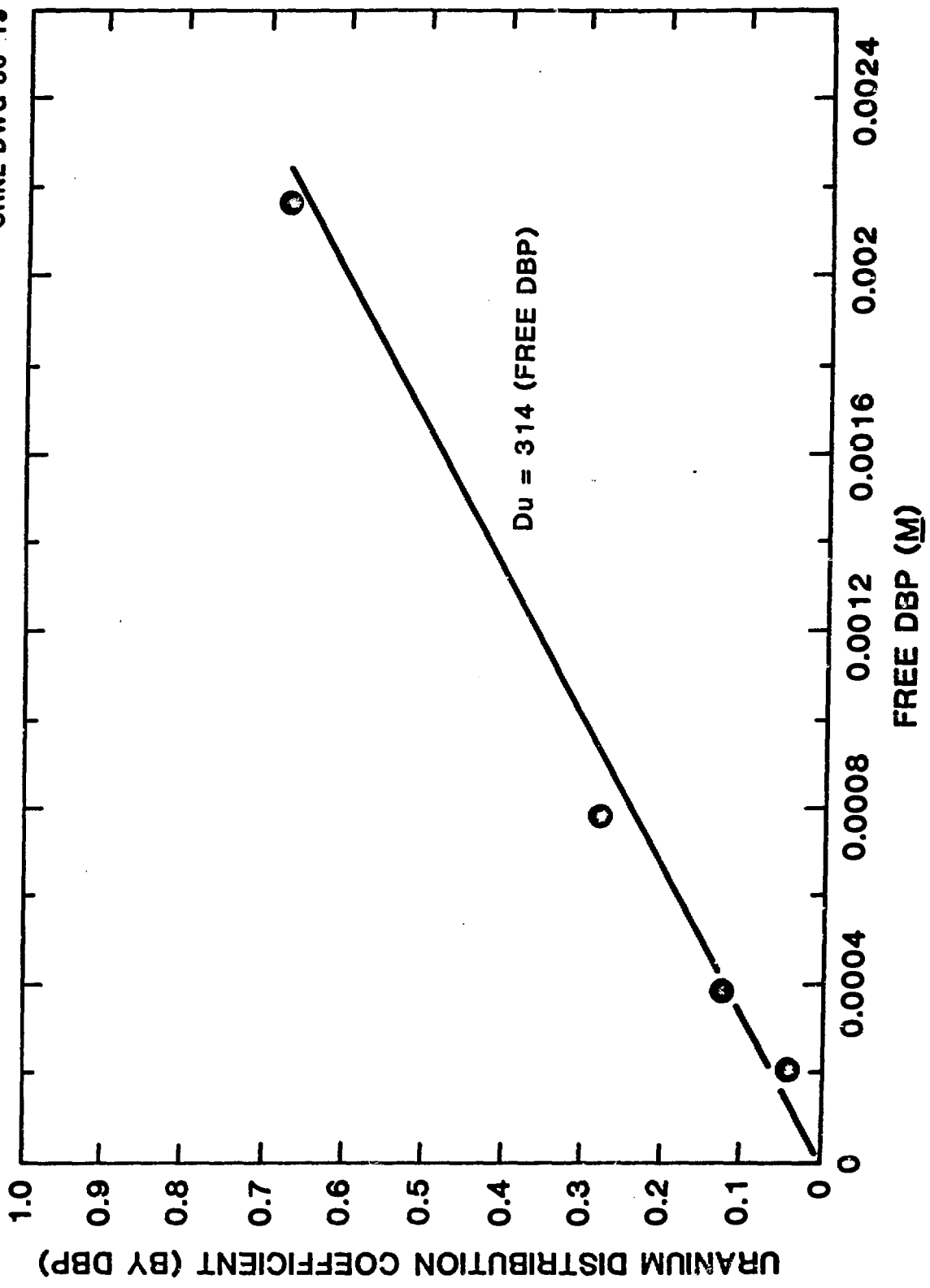


Fig. 1. Uranium extraction by HDBP. The quantity of uranium extracted was corrected by subtraction of uranium extracted by TBP. Free DBP is DBP not complexed with uranium.

```

40 CD=(A2/25.1-UT)/(0.02+A1/25.1-A2/25.1)/314-UT+A2/25.1
50 PRINT "THE DBP CONC. IS ";CD;" MOLAR"
60 PRINT:PRINT:
70 GOTO 10

```

Note that this analytical method may only be used where the nitric acid and nitrates other than uranyl nitrate are near zero.

### Small-Column Tests

The column used in the tests is shown in Fig. 2. The bed was contained in an 8-mm-OD, 6-mm-ID glass tube with a jack-leg and could be immersed in a beaker of heated water for elevated temperature tests. In all cases, the solvent passed through the beds was intended to be  $\sim 0.01$  M in both uranium and DBP (in one test the DBP concentration was found to be  $\sim 0.015$  M in the feed) and was prepared as described for the scouting tests.

Loading 20-50 mesh Bio-Rad AG MP-50 - Small-column tests used 1 mL of 20-50 mesh BIO-RAD AG MP-50 macroporous cation resin (H<sup>+</sup> form) to treat  $\sim 1$  mL/min of solvent containing  $\sim 0.01$  M of uranium and DBP. Tests were conducted at 22° (duplicates) and 52°C. Figure 3 shows effluent concentrations of the two loading tests at 22°C. Significant removal of uranium and no detectable removal of DBP were found. Figure 4 shows the uranium and DBP concentrations in the column effluent in the test at 52°C; again, uranium loaded without DBP loading. Uranium removal half-times were  $\sim 20$  s at 52°C and  $\sim 40$  s at 22°C. The apparent capacity of the resin was  $\sim 0.35$  mmol of uranium per mL of resin at 22°C and 0.56 mmol of uranium per mL of resin at 52°C (stated capacity is 1.86 meq/mL). A

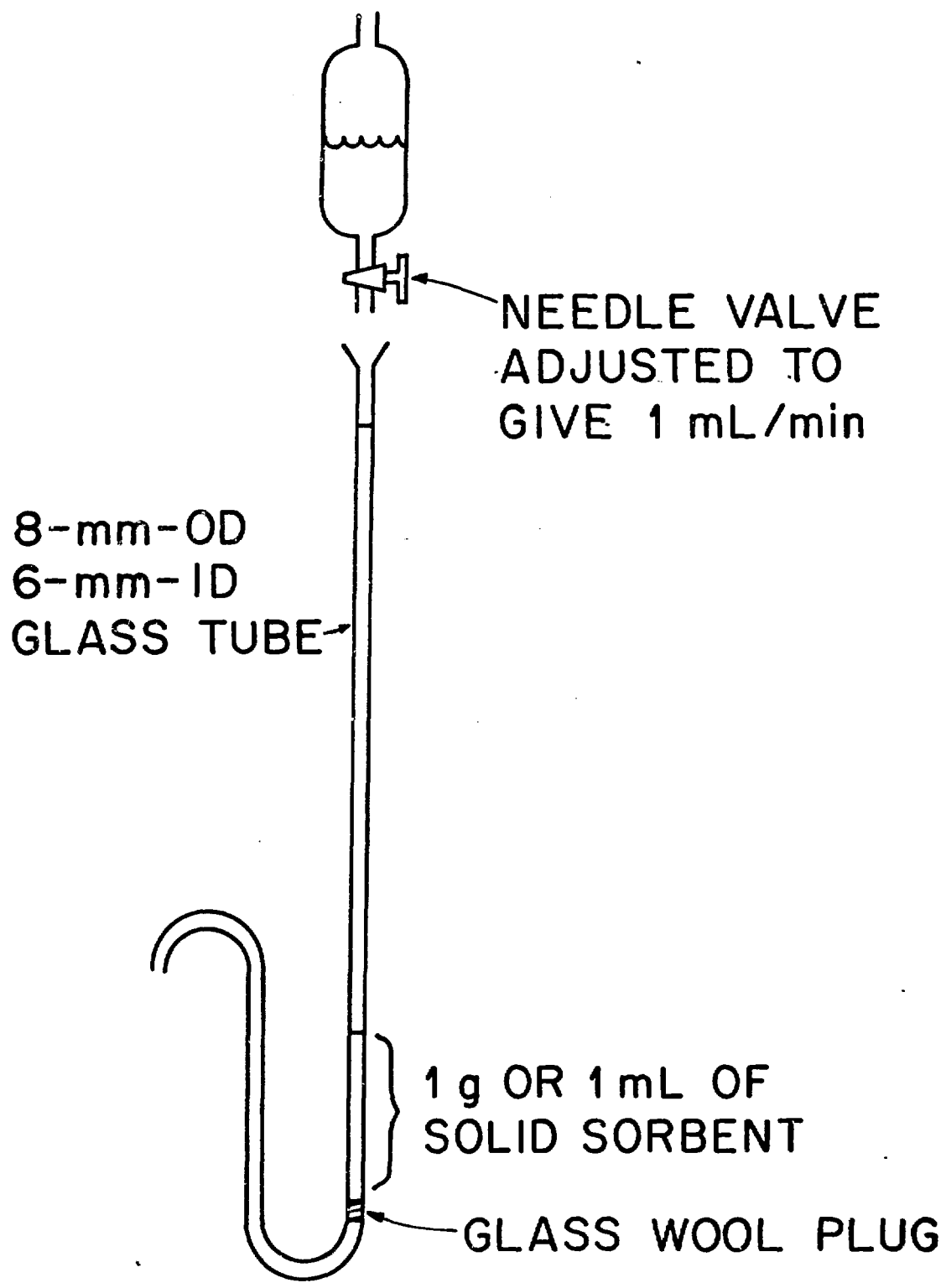


Fig. 2. Apparatus used in small-bed tests.

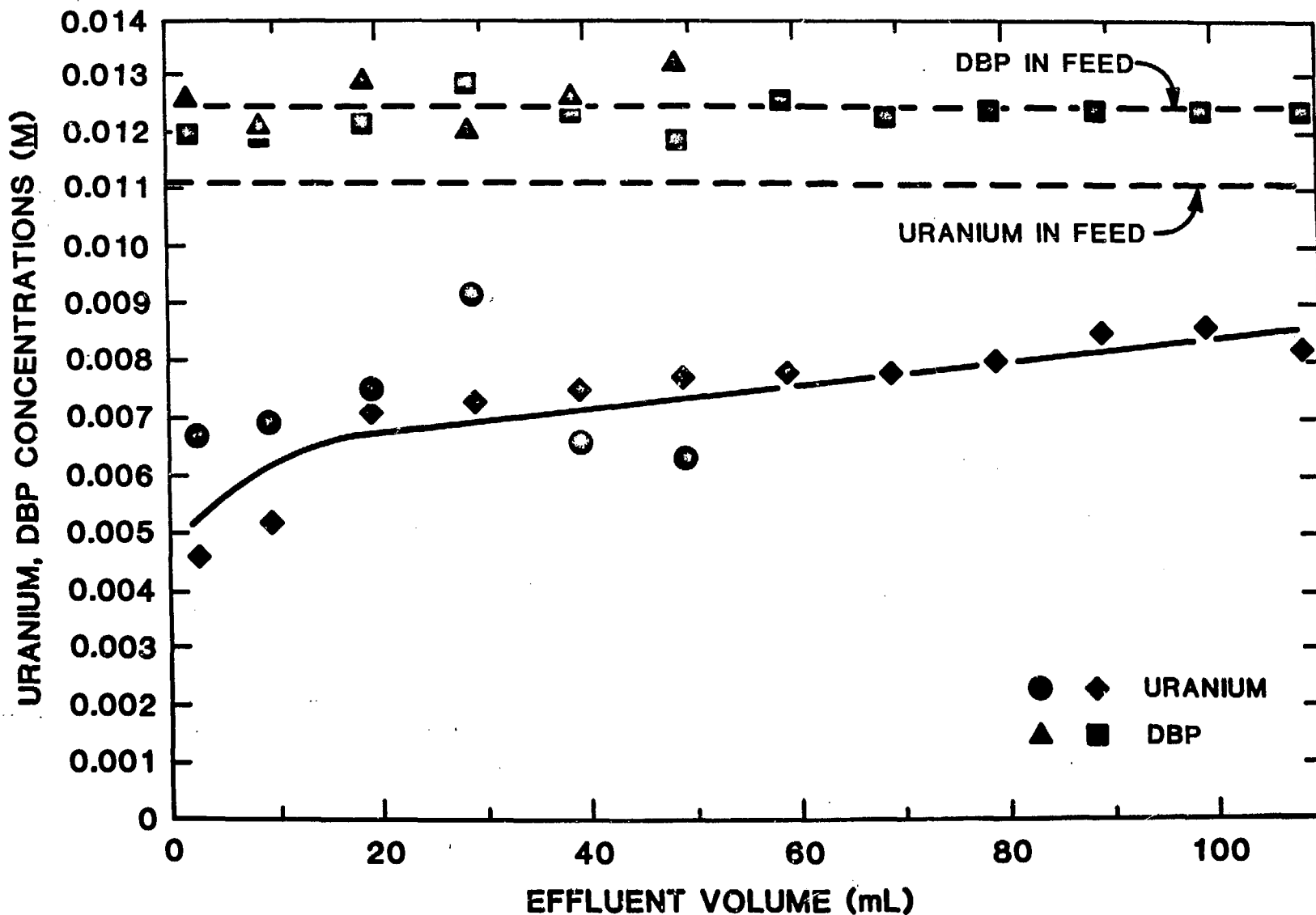


Fig. 3. Effluent uranium and DBP concentrations from duplicate test loadings of 1 mL of Dowex 50W-X4 cation exchange resin ( $H^+$  form) at 22°C. The flow rates of the solvent were 1 mL/min.



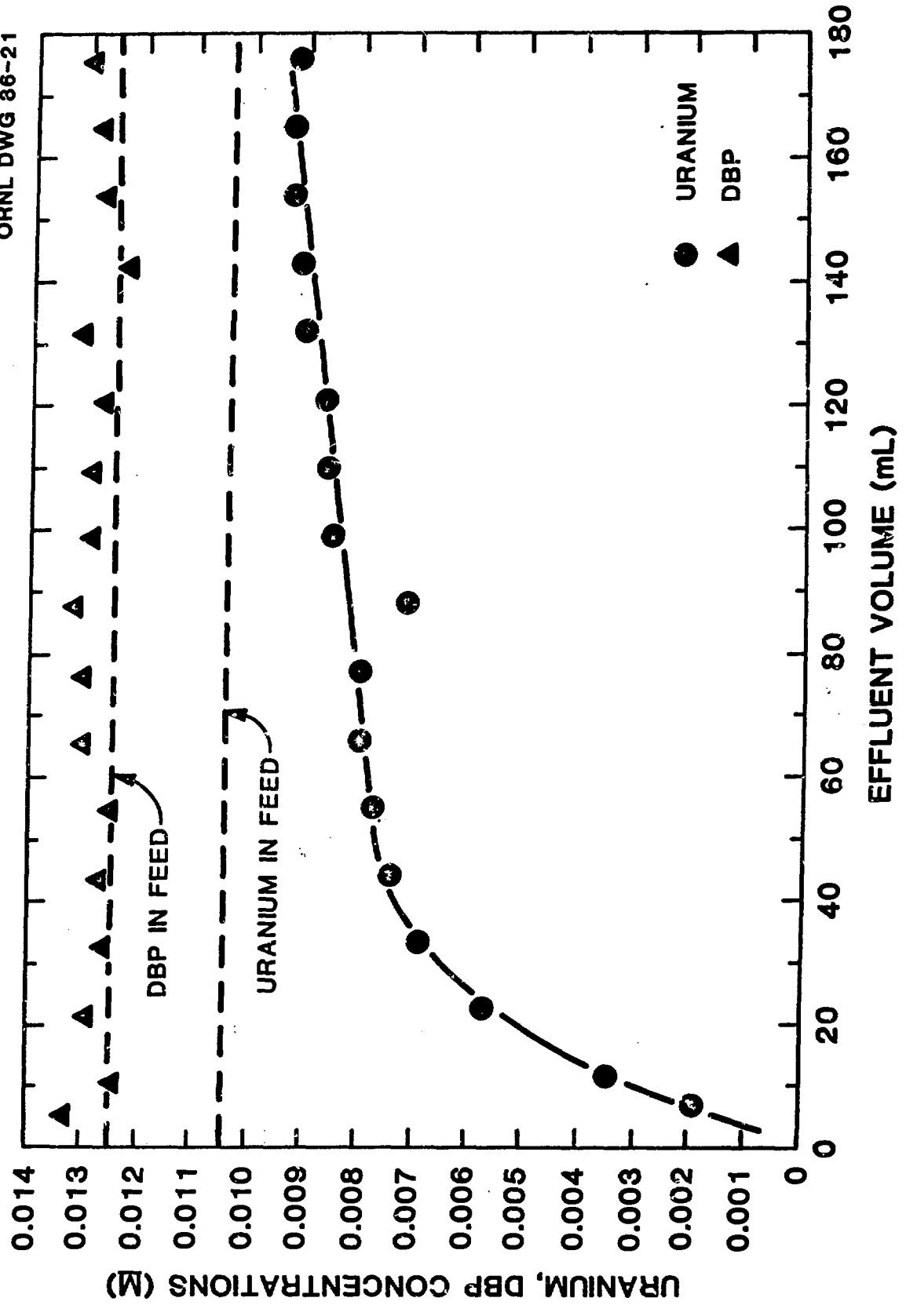




Fig. 4. Effluent uranium and DBP concentrations from a test loading of 1 mL of Dowex 50W-X4 cation exchange resin ( $H^+$  form) at  $52^{\circ}C$ . The flow rate of the solvent has 1 mL/min.

later test repeated the loading of the cation exchange resin at 50°C (Fig. 5). In this case the volume of sorbent was decreased to 0.75 mL, and the flow rate was decreased to 0.5 mL/min. This decrease in volume and flow rate gives an increase of 50% in the residence time of the solvent in the sorbent bed. DBP was not removed. The uranium removal efficiency was significantly improved over that in the earlier tests — the half-time was reduced to ~10 s, and the apparent capacity of the bed was increased to ~1 mmol of uranium per mL of resin; this value is about the theoretical capacity of the resin. In a larger bed where the residence times are larger relative to the half-times for removal, the sensitivity to flow rate may be less.

Eluting 20-50 mesh Bio-Rad AG MP-50 - Elution of the uranium loaded in the 52°C test was approximately 50% complete by the passage of 80 mL of 30% TBP containing 0.06 M HNO<sub>3</sub> at a flow rate of 1 mL/min at 22°C (Fig. 6). Uranium elution at 22°C from loaded cation resin was tested in duplicate using 30% TBP which had been equilibrated with 2 M HNO<sub>3</sub> (0.36 M HNO<sub>3</sub> in the 30% TBP) (Fig. 7). Essentially all the mobile uranium had been removed with the passage of 80 mL of solvent. The increased acidity of the solvent significantly increased the removal rate; a further increase by operating at elevated temperature should also be possible.

Loading 60-120 mesh Alcoa F-1 activated alumina - Columns containing 1 mL of damp (equilibrated with water-saturated air for about 6 weeks) and 1 mL of dry 60-120 mesh Alcoa F-1 activated alumina were tested at 22°C for the removal of uranium and DBP from damp and dry solvent (dried by sparging with air at 60°C), respectively. The column capacities were

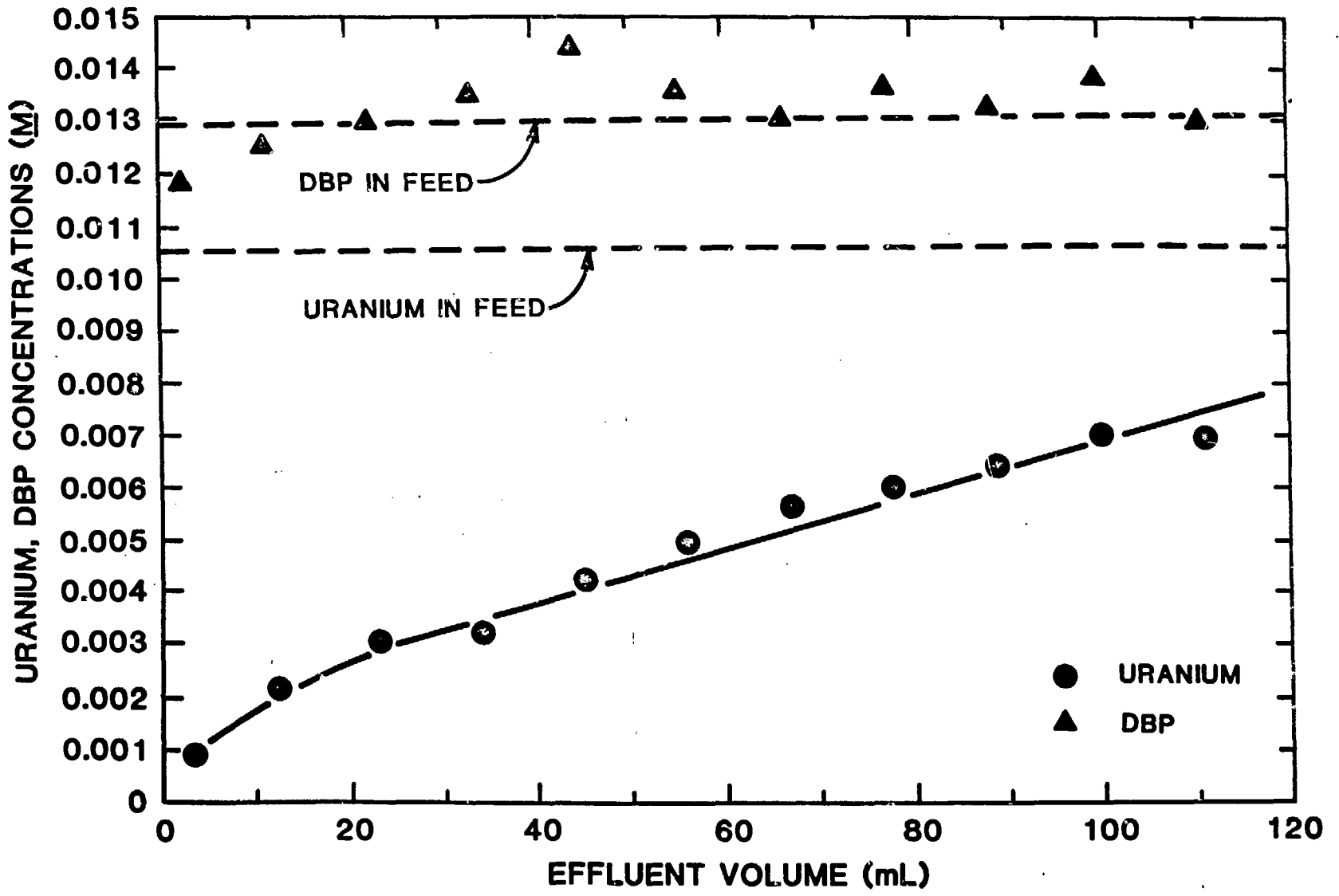


Fig. 5. Effluent uranium and DBP concentrations from a test loading of 0.75 mL of Dowex 50W-X4 cation exchange resin ( $H^+$  form) at 50°C. The flow rate of the solvent was 0.5 mL/min.

ORNL DWG 86-25

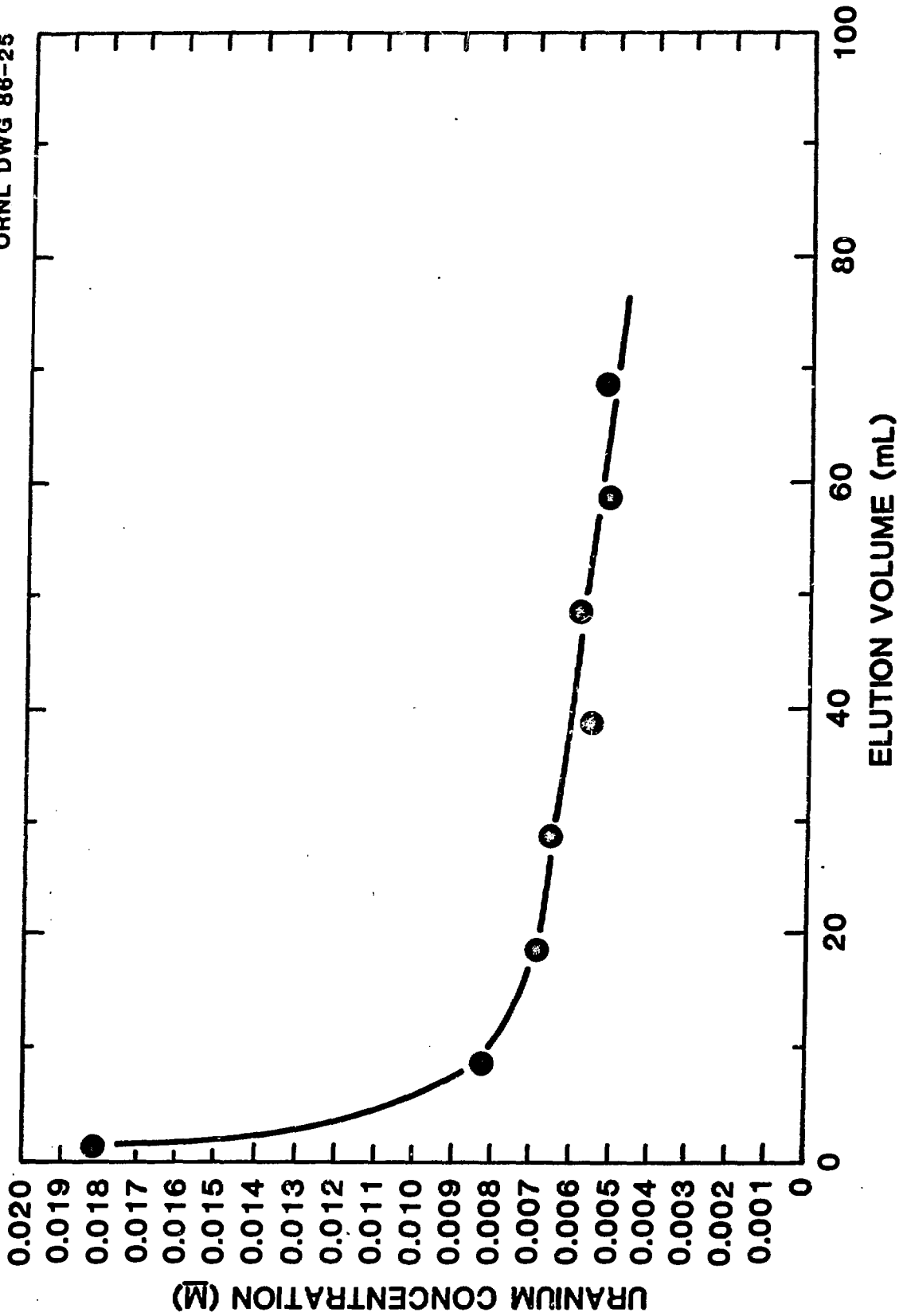


Fig. 6. Elution of uranium from 1 mL of Dowex 50W-X4 cation exchange resin ( $H^+$  form) by 30% TBP solvent containing 0.06 M  $HNO_3$  at 22°C. The solvent flow rate was 1 mL/min.

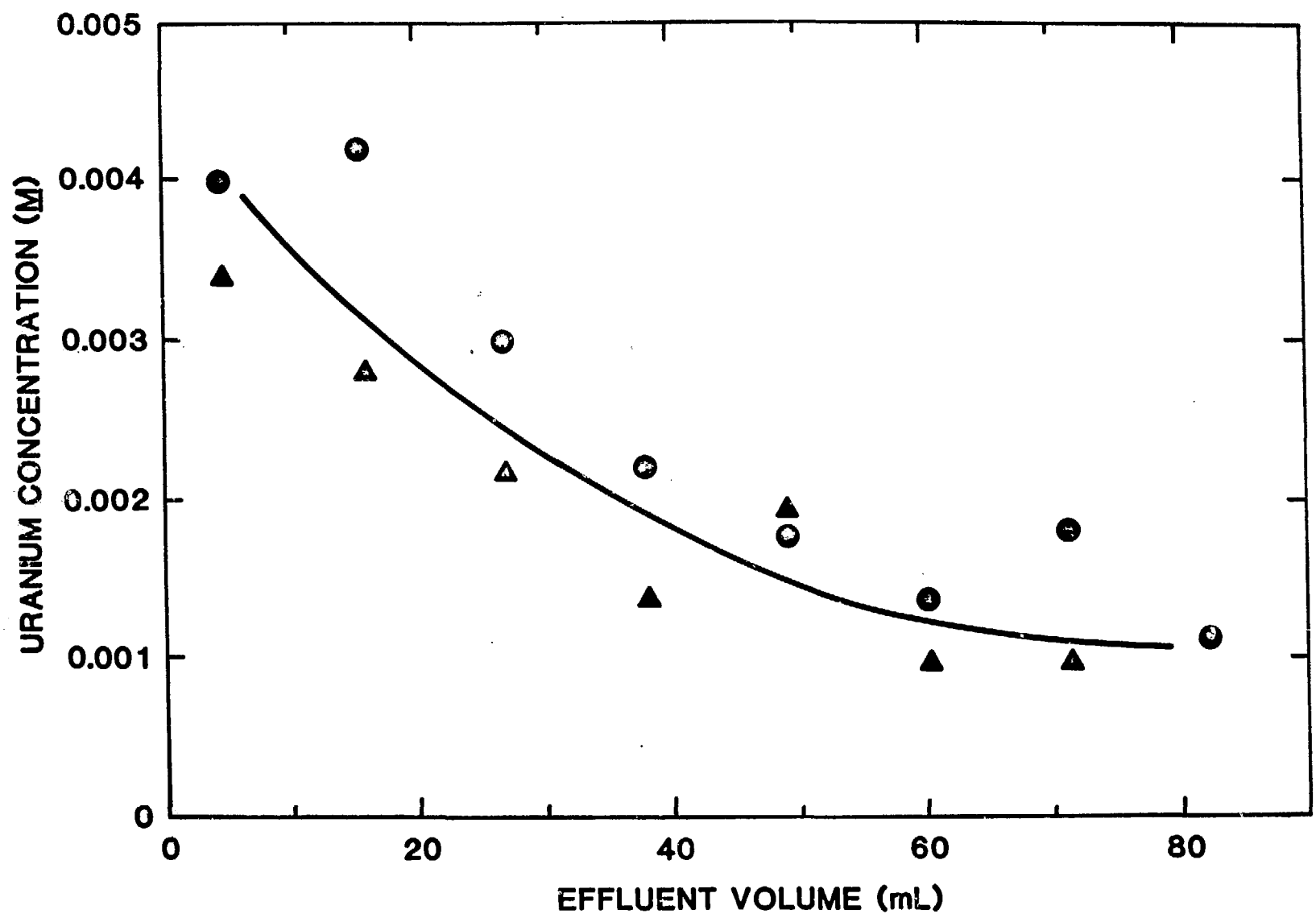




Fig. 7. Duplicate tests of elution of uranium from 1 mL of Dowex 50W-X4 cation exchange resin ( $H^+$  form) at  $22^\circ C$  with 30% TBP solvent which had been equilibrated with an equal volume of 2 M  $HNO_3$ . The flow rate of the solvent was 1 mL/min.

more than twice as great with dry alumina and dry solvent as compared with damp solvent and damp alumina. Uranium was found to load preferentially with essentially no loading of DBP. Figure 8 shows the cumulative loadings of uranium and DBP for the dry sorbent and solvent test. Both uranium and DBP were loaded in approximately the same ratio as their ratio in the solvent (solvent ratio, DBP/uranium = 1.17; sorbent ratio = 1.24).

Eluting 60-120 mesh Alcoa F-1 activated alumina - Uranium was eluted from loaded activated alumina using 30% TBP solvent containing 0.36 M  $\text{HNO}_3$ . These results are shown in Fig. 9. The uranium was more easily eluted than from the cation exchange resin, with an initial concentration in the solvent about twice that found when eluting the cation exchange resin. The volume required to elute the resin was also reduced by about one-half.

Loading a column containing DTFA on 3-mm glass beads - A column of 3-mm glass beads coated with ~0.2 g of DTPA (pH adjusted to ~7) was tested for removal of uranium and DBP from the solvent. At about 40 mL of effluent, the temperature of the column was increased from 22° to 50°C. At the lower temperature the loading of uranium and DBP was minimal; at the higher temperature the loading of uranium was significantly increased. This material appears to be usable for preferential removal of uranium from the uranium-DBP mixture. Removal of the loaded DTPA from the column is very simple since it is water-soluble. Passage of a small amount of  $\text{H}_2\text{O}$  (10-20 column volumes) through the column removed all the coating, with its uranium, from the column.

ORNL DWG 86-28

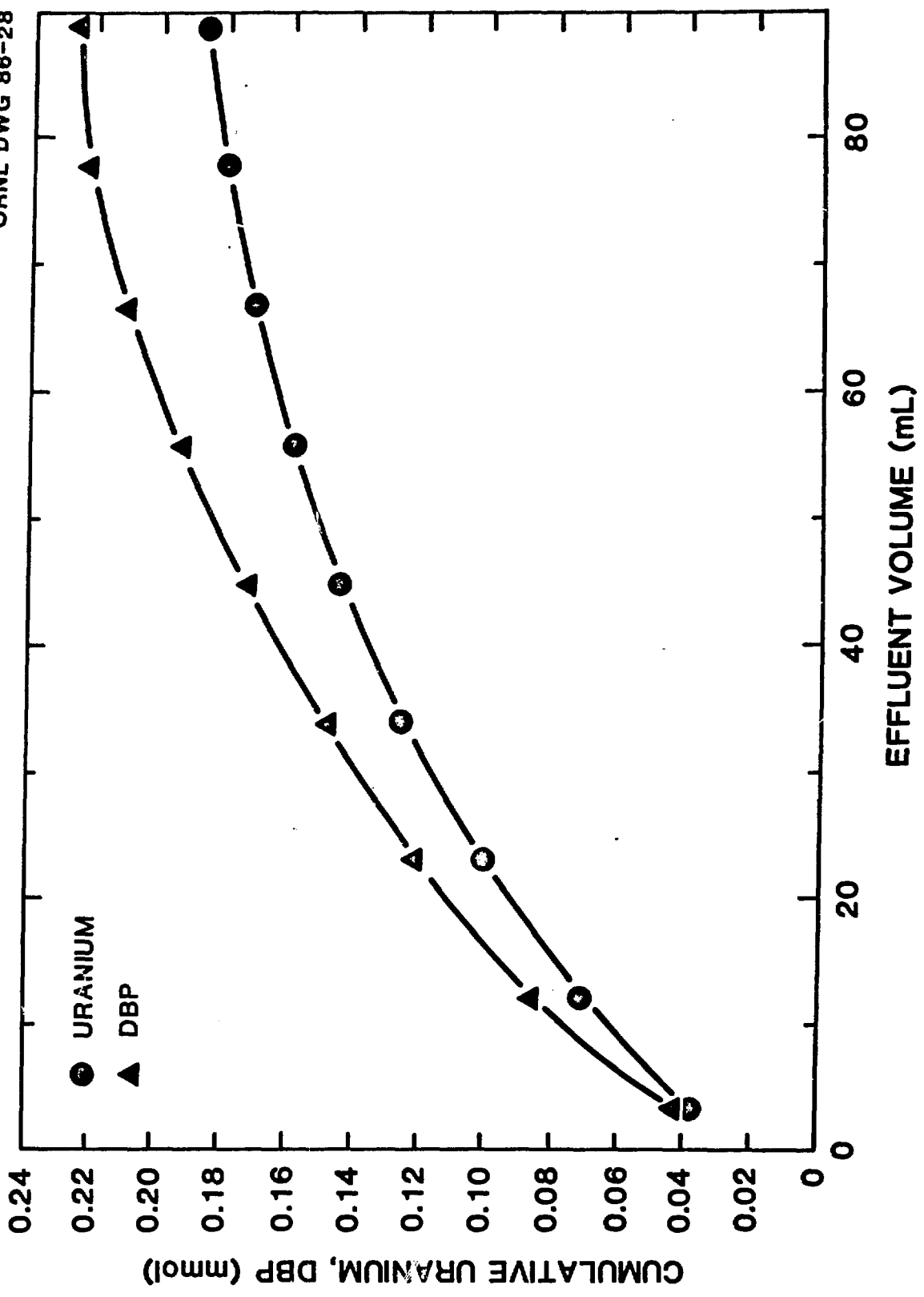


Fig. 8. Cumulative loadings of uranium and DBP on 1 mL of dry, activated alumina at 22°C. The dry solvent flow rate was 1 mL/min.

ORNL DWG 86-29

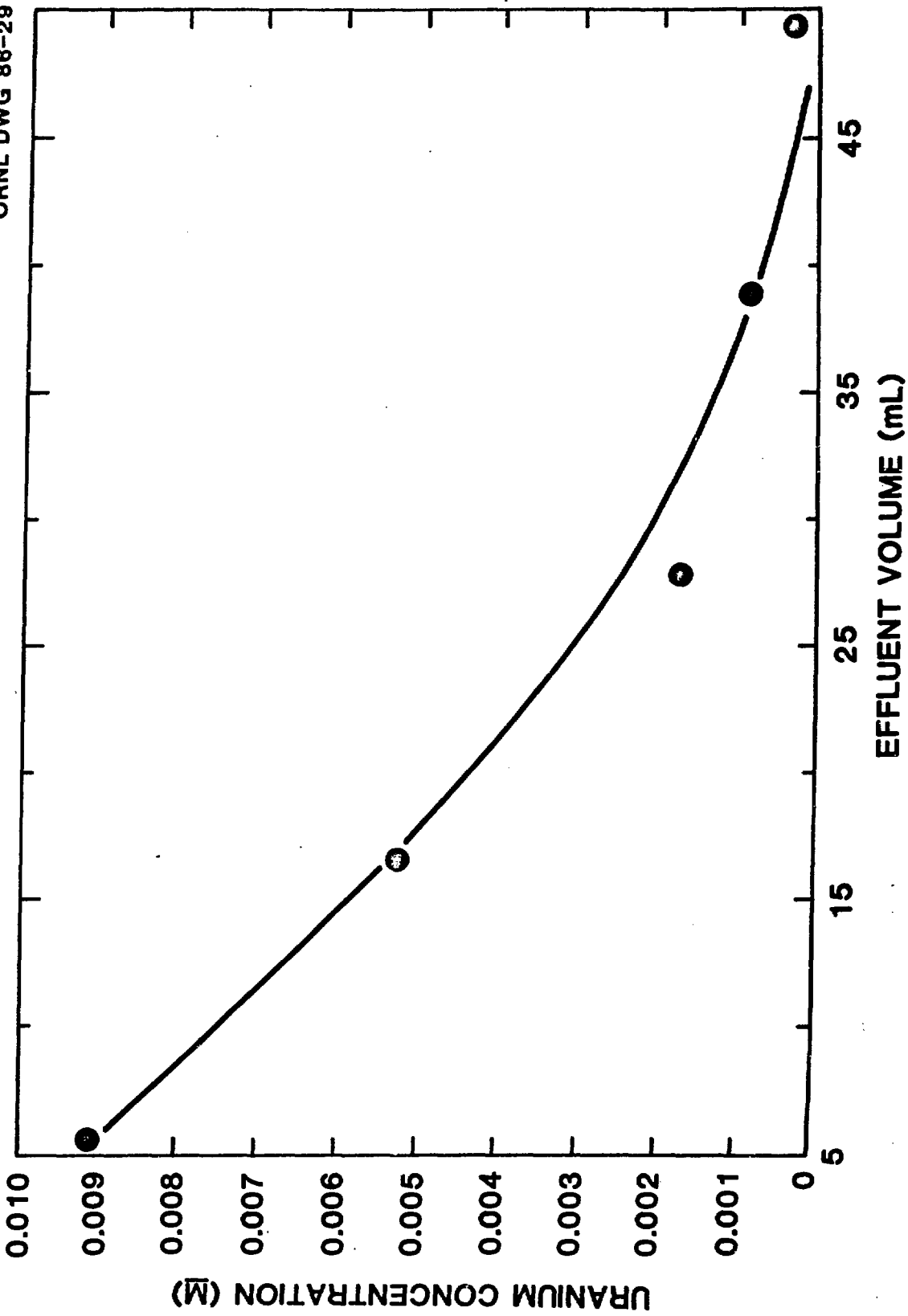


Fig. 9. Uranium removal from activated alumina by 30% TBP solvent which was equilibrated with an equal volume of 2 M HNO<sub>3</sub>. The solvent flow rate was 1 mL/min.

Loading Dowex 21K (hydroxide form) - A solvent containing  $\sim 0.01$  M uranium and  $\sim 0.015$  M DBP was used to load a hydroxide-form anion resin. Both materials were loaded in about the same ratio as their ratio in the solvent.

Separation of uranium and DBP during elution - It may be possible to separately elute uranium and DBP from a sorbent that loads both components such as hydroxide-form anion exchange resins or activated alumina. HDBP can be extracted from acidified aqueous solutions containing both uranium and DBP by 2-ethylhexanol (2). Elution of the DBP by 2-ethylhexanol containing  $\sim 0.7$  M  $\text{HNO}_3$ , followed by elution of the uranium by 30% TBP containing  $\sim 0.6$  M  $\text{HNO}_3$ , was attempted. The uranium stayed on the hydroxide-form anion exchange resin and the activated alumina during the treatment with acidified 2-ethylhexanol and was removed by the treatment with acidified TBP. Both of these observations were visual; analyses for the components in the eluates were not successful.

#### POSSIBLE APPLICATIONS

The major potential use of the cation exchange system would be to prevent the transfer of valuable metals (uranium and plutonium) to the solvent cleanup system, where they are more difficult to recover. These metals will be present in the solvent at a low level because of the strong complexes formed with DBP; low-acid stripping does not remove metals below about a 1:1 mole ratio to the DBP. Uranium and plutonium are the major metals present which form strong complexes with DBP; the plutonium complex is much stronger than the uranium complex (4). If the fuel being processed had a high uranium:plutonium ratio, as in light-water reactor fuel,

the quantity of plutonium held by the DBP would be quite small; however, in the case of breeder fuel the higher plutonium content would result in more retention of plutonium than uranium. It is possible that the uranium and plutonium could be removed from the solvent by a cation exchange resin from which they could be easily recovered; the actual behavior of plutonium is not known.

Scrubbing with sodium carbonate solutions has been observed to produce emulsions partly because of the presence of cations which form low-solubility complexes with carbonate; these include zirconium and plutonium (5,6). Treatment of the solvent with a cation exchange resin to remove the cations that cause emulsions could significantly improve the operation of the solvent cleanup system. In fact, in the absence of cations, the solvent could be scrubbed with a basic solution without the necessity of a complexing anion such as carbonate. Weak bases such as hydroxylamine hydrate, which can be readily decomposed into innocuous gases with a significant reduction of solid wastes, would be attractive.

The two applications discussed above assume that all cations can be removed from DBP solutions by cation exchange resins. Only the removal of uranium has been demonstrated; additional experiments should be undertaken to examine the behavior of zirconium and plutonium.

#### CONCLUSIONS

The tests performed show that it is relatively easy to preferentially remove uranium from solvents containing uranium and DBP, but quite difficult to remove DBP preferentially. The current methods could be used by



removing the uranium (as by a cation exchange resin) and then using either an anion exchange resin in the hydroxyl form or a conventional treatment with a basic solution to remove the DBP. Treatment of a solvent with a cation exchange resin could be useful for recovery of valuable metals from solvents containing DBP and might be used to remove cations before scrubbing a solvent with a basic solution to minimize emulsion formation.

#### ACKNOWLEDGMENTS

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Fig. 1. Uranium extraction by HDBP. The quantity of uranium extracted was corrected by subtraction of uranium extracted by TBP. Free DBP is DBP not complexed with uranium.

Fig. 2. Apparatus used in small-bed tests.

Fig. 3. Effluent uranium and DBP concentrations from duplicate test loadings of 1 mL of Dowex 50W-X4 cation exchange resin ( $H^+$  form) at 22°C. The flow rates of the solvent were 1 mL/min.

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