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THE RECOVERY OF URANIUM AND PLUTONIUM FROM STAINLESS STEEL SULFATE DECLADDING SOLUTIONS BY ION EXCHANGE

W. J. Neill
I. R. Higgins

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

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ABSTRACT

A process has been developed on a laboratory scale for the recovery of plutonium, by cation exchange resin treatment, and uranium, by anion exchange treatment, from a stainless steel decladding solution. The plutonium was recovered by treatment with Dowex 50 cation resin after diluting the decladding solution to 0.5 M $SO_4^{=}$ concentration. The plutonium product, containing >99% of the plutonium, was eluted with nitric acid and contained 4% of the stainless steel and <0.01 M sulfate ion. The uranium was recovered by passing the plutonium-free decladding solution through Dowex 1 anion resin. More than 99% of the uranium, contaminated with <0.01% of the stainless steel components, was recovered.

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1.0 INTRODUCTION

This study investigates the possibility of a simple recovery by ion exchange of uranium and plutonium from stainless steel decladding solutions. The general acceptance of heterogeneous fuel elements for power reactors suggests heterogeneous methods of processing. A solvent extraction process designed to separate unburned fuel and fission products may be greatly simplified if the bulk ions, derived from stainless steel, are removed initially. In practice this attractive method of processing heterogeneous fuels is marred by the dissolution of some uranium and plutonium from the core, above permissible loss limits, in the decladding process.

Since uranium and plutonium have a high and almost selective affinity for resins in sulfate solutions, ion exchange is an attractive method for recovering these metals and for converting them to the nitrate form for further solvent extraction purification. Fixed-bed ion exchange is recommended because of equipment simplicity and because only small quantities of uranium and plutonium are involved. Ion exchange resin damage from radiation exposure would be minimized since only trace levels of fission products and induced stainless steel activity would be expected.

Stainless steel clad UO_2 fuels look especially attractive from a decladding standpoint. In the Sulfex Process[1] decladding of an unirradiated Yankee Atomic Fuel element less than 0.1% of the total uranium was present in the decladding solution. In the decladding of Yankee Atomic Fuel pins, irradiated for 250 Mwd and decayed for 72 days, 0.023% of the uranium and 0.06% of the plutonium appeared in the decladding solution.[2] The beta activity, 1.73×10^7 c/min/ml, and the gamma activity, 3.67×10^8 c/m/ml, was due almost entirely to induced stainless steel activity.

The work presented in this report was carried out on small laboratory fixed-resin beds using a laboratory-made stainless steel solution with low levels of plutonium and fission-product tracers. It would be advantageous to undertake a hot-cell study of the proposed process using much higher levels of plutonium and fission-product activities.

The authors wish to acknowledge the analytical assistance rendered by G. R. Wilson, J. H. Cooper and their assistants, of the Analytical Chemistry Division.

2.0 PROCESS DESCRIPTION

An effective process has been developed on a laboratory scale for the recovery of plutonium, by cation exchange resin treatment, and uranium, by anion exchange treatment, from a 0.5 M $SO_4^=$ stainless steel decladding solution.

The sulfuric acid content of the proposed Sulfex decladding solution[1] was in the 4 M range and as such would be too high for either cation or anion exchange recovery of the uranium or plutonium without dilution of the solution. Uranium is commercially recovered from sulfate leach liquors,[3] in the range of 0.2-0.3 M in $SO_4^=$, by anion exchange. It was proposed, therefore, to investigate the 0.5 M in $SO_4^=$ range for uranium recovery on anion resin. At this sulfate concentration Pu(III) exists primarily as a cation[4] and since this would be the valence of the plutonium in the decladding solution a cation exchange recovery step was suggested.

The ion exchange process developed consisted of the following steps (Fig. 2.1):

1. The decladding solution is diluted to 0.5 M in $SO_4^=$.
2. This solution is passed through a cation resin bed to sorb the plutonium.
3. The cation resin is then scrubbed with a 0.5 M H_2SO_4 solution to selectively elute the bulk of the sorbed stainless steel products and uranium.
4. The Pu-loaded resin is washed with a column volume of water to remove sulfate.
5. The plutonium is eluted from the resin with nitric acid.
6. The cation column feed effluent, the 0.5 M H_2SO_4 scrub and the water wash are combined and the EMF of the composite solution is adjusted by the addition of ferric sulfate to ensure that the uranium is in the uranyl form.
7. This solution is then passed through an anion exchange column for sorption of the uranium.
8. The anion resin column is washed with a column volume of water to remove excess sulfate ion.
9. The uranium product is then eluted with nitric acid.

The principal disadvantage of this process is the dilution of the decladding solution, which increases the volume of the waste solution from the anion resin column.

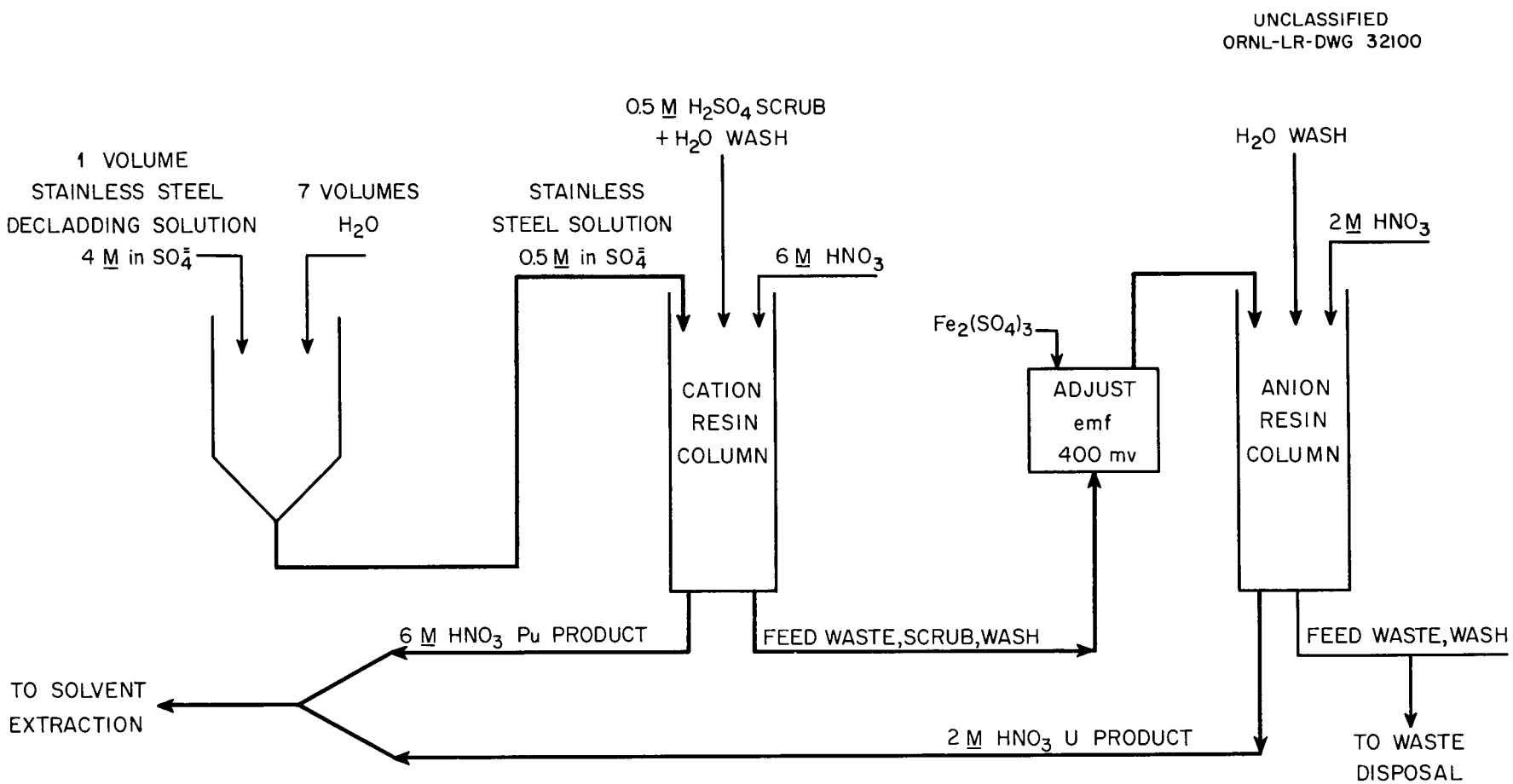

Fig. 2.1. Recovery of Plutonium and Uranium from Stainless Steel Decladding Solutions.

The principal advantage of the process is the production of separate plutonium and uranium products, separated from the bulk stainless steel contaminants, and in the nitrate form so that they may be further processed by conventional solvent extraction procedures.

3.0 PLUTONIUM RECOVERY

Optimum conditions for Pu(III) recovery were obtained by diluting the stainless steel decladding solution to approximately 0.5 M $SO_4^=$ and using Dowex 50 cation resin to sorb the plutonium. Eluting the resin with 0.5 M H_2SO_4 selectively removed the bulk of the sorbed stainless steel components. The plutonium product was eluted with nitric acid with recovery of >99% of the plutonium. The product solution was contaminated with 4% of the stainless steel and trace amounts, <0.01 M, of sulfate ion.

3.1 Decladding Solution

The stainless steel decladding solutions were prepared by dissolving 347 stainless steel in boiling 4 M H_2SO_4. Uranium trioxide was added to the solution during dissolution to give a final solution 5 g/liter in uranium. The uranium was reduced to the IV state by the stainless steel. Increments of a Pu(IV) stock solution were added in the experiments designed to trace the plutonium behavior. The ferrous ion in the decladding solution reduced the plutonium to the III state. An analysis of a typical decladding solution prepared in this manner was:

Material	Concentration (g/liter)
Uranium	5
Chromium	9
Iron	37
Nickel	5.6
Manganese	1.0
H^+	6 M
SO_4^-	3.5 M
Plutonium	10^6 (gamma counts/min/ml)

3.2 Distribution Coefficients

Distribution coefficients for plutonium between various resins and sulfuric acid indicated that Dowex 50 cation resin and a sulfate concentration range of 0.25-0.50 M were the most desirable conditions for Pu(III) absorption.

Distribution coefficients for plutonium between cation and anion resins and sulfuric acid were determined to define the behavior of plutonium in decladding solutions. The feed solution was trace plutonium(III or IV) in sulfuric acid solution. Small increments of a plutonium(IV) stock solution were added to sulfuric acid for the plutonium(IV) studies and plutonium(III) was prepared by reducing the plutonium(IV) solutions with 1 g/liter NH_2OH. The plutonium activity in the various solutions varied from 5.22×10^5 to 3.0×10^5 gamma counts/min/ml.

The distribution coefficients were calculated using the equation

$$K_D = \frac{M_r}{M_1} \times \frac{\text{volume of solution (ml)}}{\text{weight of dry resin (g)}}$$

where M_r represents the fraction of plutonium absorbed on the resin and M_1 the fraction of the plutonium in the supernatant. The resin was stirred with the solution for 4 hr. The resins were dried in an oven at 120°C until a constant weight was obtained.

Distribution coefficients varied from <0.01 for Pu(IV) between Dowex 1 anion resin and 3.2 M H_2SO_4 to 1470 for Pu(III) between Dowex 50 cation resin and 0.25 M H_2SO_4 (Table 3.1).

Table 3.1. Distribution Coefficients for the Partition of Trace Plutonium Between Various Concentrations of Sulfuric Acid and Ion Exchange Resins

		Distribution Coefficient (K_D)*		
Resin	Type	Pu(III)	Pu(IV)	H_2SO_4(M)
Duolite (C-65)	Cation	5.3	35	0.5
Dowex 50 (X8)	Cation	360	N	0.5
(X8)	Cation	3.65	N	3.6
(X12)	Cation	144	N	0.5
(X12)	Cation	1470	N	0.25
Dowex 1 (X7.5)	Anion	2.45	6.7	0.5
(X7.5)	Anion	<0.01	N	3.2

N not determined

* $K_D = \frac{M_r}{M_1} \times \frac{\text{volume of solution (ml)}}{\text{weight of dry resin (g)}}$

Table 3.2 Distribution of Plutonium, Uranium, and Stainless Steel in the Feed Effluent, Scrub Effluent and Product Effluent

Run No.	($\underline{M}$ $SO_4^{=}$)	Scrub Solution	Column[a] Volume (ml)	Resin Type[b]	Feed Effluent				Scrub Effluent				Plutonium Product	
					ml Feed / ml Resin	Pu (% of original)	SS (% of original)	U (% of original)	ml Scrub / ml Resin	Pu (% of original)	SS[c] (% of original)	U (% of original)	SS[c]	U
1	0.50	H_2O	71	Dowex 50 (x8)	28	6	75	100	3.5	.03	2.5	N	21	2.8
2	0.50	H_2O	242	Dowex 50 (x12)	16.6	<0.1	72.7	78	2.1	<.1	7	20	19.1	2.5
3	0.44	0.5 $\underline{M}$ H_2SO_4	425	Dowex 50 (x12)	15.7	<0.1	58	93	7.0	<.1	24	9.4	6.9	<0.01
4	0.55	0.5 $\underline{M}$ H_2SO_4	96	Dowex 50 (x12)	62.5	12.4	91.2	108	10.0	3.4	8.2	<.01	1.9	<0.01
5	0.62	0.5 $\underline{M}$ H_2SO_4	99.5	Dowex 50 (x8)	20	23.7	45.6	83	2.5	13.5	46	11	17	2.5
6	0.88	1.0 $\underline{M}$ H_2SO_4	103.5	Dowex 50 (x12)	19.2	30	85	95	9.7	6	11	4	2	<0.01

[a] 3/4-in. diameter

[b] 50-100 mesh

[c] Stainless steel

N Not determined

3.3 Ion Exchange Experiments

Fixed Dowex 50 cation ion beds were used to study plutonium recovery from stainless steel decladding solutions 0.44 to 0.88 M in $SO_4^=$. Plutonium recovery varied from >99% in the 0.44 M $SO_4^=$ solution to 64% in the 0.88 M $SO_4^=$. The effect of sulfuric acid as a selective eluant was evaluated and 0.5 M H_2SO_4 was chosen as a suitable scrub to give the best decontamination of the stainless steel and the uranium from the plutonium product.

The analyses of the column feed effluent, scrub effluent and plutonium product are given in Table 3.2. The stainless steel components in the plutonium product varied from 19.1% to 1.9% (Table 3.3).

A resin bed, 3/4 x 34-in., of Dowex 50 cation resin with the feed 0.5 M $SO_4^=$ gave greater than 99% recovery of the plutonium with 19.1% of the stainless steel products and 2.5% of the uranium following the plutonium product. The various elements broke through the resin bed completely in the following order: uranium, nickel, iron, manganese, and chromium (Fig. 3.1). This order was observed in subsequent experiments. The resin bed was washed with water to remove the sulfate ion and the product was eluted with 6 N HNO_3.

Since the quantity of uranium and stainless steel in the plutonium product was higher than desired, a 0.5 M H_2SO_4 elution was used in subsequent runs in an attempt to selectively elute the uranium and the stainless steel from the resin. The uranium was almost entirely eluted from the resin by the 0.5 M H_2SO_4 and the stainless steel components were reduced from 19.1% to 6% with less than 0.1% loss of plutonium.

The effect of higher sulfate concentration, 0.88 M, was investigated on a 115-ml cation resin bed and the distribution coefficient of the plutonium for the resin was 14 (Fig. 3.2) as compared with a distribution coefficient of 144 in the 0.5 M $SO_4^=$ system. The loaded resin was scrubbed with 1 M H_2SO_4 in an attempt to selectively elute the stainless steel components, particularly chromium, without losing appreciable amounts of plutonium. The plutonium and the chromium were both eluted by the 1 N H_2SO_4 (Fig. 3.3).

In order to simulate plant operating conditions, a 60 x 3/4-in. column of Dowex 50 resin was used. The performance of a plant column may be scaled up directly from the cross sectional area of the laboratory 3/4-in. column. The feed solution was 0.44 M in $SO_4^=$, 0.66 M in H^+, 0.7 g/liter U, 9.5 g/liter stainless steel and 8.2 x 10^5 gamma counts/min/ml Pu. The feed solution was pumped downflow through the resin bed;

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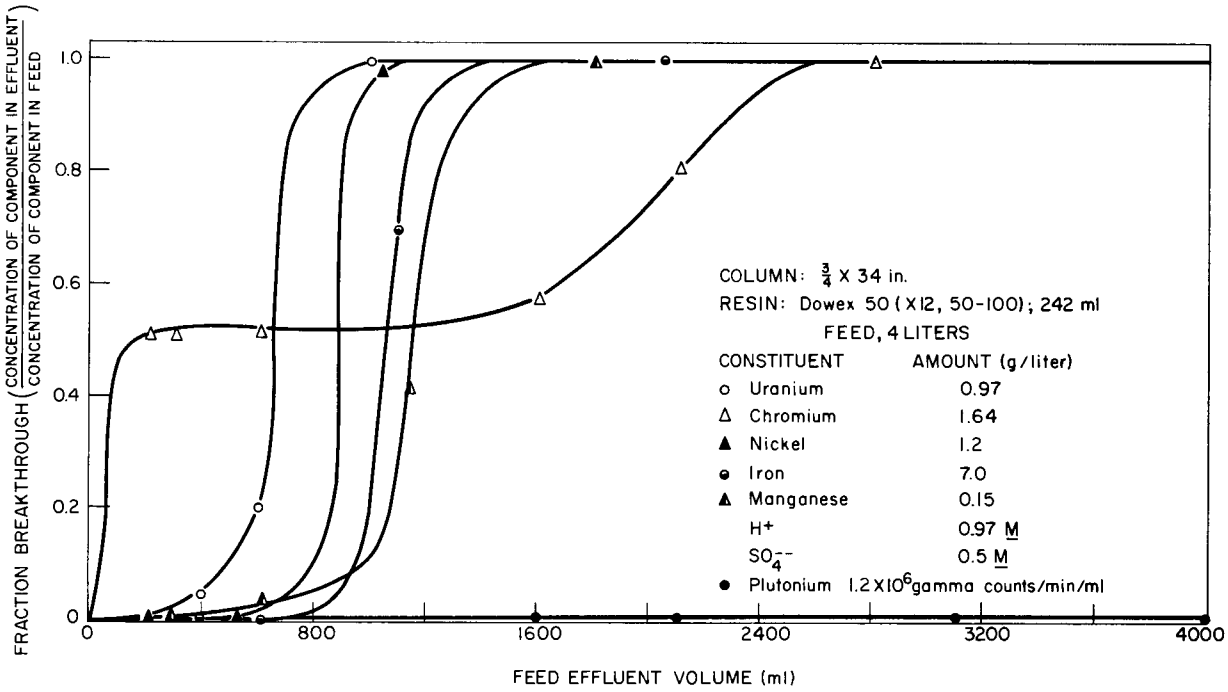

Fig. 3.1. Breakthrough Curves for Plutonium (III), Uranium, and Stainless Steel Constituents on Dowex 50 Cation Resin in 0.5 M Sulfate.

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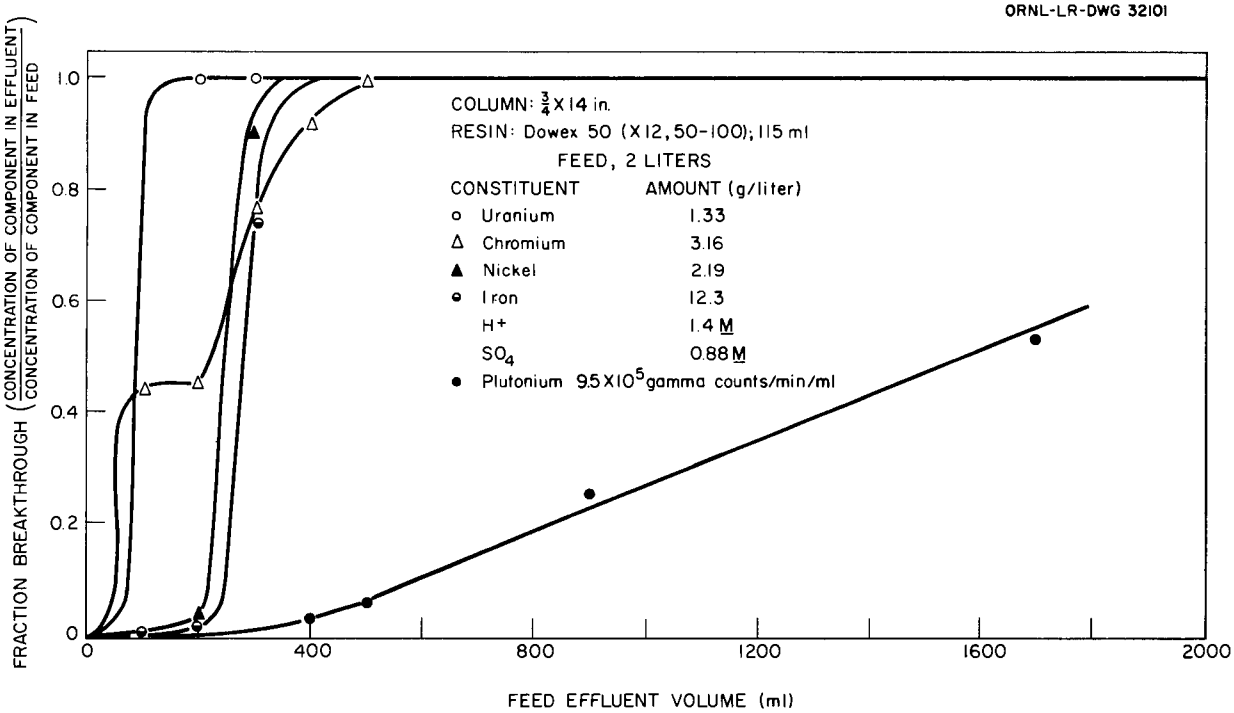

Fig. 3.2. Breakthrough Curves for Plutonium (III), Uranium, and Stainless Steel Constituents on Dowex 50 Cation Resin in 0.88 M Sulfate.

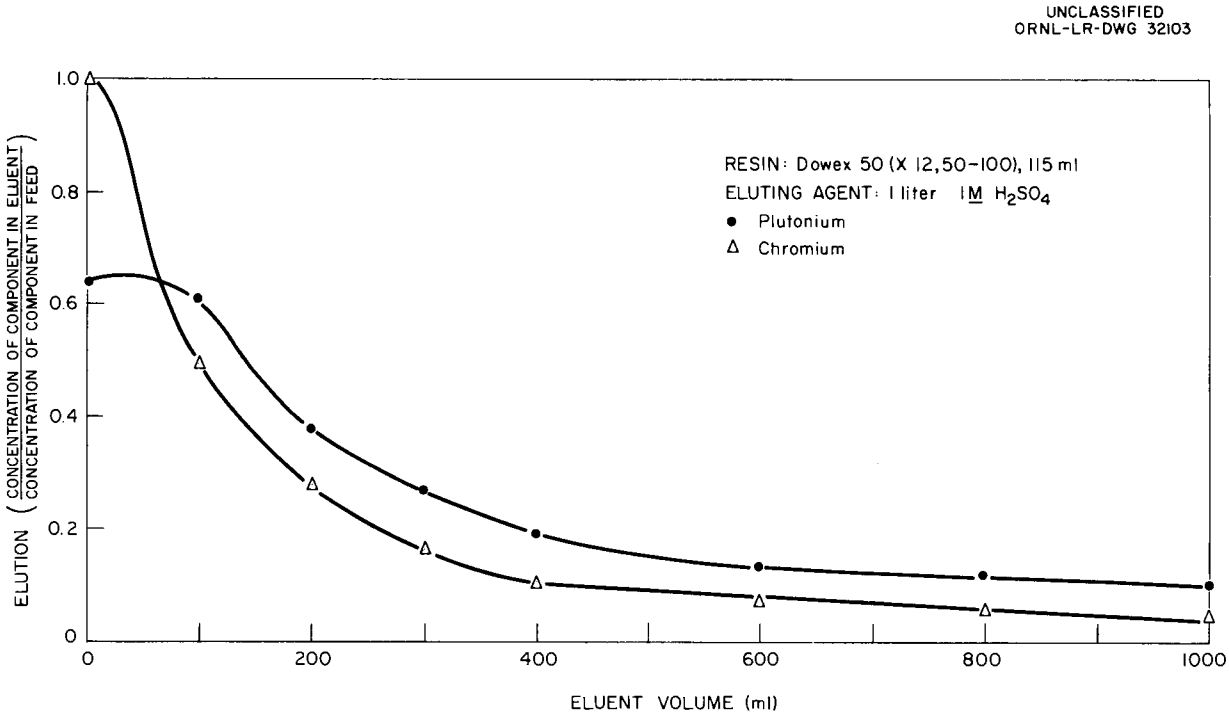

Fig. 3.3. Elution of Plutonium (III) and Chromium from Dowex 50 Cation Resin by 1 M H_2SO_4.

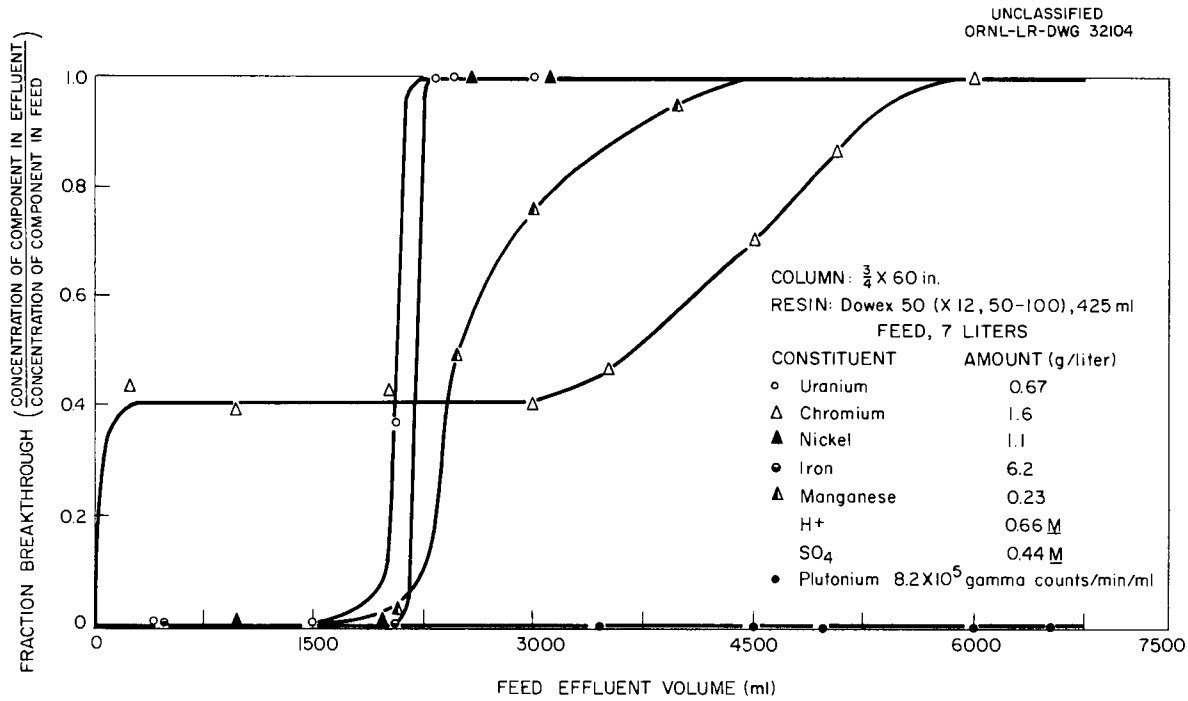

Fig. 3.4. Breakthrough Curves for Plutonium (III), Uranium and Stainless Steel Constituents on Dowex 50 Cation Resin in 0.44 M Sulfate.

Table 3.3. Contaminants in the Plutonium Product Solutions

Run No.*	Contaminant (% of original component)					
	U	Cr	Ni	Fe	Mn	Stainless Steel
1	2.8	22.7	21	21	25	21
2	2.5	1.9	2.1	22	N	19.1
3	<.01	20	<.1	5	N	6.9
4	<.01	5.1	<.1	1.3	<4	1.9
5	2.5	20	17	16	21	17
6	<.01	3	--	2	--	2

*Same runs as in Table 3.2.

N Not determined

the loaded resin was scrubbed with 0.56 M H_2SO_4; and the product was eluted with 6 N HNO_3. The feed waste contained 70% of the stainless steel, 93% of the uranium and 0.1% of the plutonium (Fig. 3.4). The 0.56 M H_2SO_4 scrub solution contained 26% of the stainless steel, 9% of the uranium and 0.05% of the plutonium (Fig. 3.5). The product plutonium solution contained 5% of the stainless steel components, primarily chromium and iron (Fig. 3.6).

In another run an excess amount of stainless steel feed, 0.55 M in $SO_4^=$, was passed through a 96-ml cation resin bed to determine the breakthrough point of the plutonium. After 60 column volumes, 38% breakthrough of the plutonium was observed (Fig. 3.7). Using the breakthrough curve from this run an optimum point at 25 column volumes was determined graphically where 99.9% of the plutonium would be loaded on the resin. At this point the final product would contain 4% of the stainless steel components.

3.4 Height of the Transfer Unit Determination

The transient behavior of an adsorption column in terms of the number of transfer units, for simplifying assumptions of linear sorption isotherm and linear kinetics, has been discussed by Marshall and Pigford.[7] Walter has shown that the general solution can be approximated by a simple function of the common error integral.[8] The error-integral form of the breakthrough curve is such that a straight line is obtained if per cent breakthrough is plotted vs the square root of effluent volume on arithmetic probability paper, with the slope of the line being a simple function of the number of transfer units.[9] One form of this relationship is

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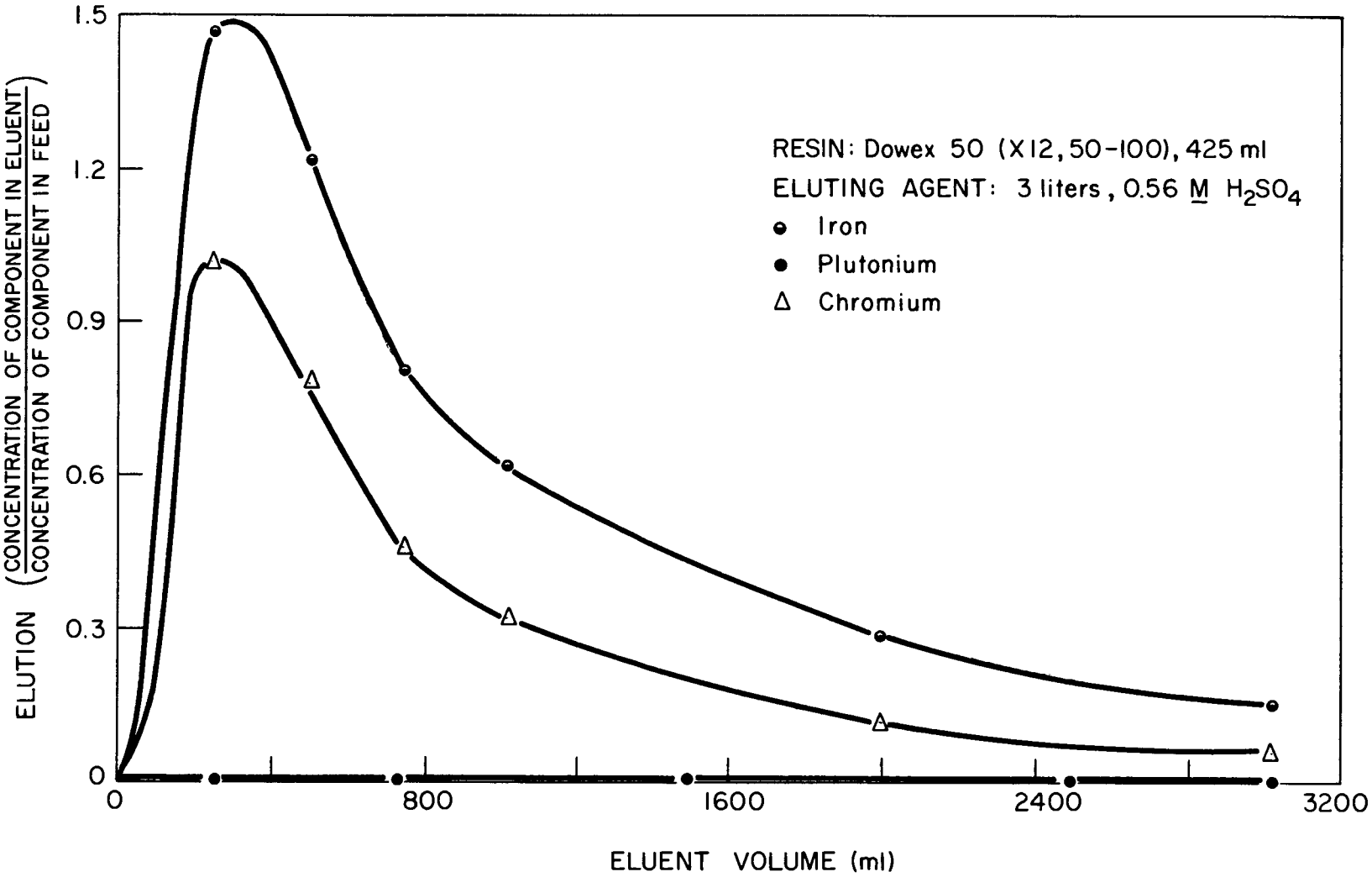

Fig. 3.5. Selective Elution of Chromium and Iron from Plutonium(III) on Dowex 50 Cation Resin by 0.56 M H_2SO_4.

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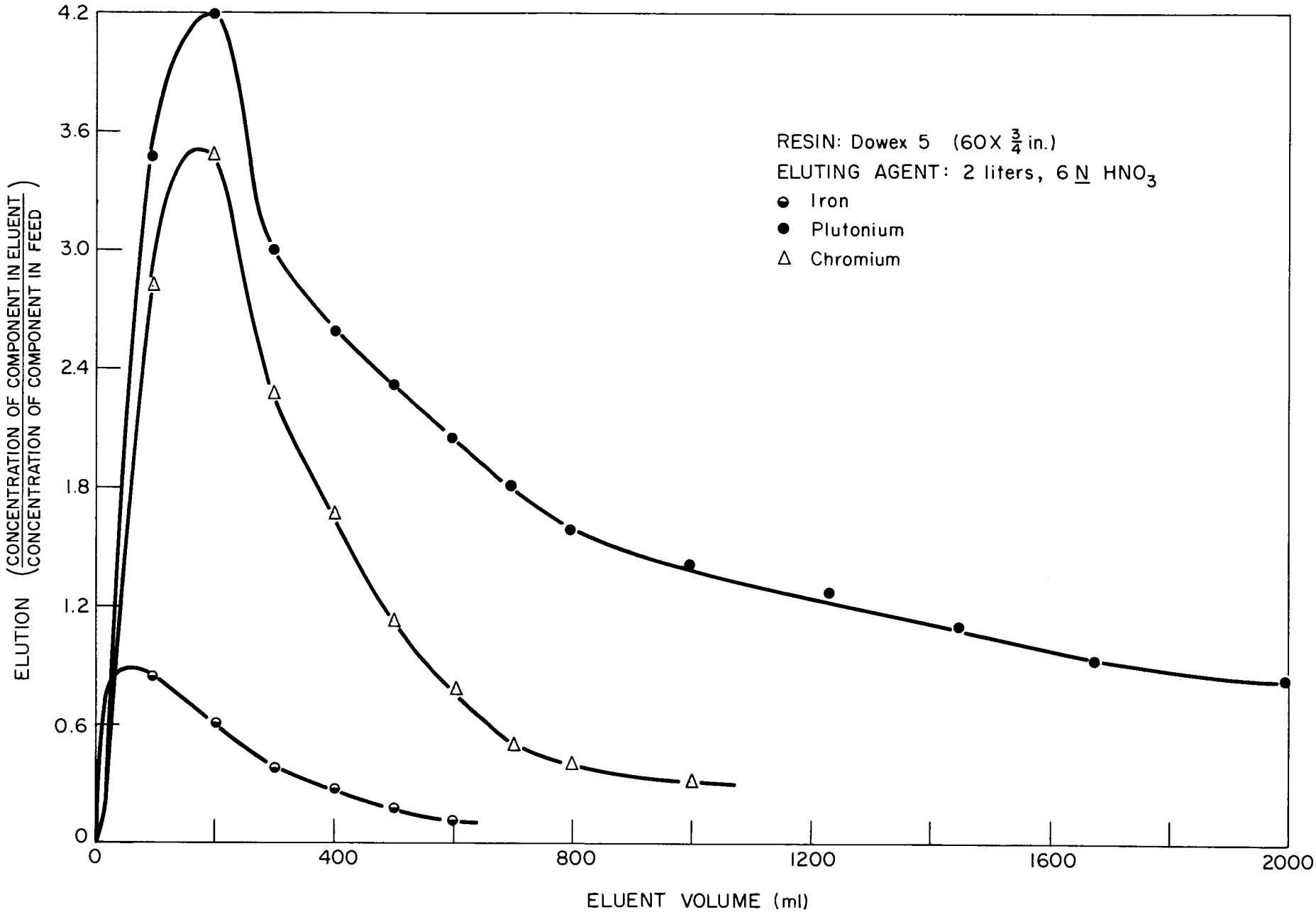

Fig. 3.6. Elution of Plutonium, Chronium and Iron from Dowex 50 Cation Resin by 6 N HNO_3.

$$\sqrt{n} = k_{1,2} \frac{\sqrt{v_2} + \sqrt{v_1}}{\sqrt{v_2} - \sqrt{v_1}}$$

where n is the number of over-all, solution-phase transfer units in the column; v_1 and v_2 are the volumes corresponding to concentrations; c_1 and c_2 on the breakthrough curve, chosen such that the sum of c_1 and c_2 is 100%, and $k_{1,2}$ is a proportionality constant, the value of which depends on the choice of c_1 and c_2. For v_1 and v_2 corresponding to the 10% and 90% breakthrough concentrations, the value of $k_{1,2}$ is 0.9062.

The plutonium breakthrough curves of Figs. 3.2 and 3.7 are replotted on arithmetic probability coordinates in Fig. 3.8. The number of transfer units in the column was determined, using the equation given above, to be about 9 in both runs, corresponding to an height of transfer units of about 1.5 inches. The fact that the number of transfer units and height of transfer units were about the same for both runs is a coincidence. In general, height of transfer units increases with increasing flow rate and with increasing solution concentration. In the two runs the effect of increased flow rate was offset by decreased concentration.

3.5 Chromium Behavior on Cation Resin

Since the $Cr(H_2O)_6^{3+}$ gives the Pu(III) the most competition for the resin it would be desirable to reprocess the solution as soon as possible after decladding the uranium fuel element or to reheat the solution and reconvert the bulk of the chromium to the $Cr(H_2O)_5SO_4^+$ form.

An unusual breakthrough curve for chromium was observed in all the plutonium recovery experiments. The shape of this curve (Fig. 3.7) indicates two forms of chromium present in the decladding solution, and one possibility considered was the presence of chromium(II) and (III). A chromium solution was prepared by dissolving 5 g of metallic chromium in sulfuric acid and this solution was divided into two portions. One portion of the solution was passed through a Dowex 50 cation exchange column immediately and the chromium breakthrough curve determined. The second portion was first treated by bubbling air through the solution for 4 hr to convert any chromium(II) to the III state and then the solution was passed through a Dowex 50 cation exchange bed and the chromium breakthrough curve determined. Identical curves were obtained in both experiments with 75% of the chromium breaking through almost immediately and the remaining 25% loading on the resin. These results indicated the two forms present were probably complexes of chromium(III).

Various texts[6] indicate a $Cr(H_2O)_5SO_4^+$ complex at boiling temperatures which converts slowly on cooling to $Cr(H_2O)_6^{3+}$. It was assumed that the $Cr(H_2O)_5SO_4^+$ form was weakly sorbed and broke through the ion exchange bed rapidly while the $Cr(H_2O)_6^{3+}$ form sorbed on the resin. It was desired

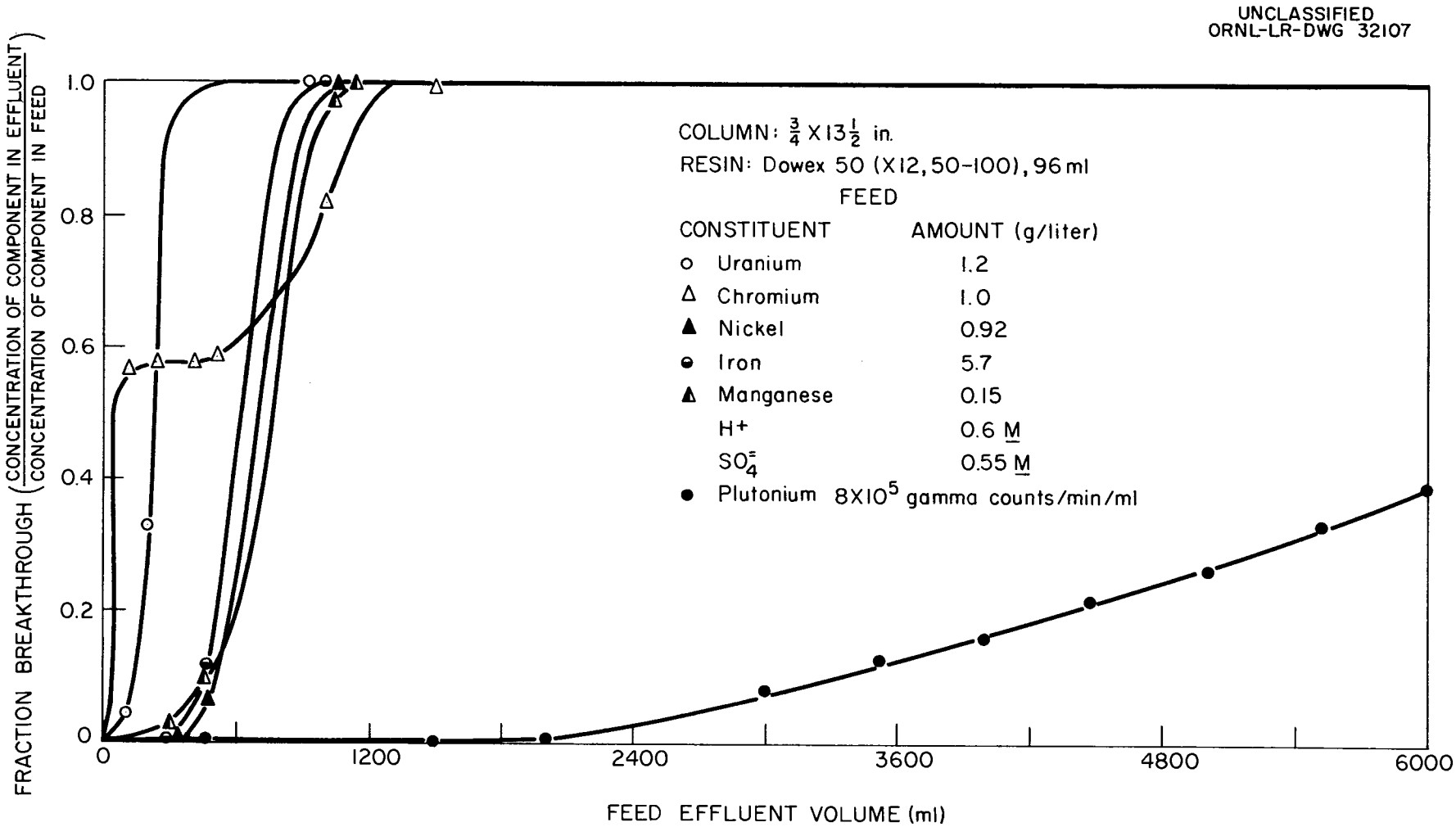

Fig.3.7. Breakthrough Curves for Plutonium (III), Uranium and Stainless Steel Constituents on Dowex 50 Cation Resin in 0.55 M Sulfate.

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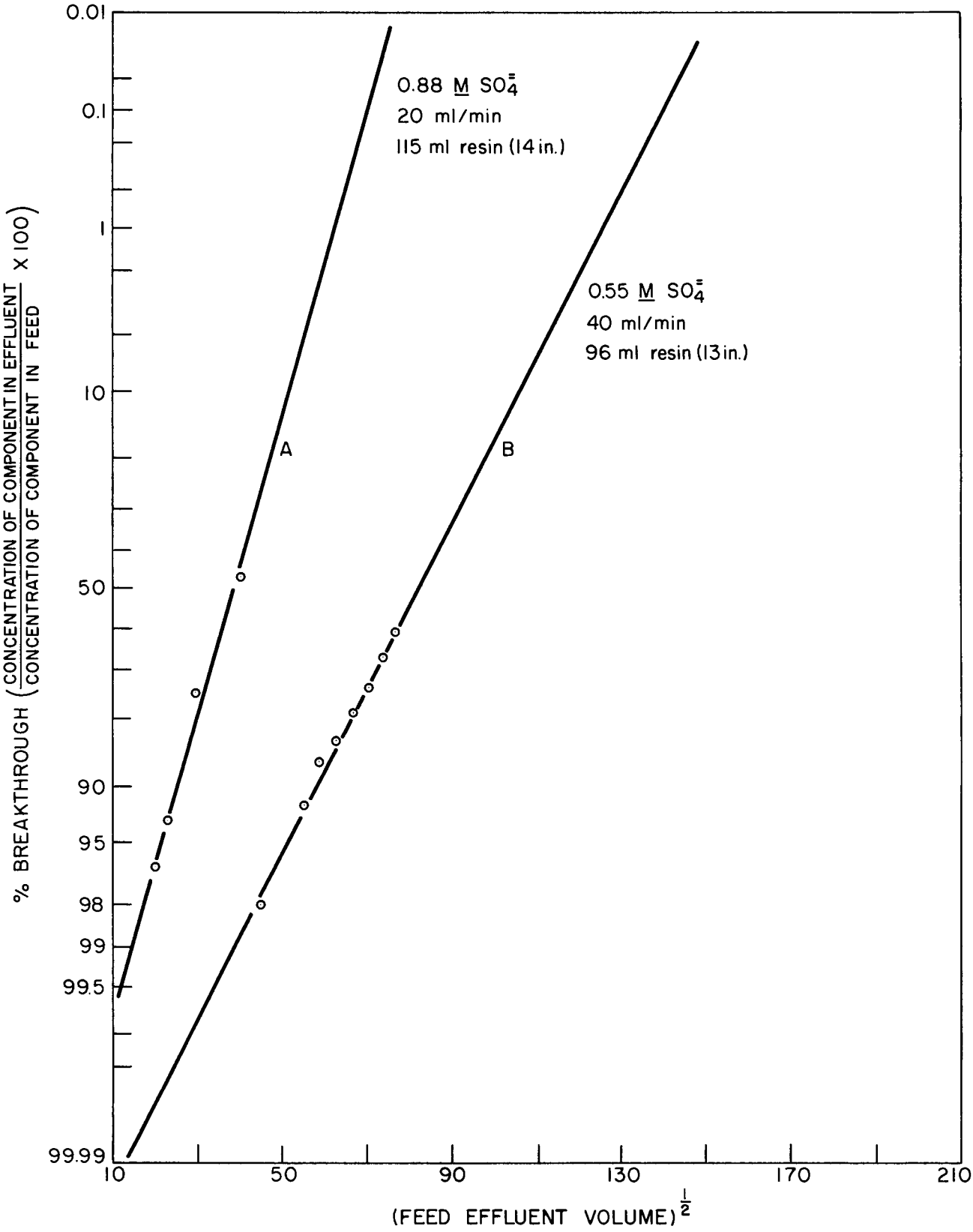

Fig. 3.8. Breakthrough Curves for Plutonium in a Sulfate Stainless Steel Decladding Solution.

to obtain information regarding the rate of conversion of the $Cr(H_2O)_5SO_4^+$ form to the $Cr(H_2O)_6^{3+}$ form in the decladding solution and also to determine whether or not the $Cr(H_2O)_5SO_4^+$ form could be regenerated by boiling.

A stock solution (4.5 g/liter Cr, 0.46 M in $SO_4^=$ and 2 x 10^4 counts/min/ml Cr^{51}) was prepared and, periodically, samples of this solution, at room temperature, were passed through a Dowex 50 cation resin bed and the fraction of the non-loading and loading forms of the chromium determined from the breakthrough curves (Fig. 3.9). Over a period of 884 hr the non-loading form of the chromium, presumably $Cr(H_2O)_5SO_4^+$, decreased from 73 to 37% of the total chromium. The half-life of the conversion was 120 hr and the rate constant was 0.0058 hr^{-1} (Fig. 3.10). The last value obtained, 37%, for the fraction of $Cr(H_2O)_5SO_4^+$ present seemed to be very close to the equilibrium value in this system.

A sample of the stock solution was boiled for thirty minutes and then passed through the resin bed while hot. The fraction of the non-loading complex was increased from 38.5% to 80% by this treatment. An additional sample was boiled for 2 hr, cooled to room temperature and then passed through the ion exchange bed. The fraction of the $Cr(H_2O)_5SO_4^+$ complex increased from 37 to 68%.

3.6 Fission-Product Behavior in Plutonium Recovery

The behavior of fission products was followed in the plutonium recovery from stainless steel decladding solution. Trace gross fission products (3.7 x 10^4 beta counts/min/ml and 5.3 x 10^4 gamma counts/min/ml) in a stainless steel solution 0.7 M in SO_4^{--} were passed through a Dowex 50 cation bed and the loaded resin scrubbed with 0.5 M H_2SO_4. The plutonium product was then eluted with 6 N HNO_3. More than 70% of the fission products appeared in the plutonium product, with 18% in the feed effluent and the 0.5 M H_2SO_4 scrub solution (Table 3.4).

Table 3.4. Distribution of Fission Products in the Recovery of Plutonium from Stainless Steel Sulfate Decladding Solutions

	Activity in Solution (% of initial)					
Sample Description	Gross Gamma	Gross Beta	Cs	Sr	Total Rare Earths	Ru
Feed Effluent	8.9	6.4	4.5	2.4	8.5	86
H_2SO_4 Scrub Effluent	7.8	3.8	12.9	3.4	14.8	9.3
HNO_3 Product Effluent	>69	>70	83.0	74.5	100	41.0

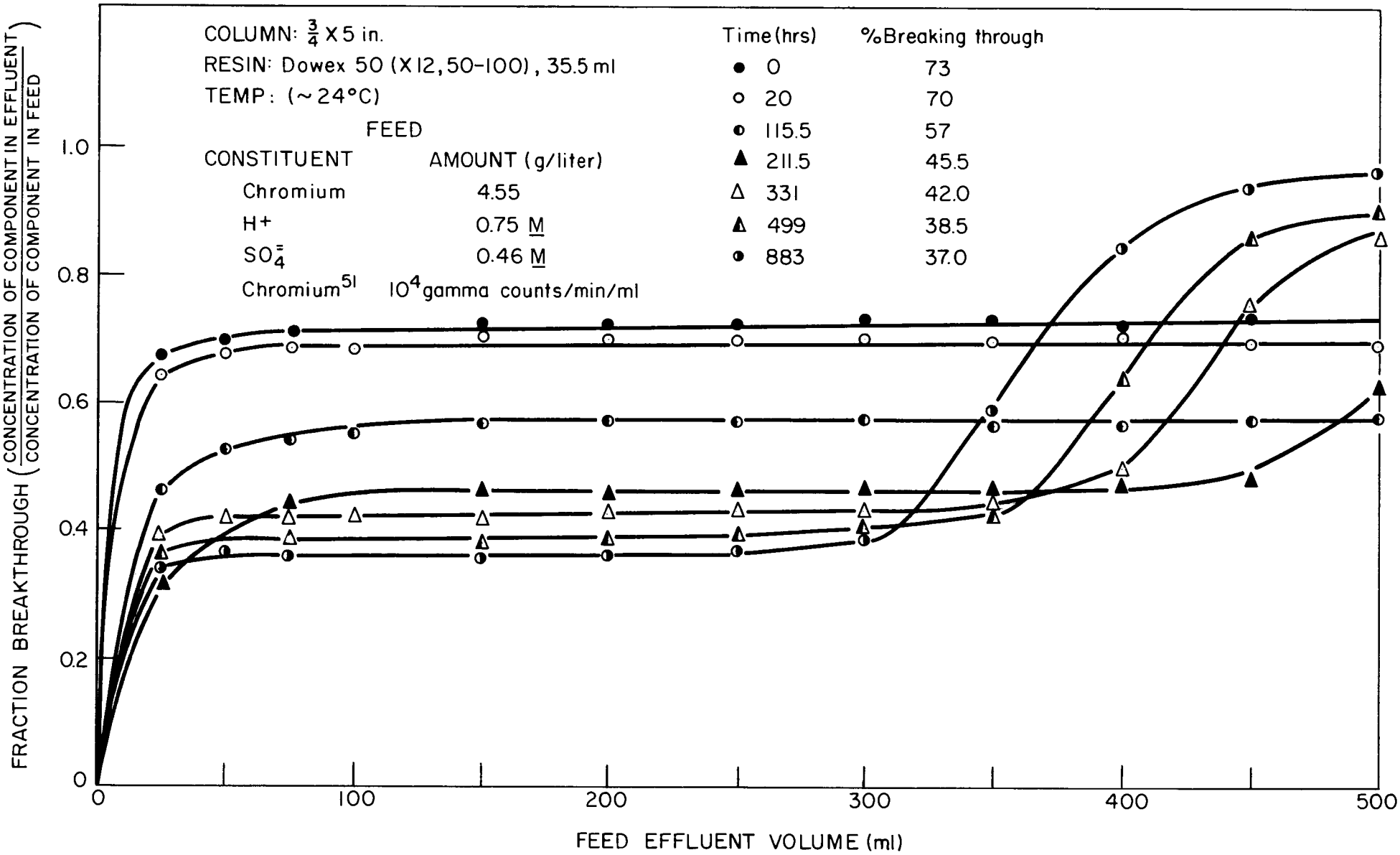

Fig. 3.9. Separation of two Cr (III) Complexes in 0.46 M Sulfate Solution by Dowex 50 Cation Resin.

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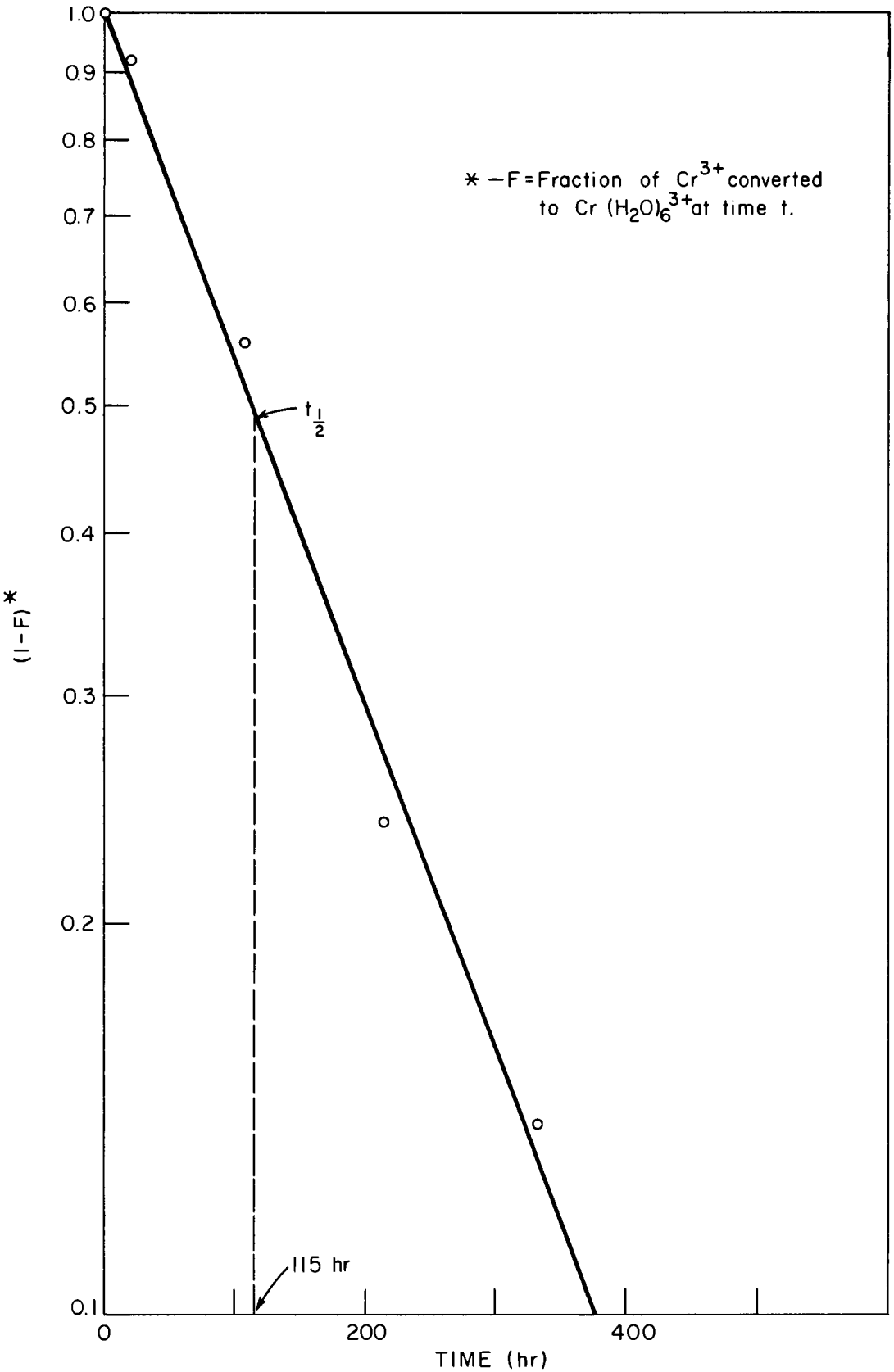

Fig. 3.10. Rate of Conversion of $Cr(H_2O)_5SO_4^+$ to $Cr(H_2O)_6^{3+}$ in 0.46 M Sulfate Solution.

4.0 URANIUM RECOVERY

Optimum conditions for uranium recovery from the stainless steel decladding solution were obtained in the 0.5 M $SO_4^=$ range using Dowex 1 anion resin. The uranium product was eluted from the resin with nitric acid and was contaminated with less than 0.01% of the stainless steel components.

Distribution coefficients were determined (Section 3.2) for uranium between Duolite C-65 cation resin and Dowex 1 anion resin and sulfuric acid in the 0.45 M to 0.56 M range. The distribution coefficients varied from 30 to 77 (Table 4.1). Duolite C-65 resin showed some possibility for uranium recovery but Dowex 1 in the 0.5 M $SO_4^=$ range was the most promising, according to the distribution coefficients.

Table 4.1 Distribution Coefficients for the Partition of Uranium Between Various Concentrations of Sulfuric Acid and Ion Exchange Resins

Resin	Type	Distribution Coefficient (K_D)*		
		U(IV)	UO_2^{+2}	$SO_4^=$ M
Duolite C-65	Cation	N	30	0.56
Dowex 1 (x 7.5)	Anion	N	51	0.56
Dowex 1 (x 7.5)	Anion	N	77	0.45
Dowex 1 (x 8)	Anion	N	7.7	1.20
Dowex 1 (x 8)	Anion	N	21.8	0.65
Dowex 1 (x 8)	Anion	N	87	0.41
Dowex 1 (x 8)	Anion	5.5	X	0.65
Dowex 1 (x 8)	Anion	16.3	X	0.38
Dowex 1 (x 8)	Anion	52.5	X	0.19

N Not determined

$$^*K_D = \frac{M_r}{M_1} \times \frac{\text{volume of solution (ml)}}{\text{weight of dry resin (g)}}$$

Fixed-bed studies were performed using a laboratory-made stainless steel solution (Section 3.1) with the sulfate ion concentration varying from 0.44 M to 0.6 M. Feed waste breakthrough curves were plotted for the various constituents. The uranium was eluted from the Dowex 1 resin with nitric acid. The uranium product solutions were analyzed for stainless steel components and these were consistently less than 0.01%. The sulfate ion concentration in the product was approximately one equivalent of sulfate for each liter of resin.

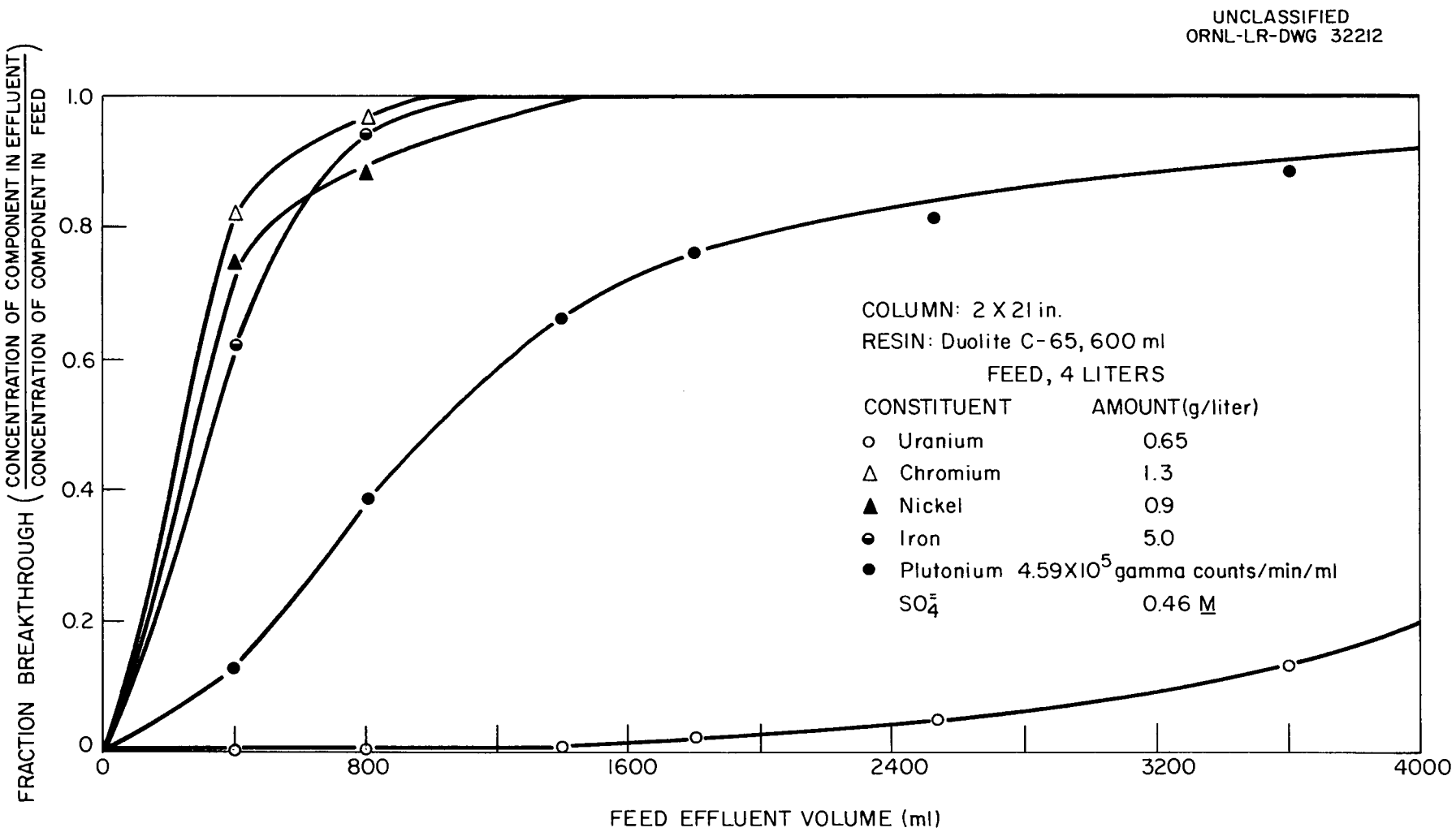

Fig. 4.1. Breakthrough Curves for Plutonium, Uranium and Stainless Steel Constituents on Duolite C-65 Cation Resin in 0.46 M $SO_4^{=}$

The recovery of uranium from a stainless steel solution, 0.46 M in $SO_4^=$, was investigated on Duolite C-65 cation resin. The stainless steel components broke through the resin bed completely after two column volumes of feed solution, the plutonium(III) after 7 column volumes and the uranium breakthrough was 20% after 13 column volumes (Fig. 4.1). The uranium product was eluted with HCl and contained 15% of the stainless steel and 25% of the plutonium. Since the decontamination of the uranium was poor and the product could not be eluted with nitric acid from this phenolic resin, further runs on Duolite C-65 resin were not undertaken.

The behavior of uranium on Dowex 1 anion resin was determined in 0.45 M and 0.60 M $SO_4^=$ decladding solutions. The stainless steel components and the plutonium broke through the resin bed completely in 5 column volumes. The uranium in the 0.45 M $SO_4^=$ system attained only 36% breakthrough in 31 column volumes (Fig. 4.2) while in the 0.60 $SO_4^=$ solution the breakthrough was 74% in 17 column volumes (Fig. 4.3). In both these runs two distinct bands appeared on the resin bed, one near the top of the column which was yellow and the second lower down which was green. These corresponded to the uranyl sulfate and the uranous sulfate, respectively. The uranium in the decladding solution was evidently initially in the (IV) state and was slowly being oxidized to the uranyl form.

The relative affinities of the uranous and uranyl forms of uranium in the stainless steel decladding solution were determined on Dowex 1 anion resin. The uranium valence in the stainless steel solution may be determined by EMF measurement[5] and it is possible to oxidize the uranous form to the uranyl without oxidizing the ferrous ion to ferric. The uranous sulfate solution was prepared by the iron reduction of uranyl sulfate and the EMF kept below 290 millivolts. The uranyl form was prepared by oxidizing the uranous ion with ferric sulfate to an EMF of 410 millivolts. The uranyl sulfate loaded in preference to the uranous sulfate by a factor of 2 (Fig. 4.4). It was thus advantageous to ensure the uranyl sulfate form of the uranium before removal of the uranium from the stainless steel solution by anion exchange.

The uranium recovery on a 60 x 3/4-in. column from a 0.44 M $SO_4^=$ decladding solution was performed with the uranium in the uranyl form. There was no uranium breakthrough after 16 column volumes and uranium nitrate product, 6 N NO_3^-, contained $<0.01\%$ of the stainless steel components (Fig. 4.5).

The behavior of fission products was followed in the uranium recovery from a stainless steel decladding solution. Trace gross fission products (6.52×10^4 beta counts/min/ml and 9.55×10^4 gamma counts/min/ml) in a solution 0.7 M in $SO_4^=$ were passed through a Dowex 1 anion bed. The uranium product was eluted with 1 N HNO_3. The product solution contained 0.3% of the gross beta activity and 0.7% of the gross gamma activity. The activity level of the product solution was too low to evaluate the fission products which followed the uranium.

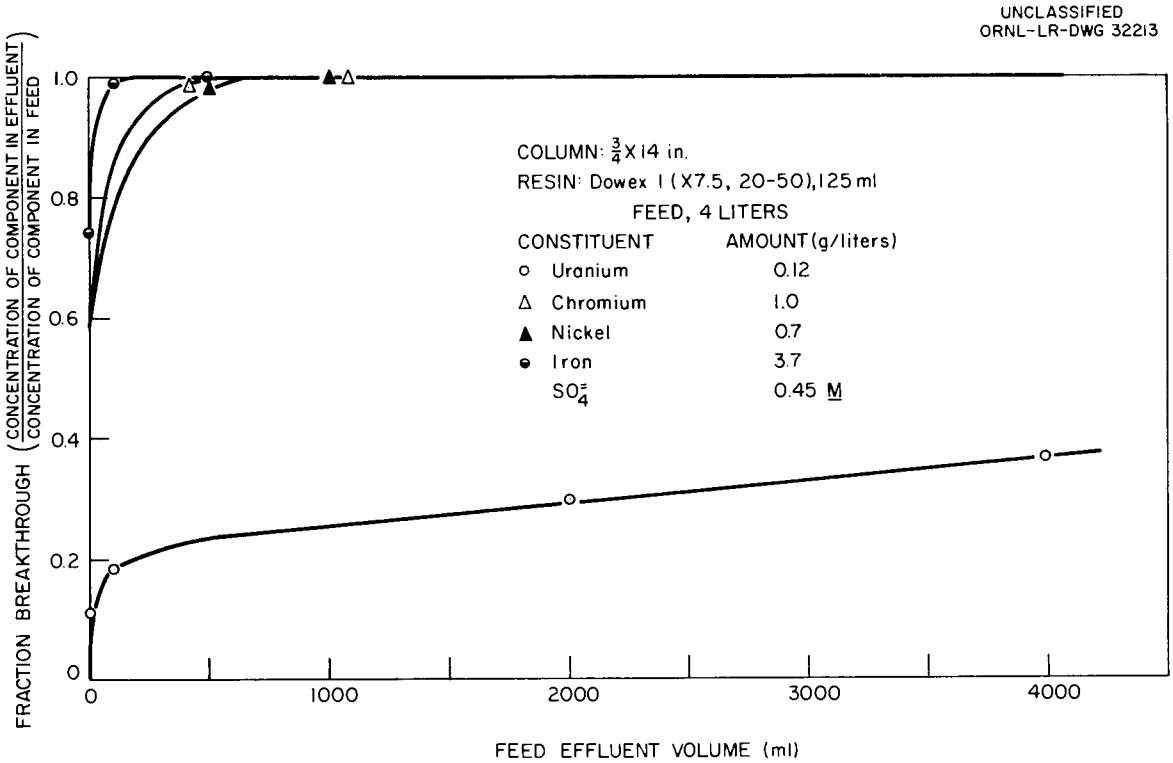

Fig. 4.2. Breakthrough Curves for Uranium and Stainless Steel Constituents on Dowex 1 Anion Resin.

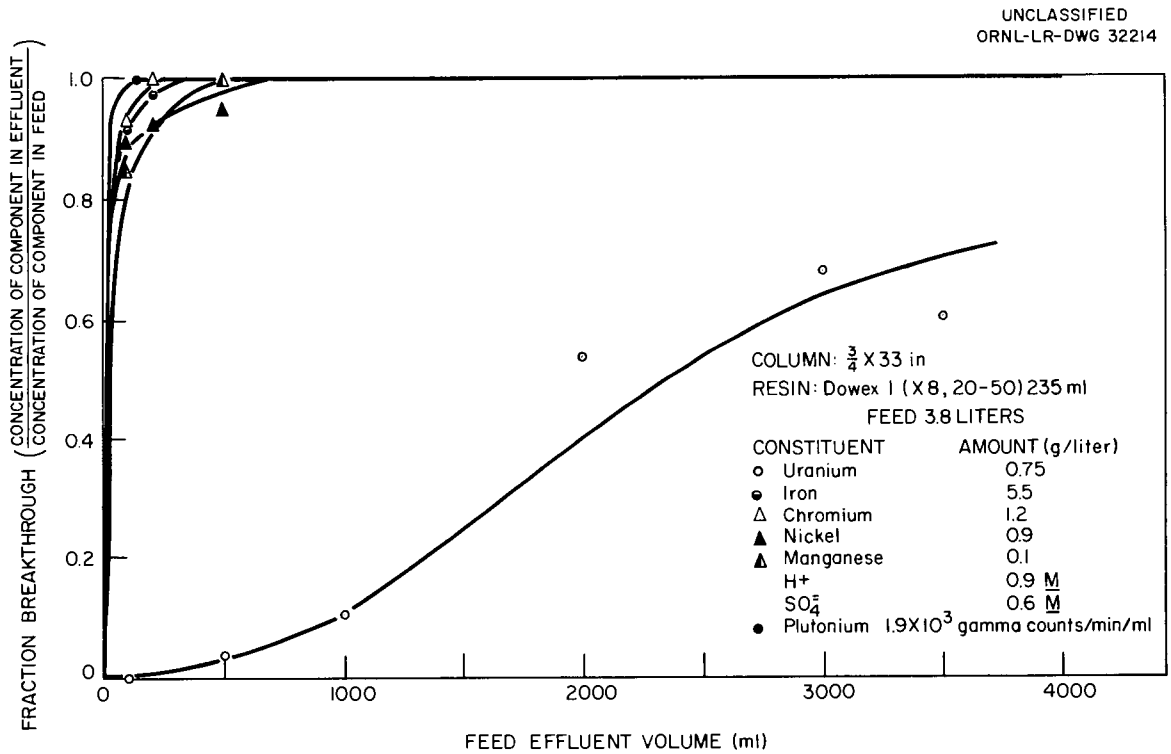

Fig. 4.3. Breakthrough Curves for Uranium, Plutonium and Stainless Steel Constituents on Dowex 1 Anion Resin.

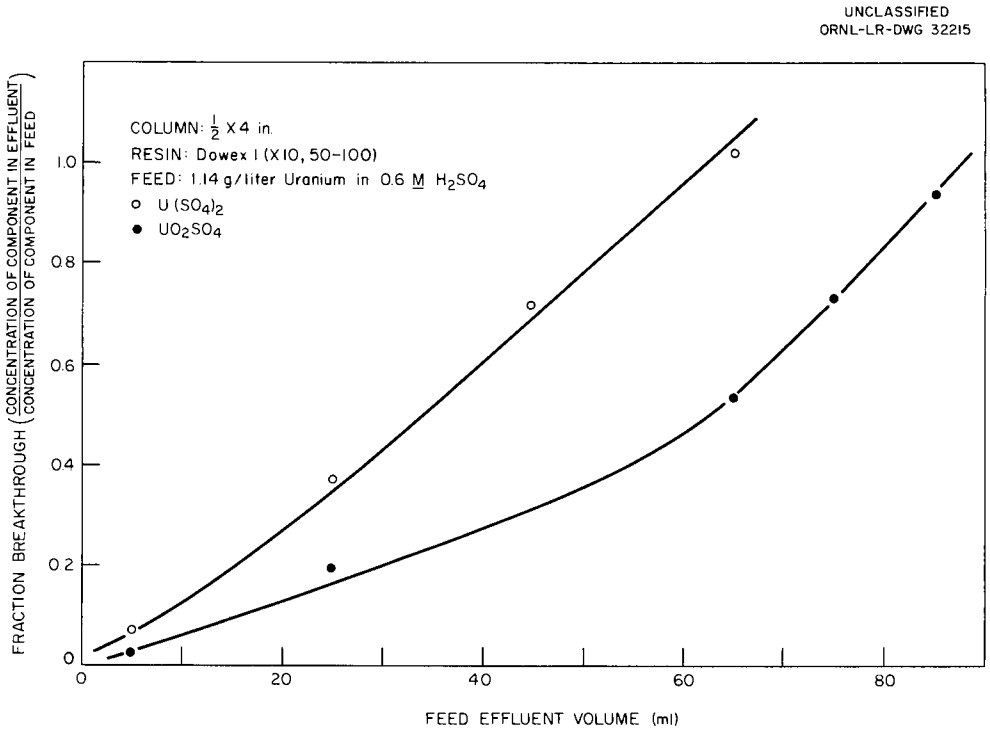

Fig. 4.4. Comparison of the Breakthrough Curves of UO_2SO_4 and $U(SO_4)_2$ on Dowex 1 Anion Resin.

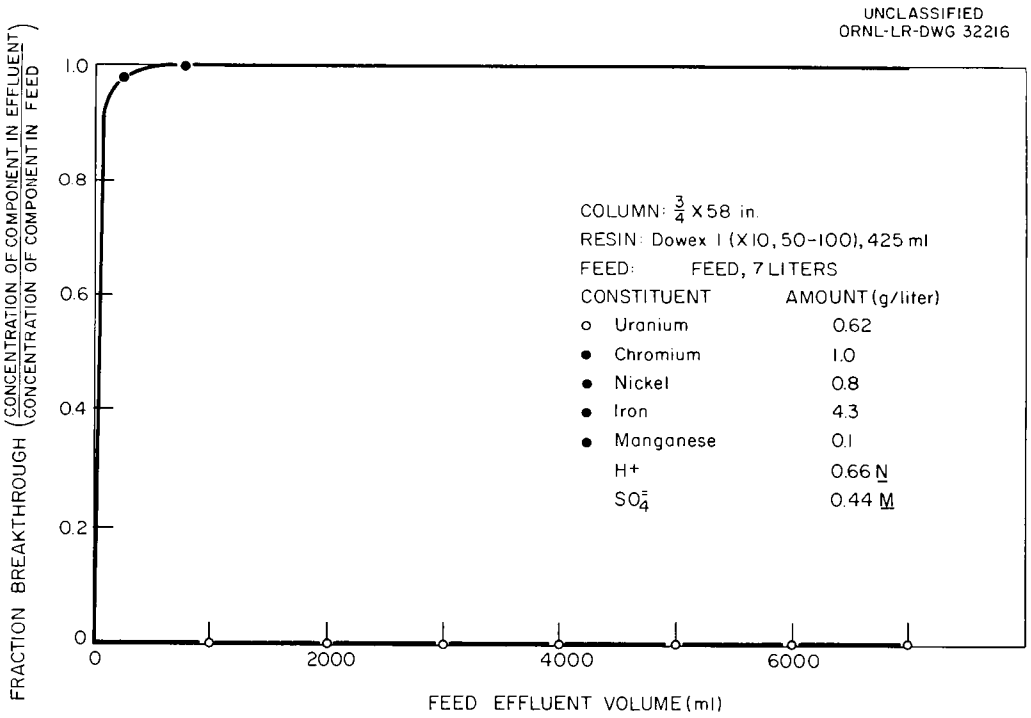

Fig. 4.5. Breakthrough Curves for Uranium and Stainless Steel Constituents on Dowex 1 Anion Resin.

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