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MINES BRANCH INVESTIGATION REPORT IR 59-95

THE REMOVAL OF URANIUM FROM AN ANION EXCHANGE RESIN
BY A STRONG CHLORIDE ELUTION PROCESS:
A PRELIMINARY INVESTIGATION

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J. C. INGLES AND E. D. KORNELSEN

EXTRACTION METALLURGY DIVISION

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J. C. Ingles* and E. D. Kornelsen**

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SUMMARY OF RESULTS

The distribution of uranium and the common impurities between an anion exchange resin and the strong chloride (3-5N) and pure water streams from a strong chloride elution scheme, has been studied in small scale tests. It is shown that a large part of the uranium is obtained in a water solution free of thorium, iron and sulphate ions, although a substantial portion of the uranium reports, along with the impurities, in the strong chloride solution. A number of methods for incorporating the strong chloride step into complete processes for the recovery of a high-grade uranium product are proposed, and some of these have been very briefly investigated. A rough economic study is also given. It is suggested that strong chloride elution should be investigated further, as a means for producing a substantially higher-grade product with the equipment and flow sheets now in use in a number of Canadian mills.

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(40 pages, 22 Tables, 15 Figures)

INTRODUCTION

Current views on improvements in the technology of uranium concentrate production suggest that the ability to produce a purer product may well be a major factor in obtaining markets when present contracts expire. This report discusses test work on some possible methods for obtaining such products with mill equipment already in use, by modifications of processes now being employed.

In 1951-52, the authors carried out a number of experiments intended principally to improve the rate of elution of uranium from the anion exchange resin IRA 400 by chloride solutions, and at the same time to effect complete displacement of chloride from the resin bed. During the course of this work, several important observations were made. The first of these was that, during the course of elution with chloride solution (1.5N in this case), the bulk of the resin was converted to the chloride form after a relatively small amount of eluting solution had passed, and that the balance of the uranium elution step was a mechanical process which could be carried out as efficiently by water as by more eluting solution. A second observation was that if the chloride concentration of the eluting solution was increased (to 3N in the study carried out) resin conversion to the chloride form occurred still more rapidly, and at the same time the proportion of the uranium appearing in the subsequent "water elution" step was substantially increased.

Thirdly, overall elution time could be reduced significantly using a short elution with concentrated chloride solution followed by a "water elution step" and fourth, the uranium solution obtained in this water elution was substantially purer than that obtained by normal elution, the impurities tending to concentrate in the strong chloride solution used for the initial conversion step.

A recent reference to the use of neutral 5N sodium chloride solution as eluant in the Higgins Moving Bed Process (1) suggested that it might be profitable to take up again and expand on the previous work, and in particular to investigate the use of neutral chloride solutions.

The program was directed to investigating the possible application of the technique to current operating practice, particularly as regards feed solutions with high thorium content. Some consideration was also given to methods of treating the resultant product streams with the idea of producing a precipitate of higher grade than present mill concentrates.

This report summarizes the results of this work to date, and includes results of studies which appeared in reports which had restricted circulation and are therefore not readily available.

The part of the report describing the details of the experimental work is divided into two sections, the first dealing with the use of strong chloride and water for elution, the second dealing

with the recovery of the uranium as a product, from these solutions.

EXPERIMENTAL PROCEDURES AND RESULTS

A. Elution Studies

1. Previous Work

In the first of the studies carried out in 1951, an attempt was made to determine the minimum amount of fresh 1.5N sodium chloride solution (0.05N in sulphuric acid) which would permit complete removal of uranium. (2)

Three columns containing 50 ml of IRA 400 were loaded with uranium using Beaverlodge leach liquors. The first of these was eluted with 100 ml of eluant, followed by 800 ml of water. The second column was eluted with 300 ml of eluant followed by 300 ml of water. The third column was eluted with 500 ml of eluant followed by 400 ml of water. In the case of the first column, which had had the shortest treatment with eluant, the column was re-eluted and the amount of retained uranium was determined. It should be emphasized that in all cases fresh (not recycled) eluant was used.

The results are shown in Table 1, in terms of cumulative percent eluted per unit of volume throughput, and the same information is shown in graphical form in Fig. 1.

The apparent difference in rate (ie the offsetting of the curves) is probably due to differences in the time of sampling, as

related to the water-eluate interface in the initial volumes passed in displacing the water in the column at the start of the tests.

TABLE I

Use of Combination of NaCl Solution and Water
for Uranium Elution: Effect of Varying Eluant
Volume

Eluant = 1.5N NaCl, 0.05N H₂SO₄
Resin = 50 ml IRA 400

Volume Throughput ml	Cumulative % Eluted		
	100 ml Eluant	300 ml Eluant	500 ml Eluant
100	32.1	10.9	26.0
200	81.3*	51.0	75.0
300	93.5	86.1	92.4
400	97.5	98.5*	97.8
500	99.1	99.9	99.5
600	99.5	99.9	99.9*
700	99.9		99.9
800	99.9		99.9
900	99.9		99.9
Fresh eluant removed }	< 0.1% } U ₃ O ₈ }	Not re-eluted	Not re-eluted

* water washing begun.

In a similar test (3), two columns, loaded from synthetic leach liquor, were eluted with 2 bed volumes of 1.5N NaCl; 0.05N H₂SO₄ eluant, followed by 5 bed volumes of water. The results are given in Table 2.

TABLE 2

Use of Combination of Eluant and Wash Water for Uranium Elution, Reproducibility Test for Fixed Ratio of Eluant and Water; Eluant = 1.5N NaCl; 0.05N H₂SO₄.

Eluant	Bed Volumes	U ₃ O ₈ , % Eluted	
		Test 1	Test 2
Chloride Solution	2	62	59
Water	5	35	37
Left on Resin		3	4

A third study (4) was designed to establish in what part of the ion exchange column the various constituents were to be found after this type of elution.

A 50 ml column of resin, made up of five 10 ml sections joined together, was loaded with uranium from a sulphate solution containing 1g/l U₃O₈ and 4 g/l Fe. The column was then eluted with 2 bed volumes of 1.5N NaCl; 0.05N H₂SO₄ eluant, at a flow rate of 5 ml/min (R. T. = 4 mins) followed by 5 bed volumes of water at a flow rate of 15 ml/min (R. T. = 1.3 min). The column was taken apart, and the sections eluted separately with ammonium nitrate-nitric acid eluant. All the solutions were analyzed for uranium and sulphate. The results are summarized, as far as the distribution of the ions between the two solutions and the resin are concerned, in Table 3, and their location on the resin, in Table 4.

TABLE 3

Elution with NaCl Solution followed by Water Wash
Sectional Column Study

Distribution of Uranium and Sulphate between
Solutions and Resin

Eluant = 1.5N NaCl; 0.05M H₂SO₄

	U ₃ O ₈		SO ₄
	g	%	meq
Eluate (2 BV)	1.95	60.2	45
Water (5 BV)	1.19	36.7	12
Left on Resin	.10	3.1	4.3

TABLE 4

Elution with NaCl Solution followed by Water Wash
Sectional Column Study

Distribution of Uranium, Chloride and Sulphate
in the Sections

Eluant = 1.5N NaCl; 0.05M H₂SO₄

Ions	Section (10 ml volume)				
	Top				Bottom
	1	2	3	4	5
Chloride (meq)	12	11.7	11	9	8
Sulphate (meq)	<.05	.3	.12	1.6	2.6
U ₃ O ₈ (mg)	2.8	5.0	13	29	51

The previous tests, though not intended to establish this point, showed that even with rapid flow rates the conversion of the resin to the chloride form could be very largely completed with a small number of bed volumes of chloride eluant.

Tests were therefore carried out to see whether the rate and completeness of conversion could be improved using a strong chloride solution (5). For this purpose, the eluant was made 3N in NaCl and 0.1N in H_2SO_4 . Resin loaded from synthetic leach liquor was eluted with 2.4 bed volumes of this solution (R. T. = 10 min) followed by 3.2 bed volumes of water (R. T. = 12.5 min). The results are given in Table 5.

TABLE 5

Elution with Strong Chloride Eluant followed by
Water Wash

Eluant - 3.0N NaCl, 0.1N H_2SO_4 R. T. = 10 min
Water, R. T. = 12.5 min :

Solution	Bed Volumes	Fe		SO ₄		U ₃ O ₈	
		g/l	%	g/l	%	g/l	%
Eluant	0.8	4.5	49.5	29.4	86.0	20.2	26.4
	0.8	2.0	22.0	2.4	7.0	15.2	19.7
	0.8	2.0	22.0	--	--	8.1	10.6
	(water displacement)	0.8	.2	2.2	2.1	6.1	11.2
Water	0.8	.4	4.3	.3	.9	20.7	27.1
	0.8	--	--	--	--	.9	1.2
	0.72	--	--	--	--	.3	.4
	0.08	--	--	--	--	.1	.1

2. Current Work

Three series of tests were carried out. In series 1, resin loaded with uranium and sulphate only was eluted with concentrated neutral sodium chloride solutions followed by the water wash treatment. The chloride concentration was varied from 5N to 2N. The relative proportion of the water to the chloride solutions was varied. Determinations of uranium and sulphate were carried out on each bed volume of effluent. The results are given in Tables 6 to 12, plotted in Figures 2 to 8, and summarized in comparison with all the data, in Table 20. In series 2, similar tests were carried out, using, in place of the concentrated neutral chloride solutions, solutions that had been made 0.05N in hydrochloric acid. Since it was not believed that the presence of the acid would have any significant effect, this series was restricted to the minimum number of tests to establish this belief. The results will be found in Tables 13 to 16, are plotted in Figures 9 to 12, and summarized in Table 20. series 3, consisted of a series of tests using the concentrated neutral chloride eluant on a resin which had been loaded from a synthetic solution containing thorium in addition to uranium and sulphate. The effluent samples were also analyzed for thorium. The results are given in Tables 17 to 19, plotted in Figures 13 to 15, and summarized in Table 20.

TABLE 6

Effluent Solution Analyses; Series 1, Test 1
Neutral 5N Chloride Solution;
 1 Volume Chloride, 7 Volumes Water

Eluting Solution	Volume Throughput		Effluent Analyses				
			Cl	SO ₄		U ₃ O ₈	
	ml	BV	g/l	g/l	g	g/l	g
5N NaCl	0-25	1	1.36	47.61	1.190	12	.30
Water	25-50	2	93.3	49.62	1.240	43	1.08
Water	50-75	3	4.36	.99	.025	18	.45
Water	75-100	4	1.00	.30	.008	2.7	.07
Water	100-125	5	.46	<0.03		1.3	.03
Water	125-150	6	.28	<0.03		.78	.02
Water	150-175	7	.25	<0.03		.9	.02
Water	175-200	8	.12	<0.03		.33	.008
N HCl	200-300	9-12	--	2.13		.21	.021
Total					2.46		2.00

Resin volume = 25 ml

Average retention time = 8.7 min

TABLE 7

Effluent Solution Analyses; Series 1, Test 2
Neutral 5N Chloride Solution;
 2 Volumes Chloride, 5 Volumes Water

Eluting Solution	Volume Throughput		Effluent Analyses				
			Cl	SO ₄		U ₃ O ₈	
	ml	BV	g/l	g/l	g	g/l	g
5N NaCl	0-25	1	3.7	56.1	1.40	17.2	0.43
5N NaCl	25-50	2	142	37.7	.94	13.5	.34
Water	50-75	3	138	4.9	.12	33.1	.83
Water	75-100	4	4.8	.48	.01	14	.35
Water	100-125	5	1.3	<.03	--	1.9	.05
Water	125-150	6	.3	<.03	--	.5	.01
Total					2.47		2.01

Resin volume = 25 ml

Average retention time = 8.6 min

TABLE 8

Effluent Solution Analyses; Series 1, Test 3
Neutral 5N Chloride Solution;
 6 Volumes Chloride, 4 Volumes Water

Eluting Solution	Volume		Effluent Analyses				
	Throughput		Cl	SO ₄		U ₃ O ₈	
	ml	BV	g/l	g/l	g	g/l	g
5N NaCl	0-25	1	1.9	48.9	1.22	20(est)	.5
5N NaCl	25-50	2	127	46.9	1.17	15	.38
5N NaCl	50-75	3	173	5.3	.13	1.6	.04
5N NaCl	75-100	4	175	2.3	.06	1.1	.03
5N NaCl	100-125	5	176	1.8	.04	.80	.02
5N NaCl	125-150	6	177	.84	.02	.79	.02
Water	150-175	7	135	.66		29.1	.73
Water	175-200	8	3.3	< .03	--	10	.25
Water	200-225	9	.7	< .03	--	.36	.01
Water	225-250	10	.1	< .03	--	.15	.004
Total					2.66		2.0

Resin volume = 25 ml

Average retention time = 8.7 min

TABLE 9

Effluent Solution Analyses; Series 1, Test 4
Neutral 4N Chloride Solution;
 3 Volumes Chloride, 5 Volumes Water

Eluting Solution	Volume		Effluent Analyses				
	Throughput		Cl	SO ₄		U ₃ O ₈	
	ml	BV	g/l	g/l	g	g/l	g
4N NaCl	0-25	1	0.6	40.6	1.01	9.4	.23
4N NaCl	25-50	2	97.2	50.8	1.27	25	.63
4N NaCl	50-75	3	133	6.3	.16	3.2	.08
Water	75-100	4	113	3.5	.09	30	.75
Water	100-125	5	4.8	.2	.005	13.3	.33
Water	125-150	6	1.4	< .03	--	1.3	.03
Water	150-175	7	.4	< .03	--	.9	.02
Water	175-200	8	.1	< .03	--	.2	.005
Total					2.53		2.08

Resin volume = 25 ml

Average retention time = 8.7 min

TABLE 10

Effluent Solution Analyses; Series I, Test 5,
Neutral 4N Chloride Solution;
 7 Volumes Chloride, 3 Volumes Water

Eluting Solution	Volume		Effluent Analyses				
	Throughput		Cl g/l	SO ₄		U ₃ O ₈	
	ml	BV		g/l	g	g/l	g
4N NaCl	0-25	1	.97	43.9	1.10	9.8	.25
4N NaCl	25-50	2	98.5	49.0	1.22	21.7	.54
4N NaCl	50-75	3	136	6.2	.16	3.5	.09
4N NaCl	75-100	4	139	3.1	.08	2.3	.06
4N NaCl	100-125	5	139	2.3	.06	3.1	.08
4N NaCl	125-150	6	141	.8	.02	2.1	.05
4N NaCl	150-175	7	142	.6	.01	1.9	.05
Water	175-200	8	115	.5	.01	26	.65
Water	200-225	9	3.6	< .03	--	9	.22
Water	225-250	10	.8	< .03	--	.5	.01
Total					2.66		2.00

Resin volume = 25 ml

Average retention time = 8.6 min

TABLE 11

Effluent Solution Analyses; Series I, Test 6
Neutral 3N Chloride Solution;
 7 Volumes Chloride, 3 Volumes Water

Eluting Solution	Volume		Effluent Solution Analyses				
	Throughput		Cl g/l	SO ₄		U ₃ O ₈	
	ml	BV		g/l	g	g/l	g
3N NaCl	0-25	1	.24	34.1	.85	6.3	.16
3N NaCl	25-50	2	67	56.6	1.42	30	.75
3N NaCl	50-75	3	102	7.6	.19	7.5	.19
3N NaCl	75-100	4	104	3.7	.09	5.2	.13
3N NaCl	100-125	5	105	2.5	.06	4.4	.11
3N NaCl	125-150	6	97	1.1	.03	3.3	.08
3N NaCl	150-175	7	90	.7	.02	3.2	.08
Water	175-200	8	74	.5	.01	15	.38
Water	200-225	9	.7	< .03	--	3	.07
Water	225-250	10	.01	< .03	--	.2	.005
Total					2.67		1.95

Resin volume = 25 ml

Average retention time = 9.0 min

TABLE 12

Effluent Solution Analyses; Series 1, Test 7
Neutral 2N Chloride Solution;
 8 Volumes Chloride, 2 Volumes Water

Eluant	Volume Throughput		Effluent Solution Analyses				
			Cl	SO ₄		U ₃ O ₈	
	ml	BV	g/l	g/l	g	g/l	g
2N NaCl	0-25	1	.025	24.1	.60	3.3	.08
2N NaCl	25-50	2	32.5	57.9	1.45	30.1	.75
2N NaCl	50-75	3	64.2	12.9	.32	13.5	.34
2N NaCl	75-100	4	67.8	5.6	.14	8.7	.22
2N NaCl	100-125	5	79.2	2.9	.07	7.4	.19
2N NaCl	125-150	6	70.5	1.8	.04	4.1	.10
2N NaCl	150-175	7	70.5	1.1	.03	3.1	.08
2N NaCl	175-200	8	70.2	.63	.02	2.2	.05
Water	200-225	9	51.1	.48	.01	4.9	.12
Water	225-250	10	.30	< .03		.6	.01
Total					2.68		1.94

Resin volume = 25 ml

Average retention time = 8.3 min

TABLE 13

Effluent Solution Analyses; Series 2, Test 1,
Acidified 5N Chloride Solution (0.05N HCl);
 4 Volumes Chloride, 3 Volumes Water

Eluant	Volume Throughput		Effluent Solution Analyses				
			Cl	SO ₄		U ₃ O ₈	
	ml	BV	g/l	g/l	g	g/l	g
5N NaCl	0-25	1	1	49.0	1.22	15.4	.38
5N NaCl	25-50	2	131	48.5	1.21	15.5	.39
5N NaCl	50-75	3	172	5.07	.13	.8	.02
5N NaCl	75-100	4	175	1.86	.05	1	.02
Water	100-125	5	141	.48	.01	35	.88
Water	125-150	6	5.5	< .03		12.3	.31
Water	150-175	7	.7	< .03		.4	.01
Total					2.62		2.01

Resin volume = 25 ml

Average retention time = 8.8 min

TABLE 14

Effluent Solution Analyses; Series 2, Test 2
Acidified 4N Chloride Solution, 0.05N HCl;
 7 Volumes Chloride, 3 Volumes Water

Eluant	Volume		Effluent Solution Analyses				
	Throughput		Cl	SO ₄		U ₃ O ₈	
	ml	BV	g/l	g/l	g	g/l	g
4N NaCl	0-25	1	.6	40.6	1.02	9.8	.25
4N NaCl	25-50	2	105	54.9	1.37	21.6	.54
4N NaCl	50-75	3	134	6.45	.16	2.9	.07
4N NaCl	75-100	4	141	2.85	.07	2.1	.05
4N NaCl	100-125	5	140	1.17	.03	2.0	.05
4N NaCl	125-150	6	132	.69	.02	3.0	.08
4N NaCl	150-175	7	134	.45	.01	1.8	.04
Water	175-200	8	111	.30	.008	25.4	.64
Water	200-225	9	4.6	<.03	.008	12.6	.31
Water	225-250	10	.6	<.03	.008	0.3	.03
Total					2.70		2.04

Resin volume = 25 ml

Average retention time = 8.5 min

TABLE 15

Effluent Solution Analyses; Series 2, Test 3
Acidified 3N Chloride Solution; 0.05N HCl
 7 Volumes Chloride, 3 Volumes Water

Eluant	Volume		Effluent Solution Analyses				
	Throughput		Cl	SO ₄		U ₃ O ₈	
	ml	BV	g/l	g/l	g	g/l	g
3N NaCl	0-25	1	.5	36.0	.90	6.4	.16
3N NaCl	25-50	2	66	55.8	1.40	26.5	.66
3N NaCl	50-75	3	103	8.2	.20	7.4	.19
3N NaCl	75-100	4	107	3.6	.09	4.4	.11
3N NaCl	100-125	5	108	1.7	.04	4.8	.12
3N NaCl	125-150	6	116	1.1	.03	3.2	.08
3N NaCl	150-175	7	108	.66	.02	3.2	.08
Water	175-200	8	83	.45	.01	16	.40
Water	200-225	9	1.7	<.03		3.4	.08
Water	225-250	10	.6	<.03		.1	.004
Total					2.69		1.88

Resin volume = 25 ml

Average retention time = 8.6 min

TABLE 16

Effluent Solution Analyses; Series 2, Test 4
Acidified 2N Chloride Solution; 0.05N HCl
 7 Volumes Chloride, 3 Volumes Water

Eluant	Volume		Effluent Analyses				
	Throughput		Cl g/l	SO ₄		U ₃ O ₈	
	ml	BV		g/l	g	g/l	g
2N NaCl	0-25	1	.015	27.1	.68	4.6	.11
2N NaCl	25-50	2	32	57.5	1.44	27.2	.68
2N NaCl	50-75	3	63	12.0	.30	11.5	.29
2N NaCl	75-100	4	61	5.0	.12	11.0	.28
2N NaCl	100-125	5	65	2.6	.066	6.9	.17
2N NaCl	125-150	6	66	1.3	.033	4.6	.12
2N NaCl	150-175	7	66	.66	.016	2.2	.05
Water	175-200	8	48	.36	.009	5.7	.14
Water	200-225	9	.44	<.03	--	.8	.02
Water	225-250	10	.44	<.03	--	.03	.001
Total					2.66		1.86

Resin volume = 25 ml

Average retention time = 8.6 min

TABLE 17

Effluent Solution Analyses; Series 3, Test 1
(Thorium on Resin) Neutral 5N Chloride Solution;
 2 Volumes Chloride, 4 Volumes Water

Eluant	Volume		Effluent Solution Analyses						
	Throughput		Cl g/l	SO ₄		ThO ₂		U ₃ O ₈	
	ml	BV		g/l	g	g/l	g	g/l	g
5N NaCl	0-25	1	1.0	52.1	1.30	.64	.016	9.1	.23
5N NaCl	25-50	2	119	48.0	1.20	.44	.011	12.3	.31
Water	50-75	3	15.	3.7	.09	<.01	--	24.1	.60
Water	75-100	4	7.	0.6	.00	<.01	--	22.9	.57
Water	100-125	5	.4	<.03	--	<.03	--	0.93	.02
Water	125-150	6	.1	<.03	--	<.005	--	0.41	.01
Total			--		2.61		.027	--	1.74

Resin volume = 25 ml

Average retention time = 10.2 min

TABLE 18

Effluent Solution Analyses; Series 3, Test 2
(Thorium on Resin)-Neutral 4N Chloride Solution;
 2 Volumes Chloride, 5 Volumes Water

Eluant	Volume		Effluent Solution Analyses						
	Throughput		Cl	SO ₄		Th O ₂		U ₃ O ₈	
	ml	BV	g/l	g/l	g	g/l	g	g/l	g
4N NaCl	0-50	1	1.5	57.2	2.86	0.76	.038	11	0.55
4N NaCl	50-100	2	12.5	40.5	2.02	0.36	.018	12	0.60
Water	100-150	3	107.	3.3	.16	<.01	--	27.7	1.38
Water	150-200	4	4.4	.45	.02	<.01	--	16.0	.80
Water	200-250	5	.86	<.03	--	<.001	--	1.5	.07
Water	250-300	6	.16	<.03	--	<.001	--	.8	.04
Water	300-350	7	.03	<.03	--	<.001	--	.14	.007
Total					5.07		.056		3.45

Resin volume = 50 ml

Average retention time = 9.7 min

TABLE 19

Effluent Solution Analyses; Series 3, Test 3
(Thorium on Resin), Neutral 3N Chloride Solution;
 2 Volumes Chloride, 4 Volumes Water

Eluant	Volume		Effluent Solution Analyses						
	Throughput		Cl	SO ₄		Th O ₂		U ₃ O ₈	
	ml	BV	g/l	g/l	g	g/l	g	g/l	g
3N NaCl	0-50	1	.5	52.7	2.64	.69	.034	8.6	.43
3N NaCl	50-100	2	81.	42.6	2.13	.38	.019	18.3	.92
Water	100-150	3	82.	4.5	.22	.11	.006	25.8	1.29
Water	150-200	4	3.5	0.5	.02	.03	.002	11.4	.57
Water	200-250	5	.50	<.03	--	<.001	--	2.1	.11
Water	250-300	6	.14	<.03	--	<.001	--	0.9	.04
Total					5.01		.061		3.36

Resin volume = 50 ml

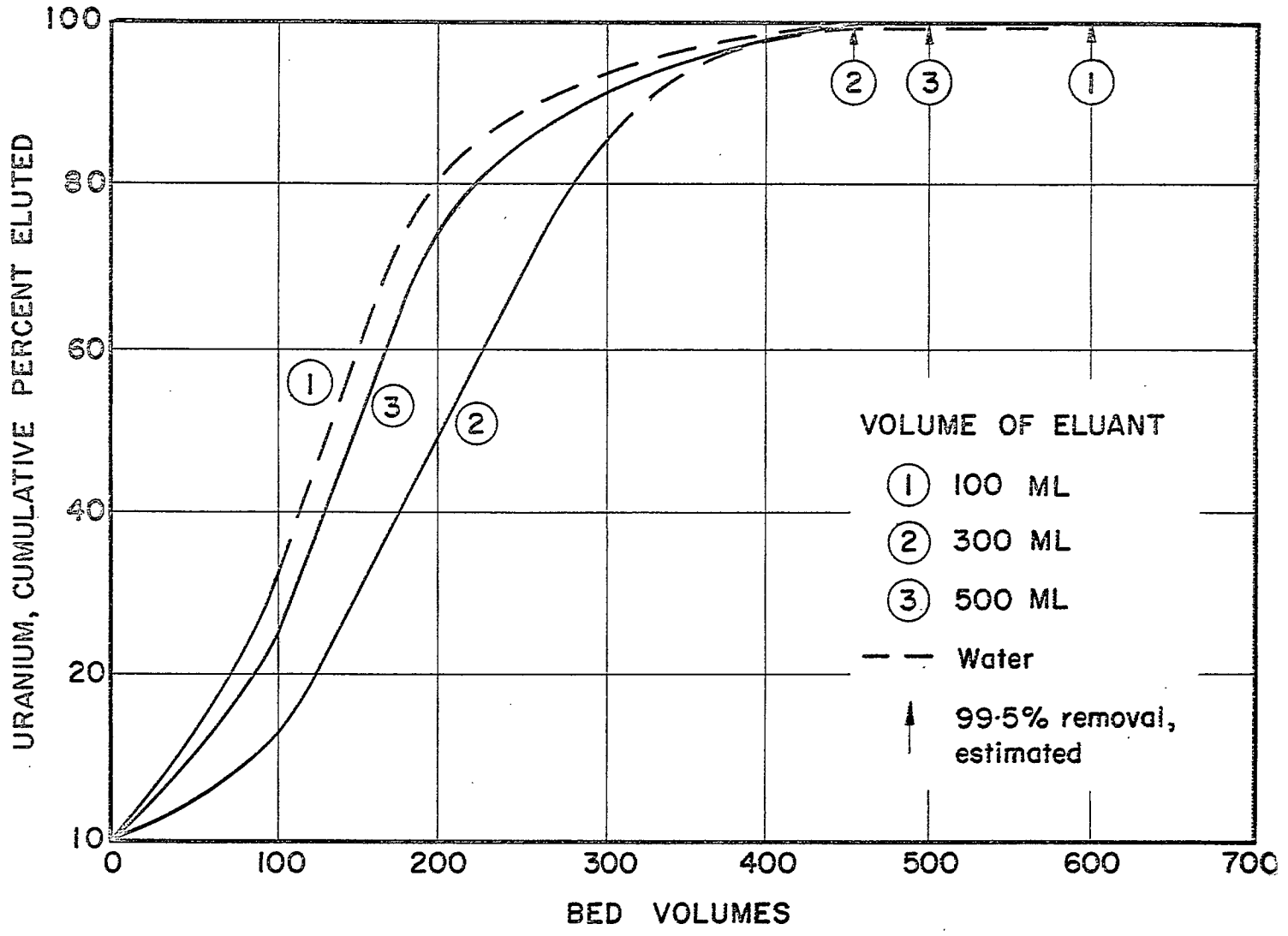
Average retention time = approx. 9 min

TABLE 20

Summary of Strong Chloride Elution Results, Showing Percent Distribution of Solution Components between Concentrated Chloride Eluate and Water Wash, for Chloride Concentrations from 2 to 5N, and for Various Combinations of Recycle

Table No.	N NaCl Solution	Bed Volumes of NaCl Solution Used	Bed Volumes of Water Used	Proposed Recycle Eluate Contained in 1st n Bed Volumes				Proposed Precipitation Feed Contained in next m Bed Volumes			
				n	SO ₄	ThO ₂	U ₃ O ₈	m	SO ₄	ThO ₂	U ₃ O ₈
					%	%	%		%	%	%
6	5	1	7	1	44.4	--	15.0	7	55.6	--	85.0
				2	91.0	--	68.3	6	9.0	--	31.7
7	5	2	5	2	94.7	--	38.5	4	5.3	--	61.5
				3	99.6	--	79.4	3	.4	--	20.6
8	5	6	4	2	89.8	--	44.4	8	10.2	--	55.6
				3	91.4	--	46.0	7	8.6	--	54.0
				6	99.6	--	50.0	4	.4	--	50.0
13	5 (acidified)	4	3	2	93.3	--	38.3	5	6.7	--	61.7
				3	98.2	--	39.3	4	1.8	--	60.7
				4	99.6	--	40.3	3	.4	--	59.7
17	5	2	4	2	95.8	95. +	31.0	4	4.2	< 5	69.0
				3	99.4	95. +	65.5	3	.6	< 5	34.5
9	4	3	5	2	90.3	--	41.3	6	9.7	--	58.7
				3	96.6	--	45.2	5	3.4	--	54.8
10	4	7	3	2	87.2	--	39.5	8	12.8	--	60.5
				3	93.3	--	44.0	7	6.7	--	56.0
				7	99.6	--	55.5	3	.4	--	44.5
14	4 (acidified)	7	3	2	88.7	--	38.8	8	11.3	--	61.2
				3	96.2	--	42.2	7	3.8	--	57.8
				7	99.6	--	62.9	3	.4	--	37.1
18	4	2	5	2	93.1	95 +	33.7	5	6.9	< 5	66.3
				3	99.2	95 +	73.8	4	.8	< 5	26.2
11	3	7 *	3	2	85.0	--	46.5	8	15.0	--	53.5
				3	92.1	--	55.5	7	7.9	--	44.5
				7	99.6	--	76.9	3	.4	--	23.1
15	3 (acidified)	7 *	3	2	85.5	--	43.6	8	14.5	--	56.4
				3	92.9	--	54.8	7	1.1	--	45.2
				7	99.6	--	74.0	3	.4	--	26.0
19	3	2	4	2	95.2	87	40.0	4	4.8	13	60.0
				3	99.6	97	78.6	3	.4	3	21.4
12	2	8 *	2	2	76.4	--	42.8	8	23.6	--	57.2
				3	88.4	--	60.3	7	11.6	--	39.7
				8	99.6	--	92.6	2	.4	--	7.4
16	2 (acidified)	7 *	3	2	79.7	--	42.4	8	20.3	--	57.6
				3	91.0	--	58.1	7	9.0	--	41.9
				7	99.6	--	91.4	3	.4	--	8.6

* Elution probably not complete.



from AD 5/51

FIGURE 1

USE OF COMBINATION OF ELUANT
AND WATER WASH FOR URANIUM ELUTION

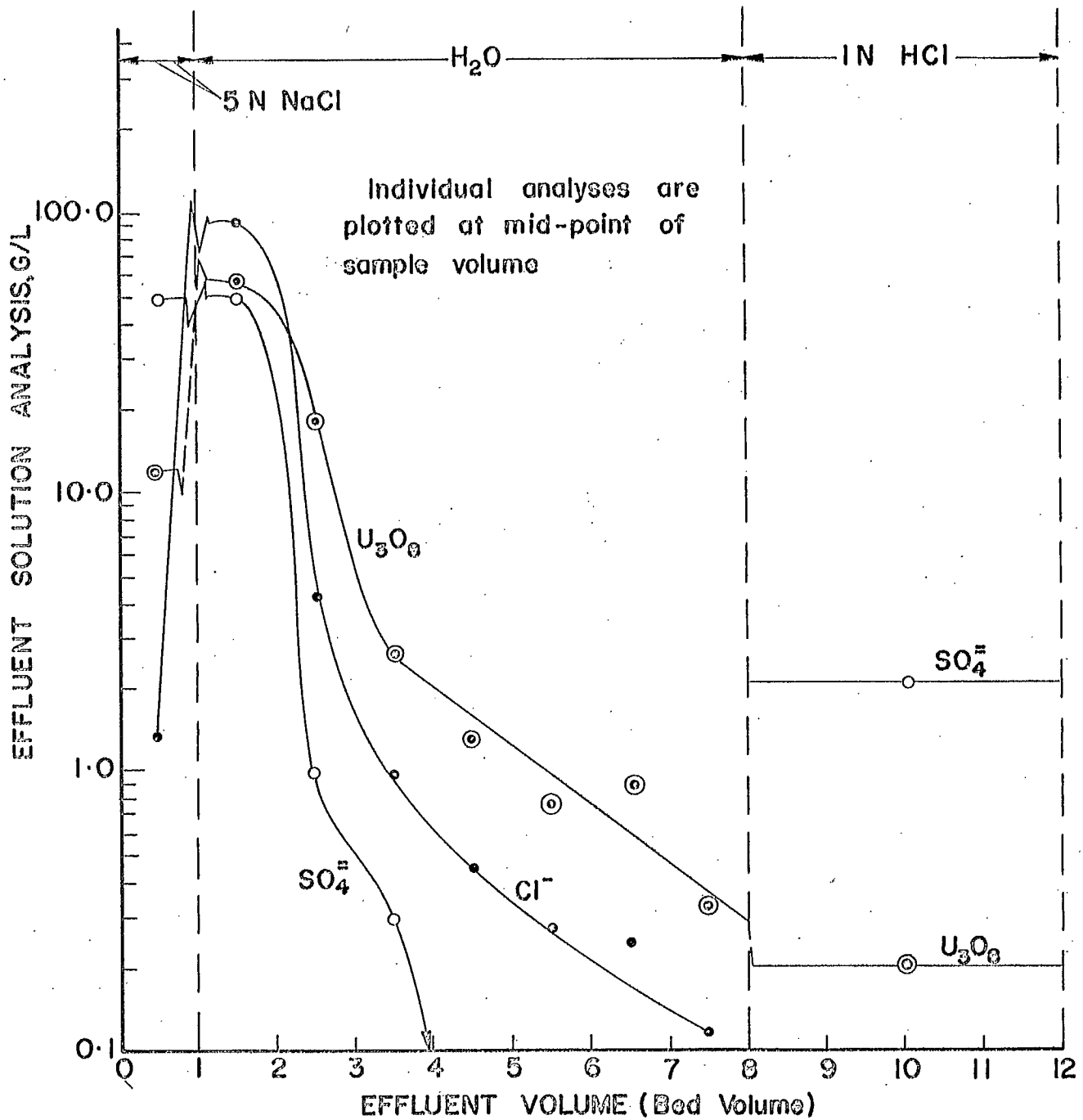


FIGURE 2

ELUTION CURVES FOR NEUTRAL 5N CHLORIDE SOLUTION
 SERIES I (See Table 6)

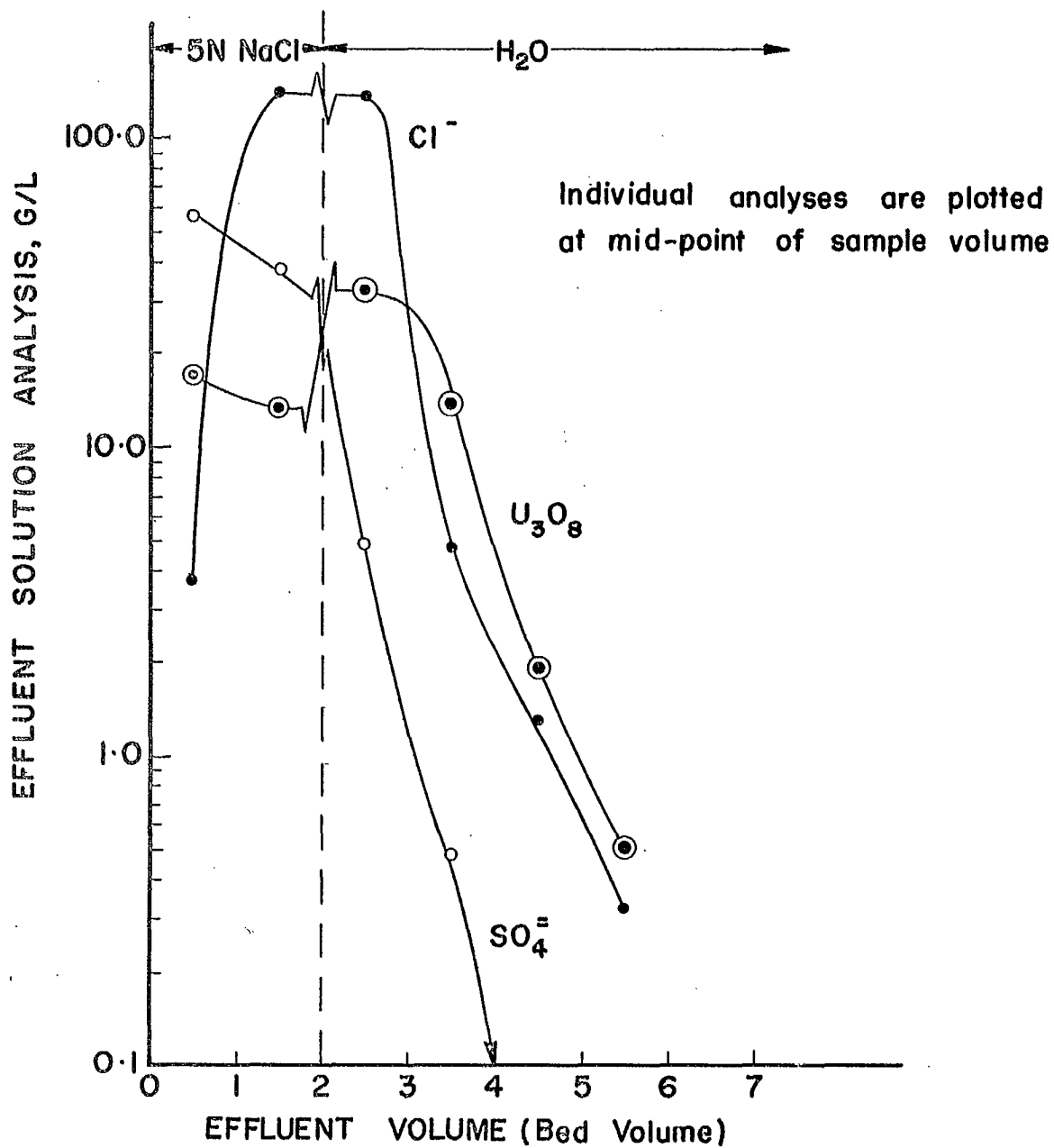


FIGURE 3

ELUTION CURVES FOR NEUTRAL 5N CHLORIDE SOLUTION
 SERIES I (See Table 7)

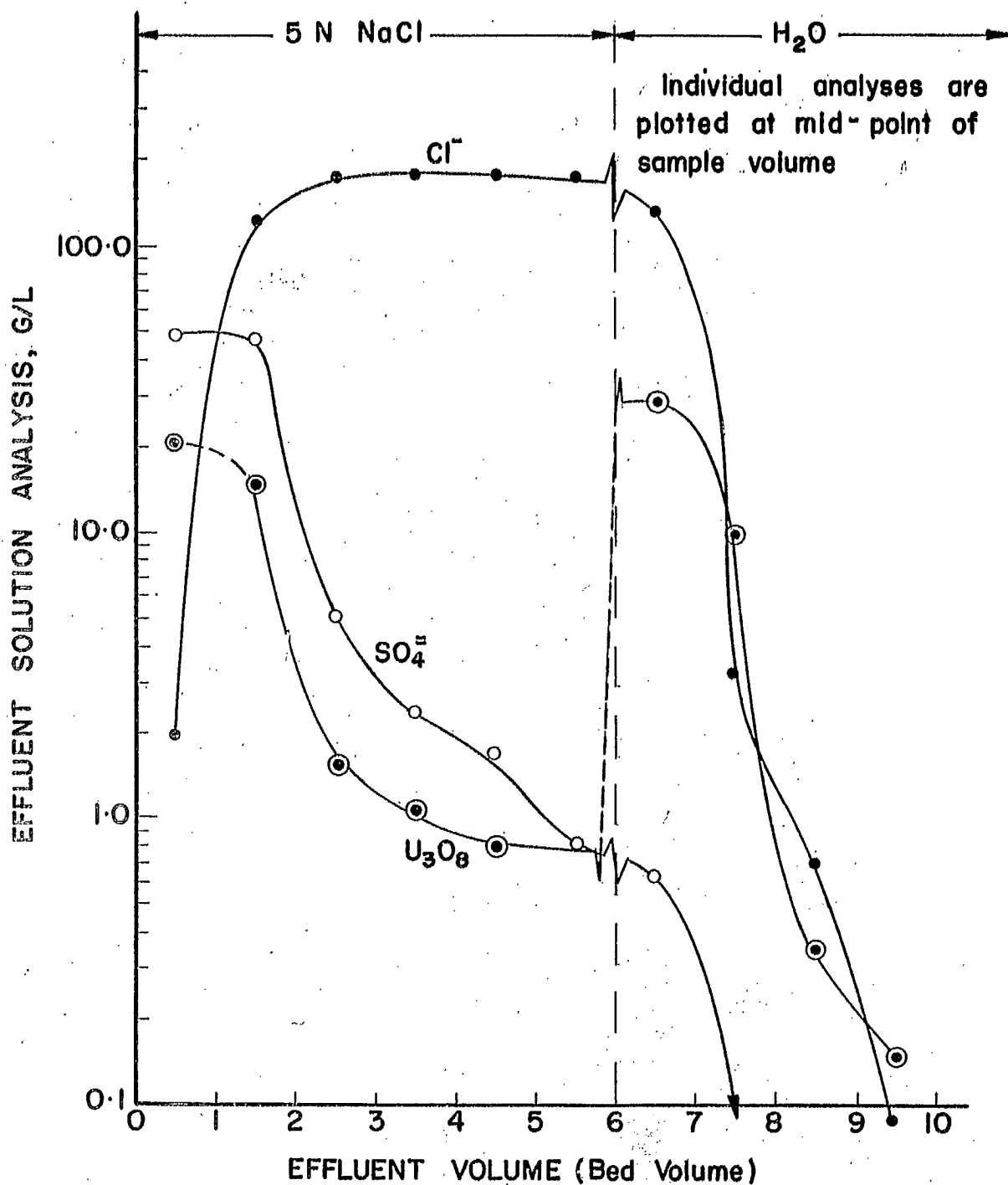


FIGURE 4

ELUTION CURVES FOR NEUTRAL 5N CHLORIDE SOLUTION
SERIES I (See Table 8)

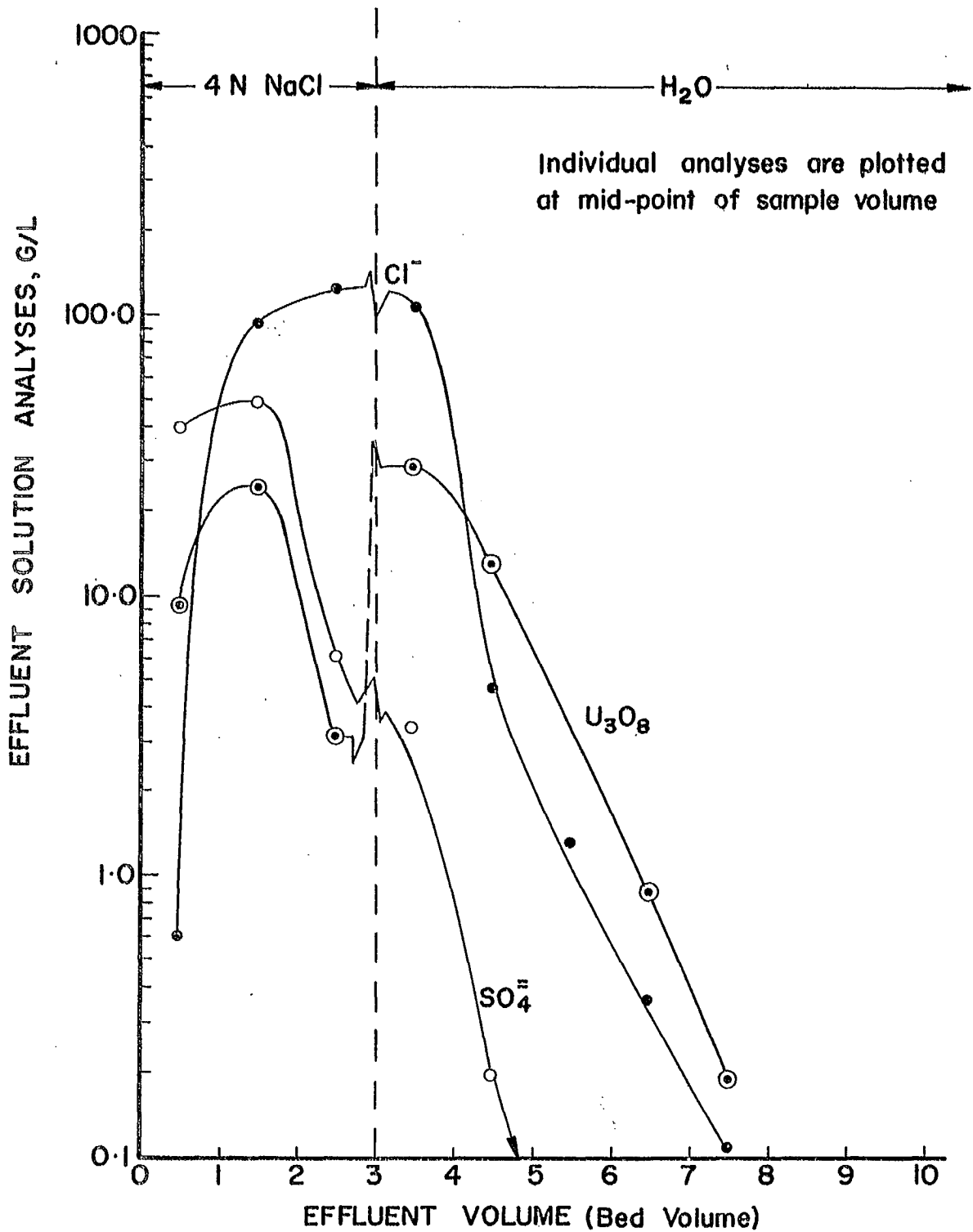


FIGURE 5

ELUTION CURVES FOR NEUTRAL 4 N CHLORIDE SOLUTION
SERIES I (See Table 9)

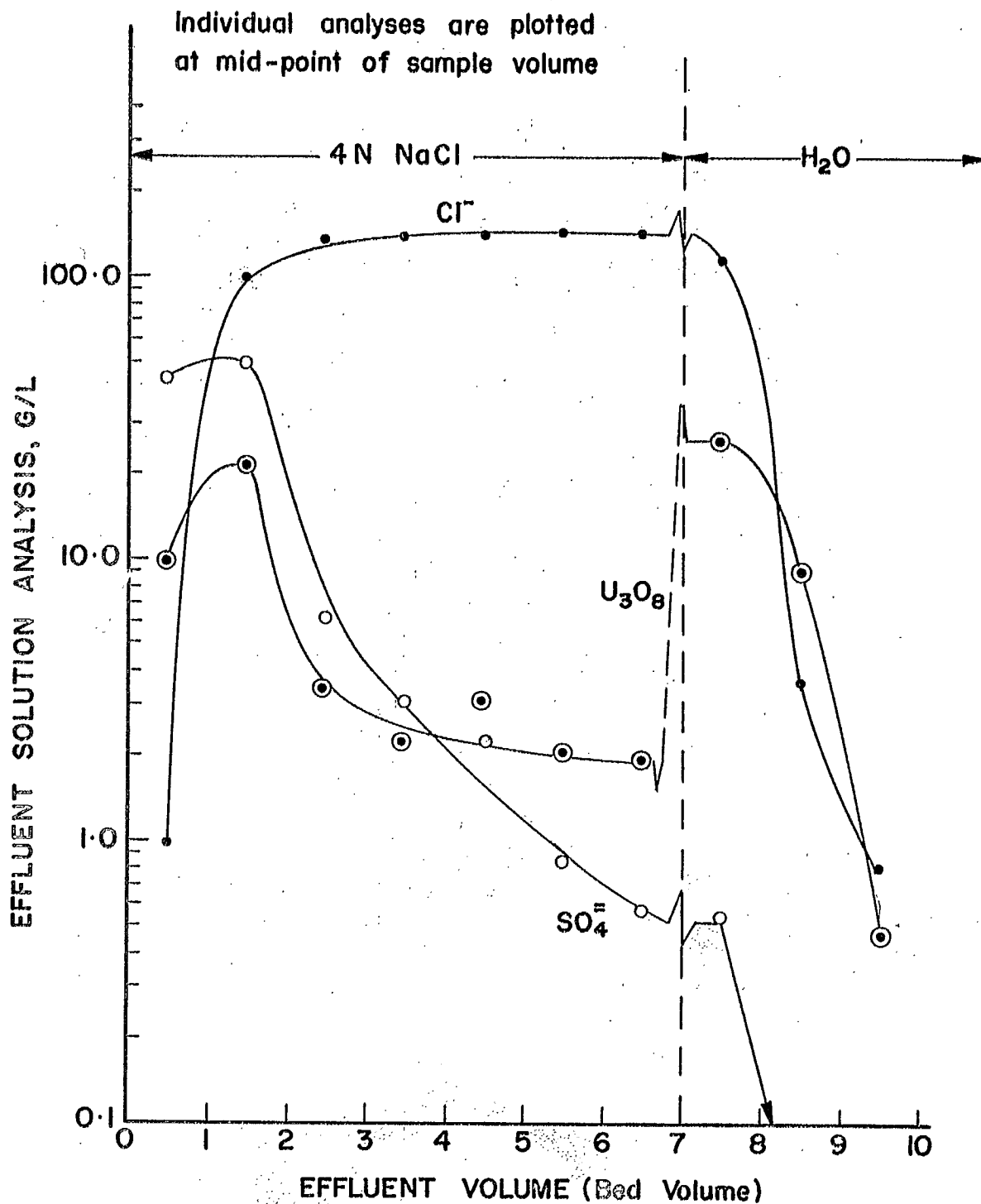


FIGURE 6

ELUTION CURVES FOR NEUTRAL 4 N CHLORIDE SOLUTION
SERIES I (See Table 10)

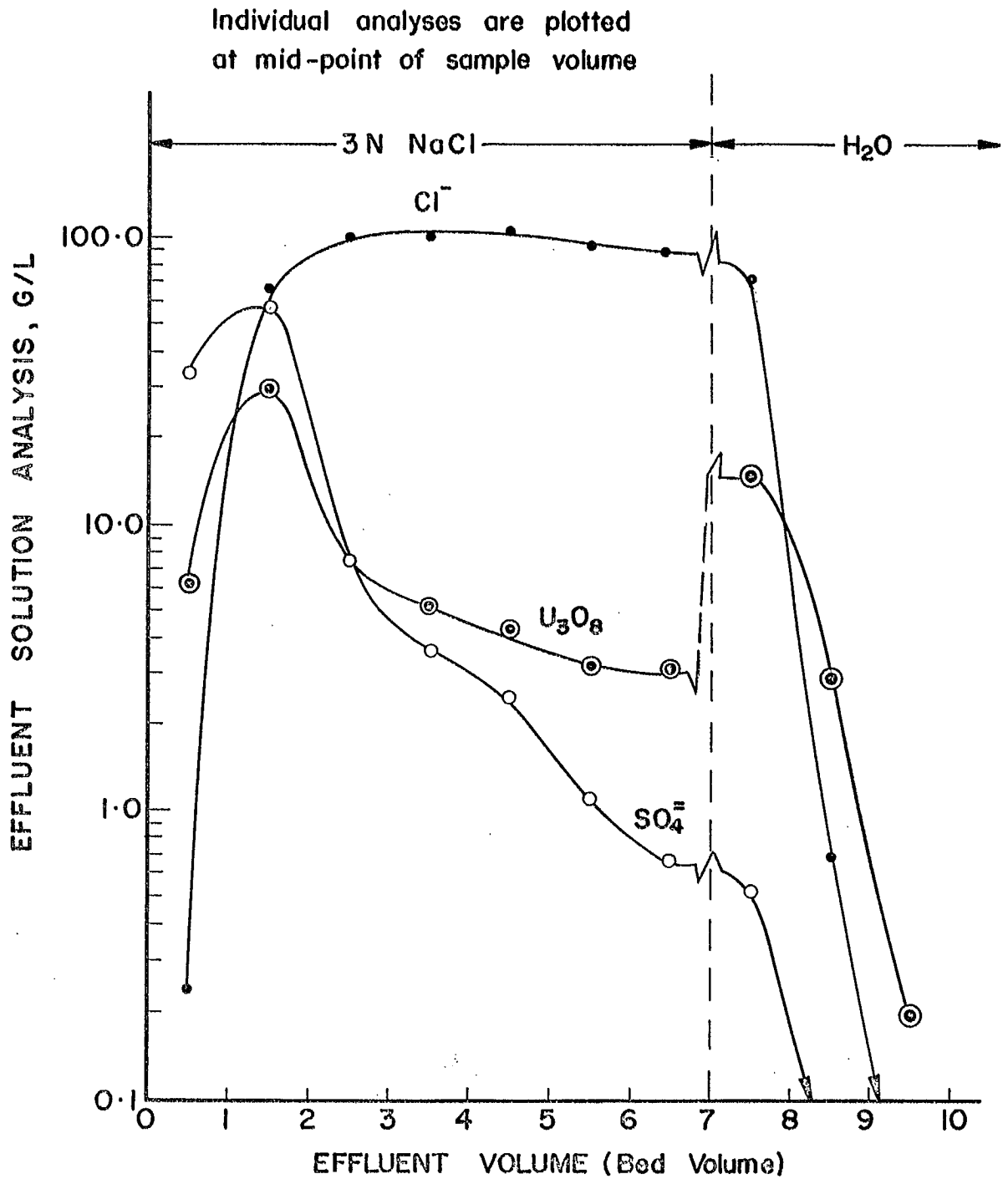


FIGURE 7

ELUTION CURVES FOR NEUTRAL 3N CHLORIDE SOLUTION
SERIES I (See Table II)

Individual analyses are plotted
at mid-point of sample volume

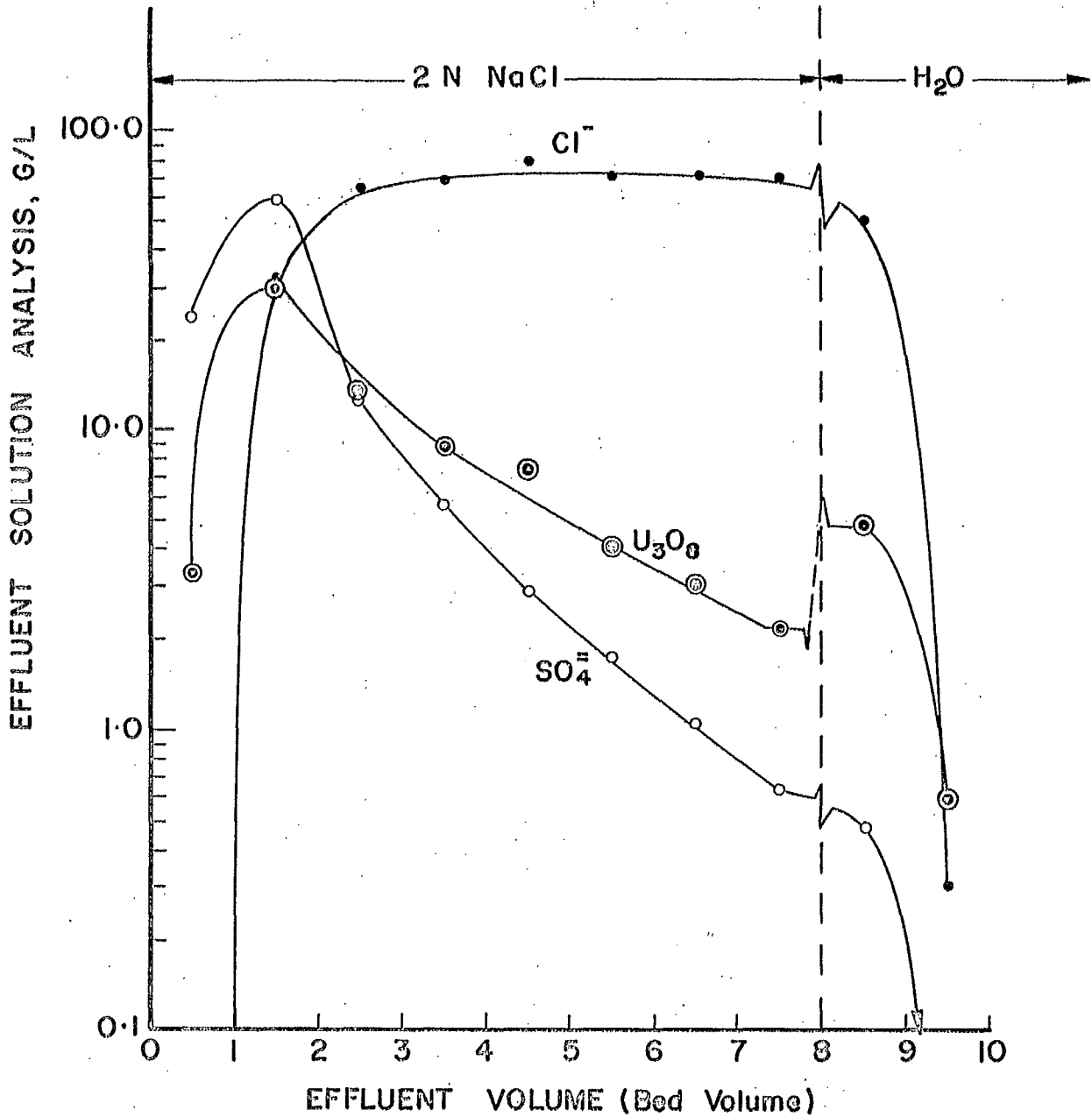


FIGURE 8

ELUTION CURVES FOR NEUTRAL 2N CHLORIDE SOLUTION
SERIES 1 (See Table 12)

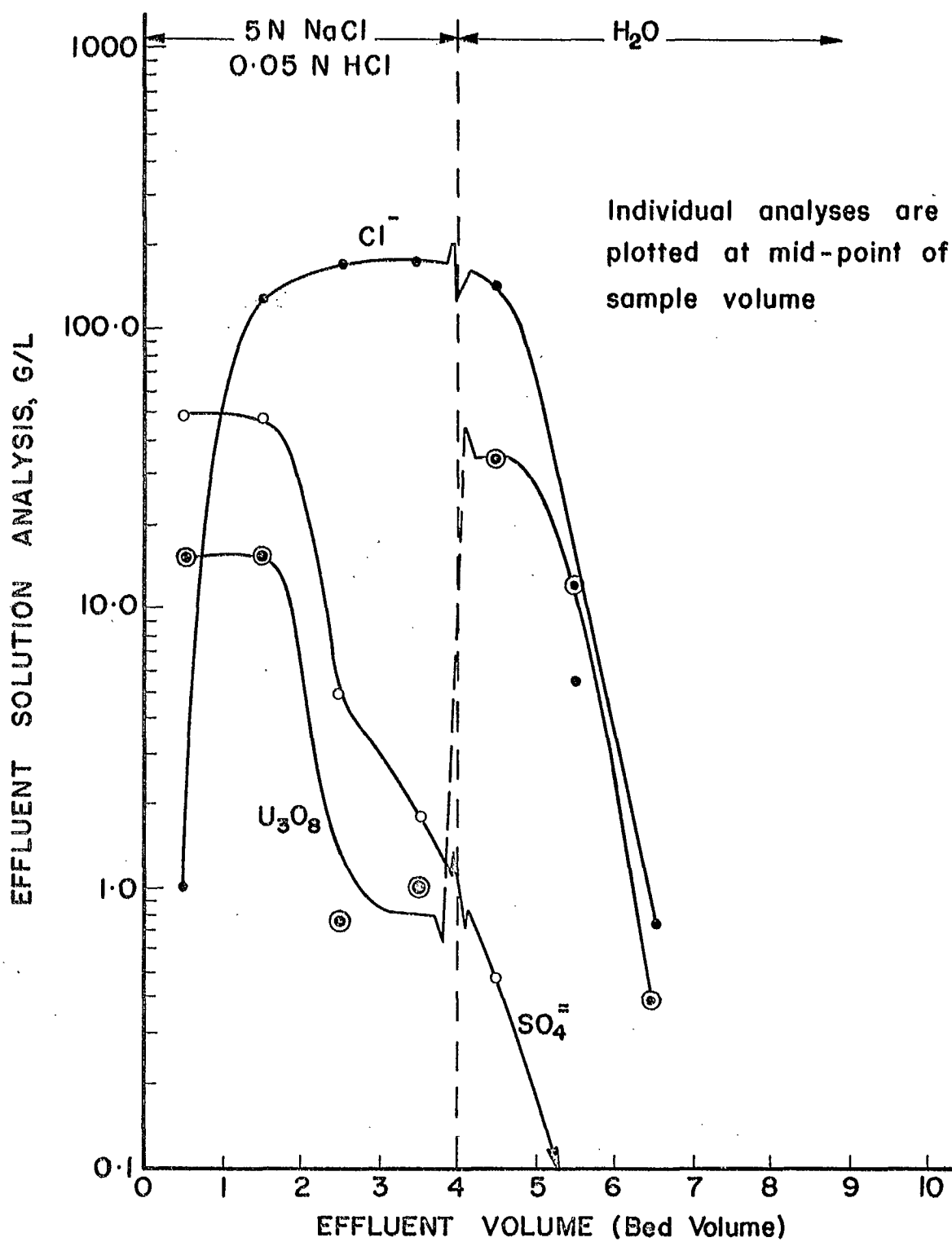


FIGURE 9

ELUTION CURVES FOR ACIDIFIED 5N CHLORIDE SOLUTION
SERIES 2 (See Table 13)

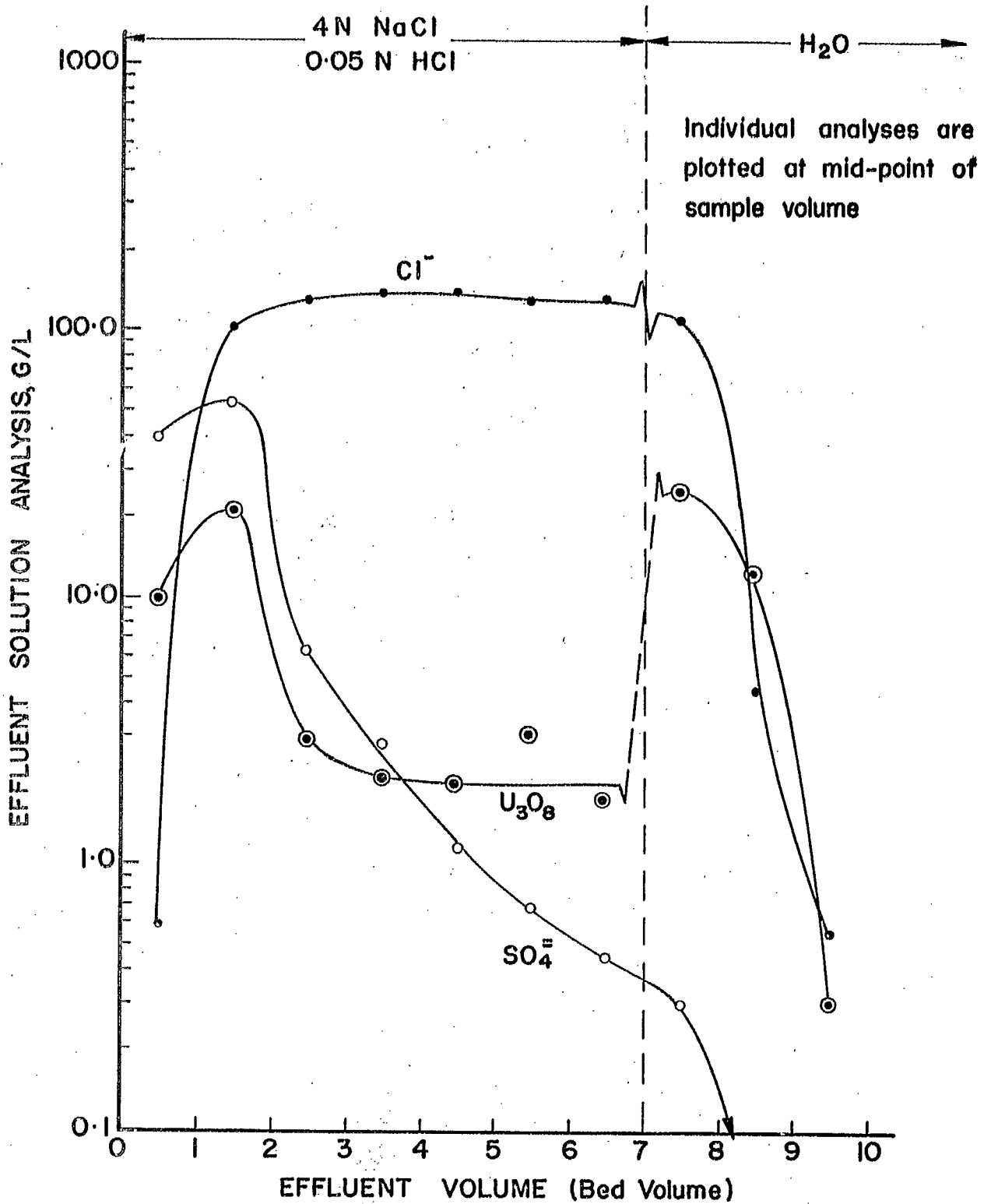


FIGURE 10

ELUTION CURVES FOR ACIDIFIED 4N CHLORIDE SOLUTION
SERIES 2 (See Table 14)

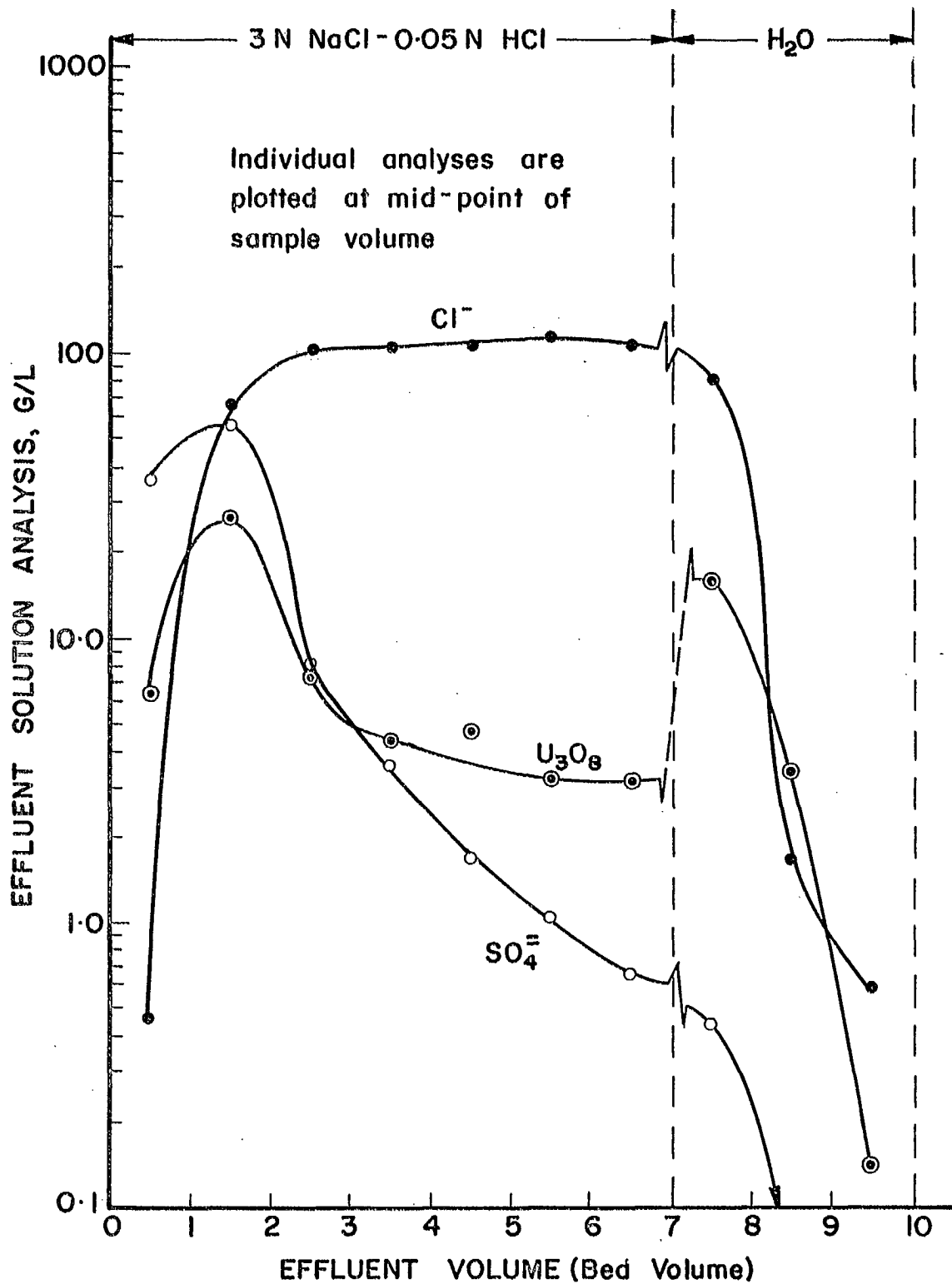


FIGURE II
 ELUTION CURVES FOR ACIDIFIED 3N CHLORIDE SOLUTION
 SERIES 2 (See Table 15)

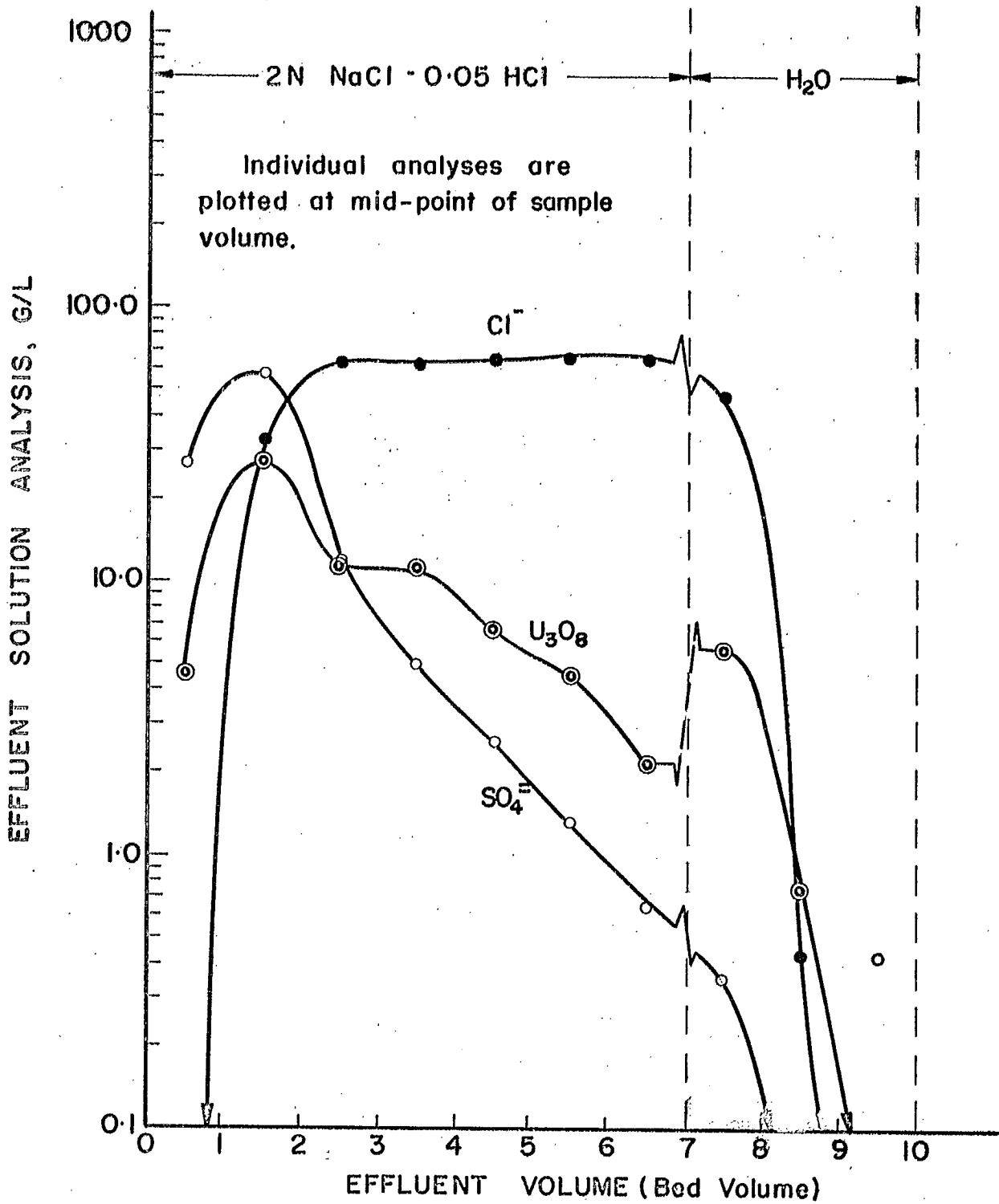


FIGURE 12

ELUTION CURVES FOR ACIDIFIED 2N CHLORIDE SOLUTION
 SERIES 2 (See Table 16)

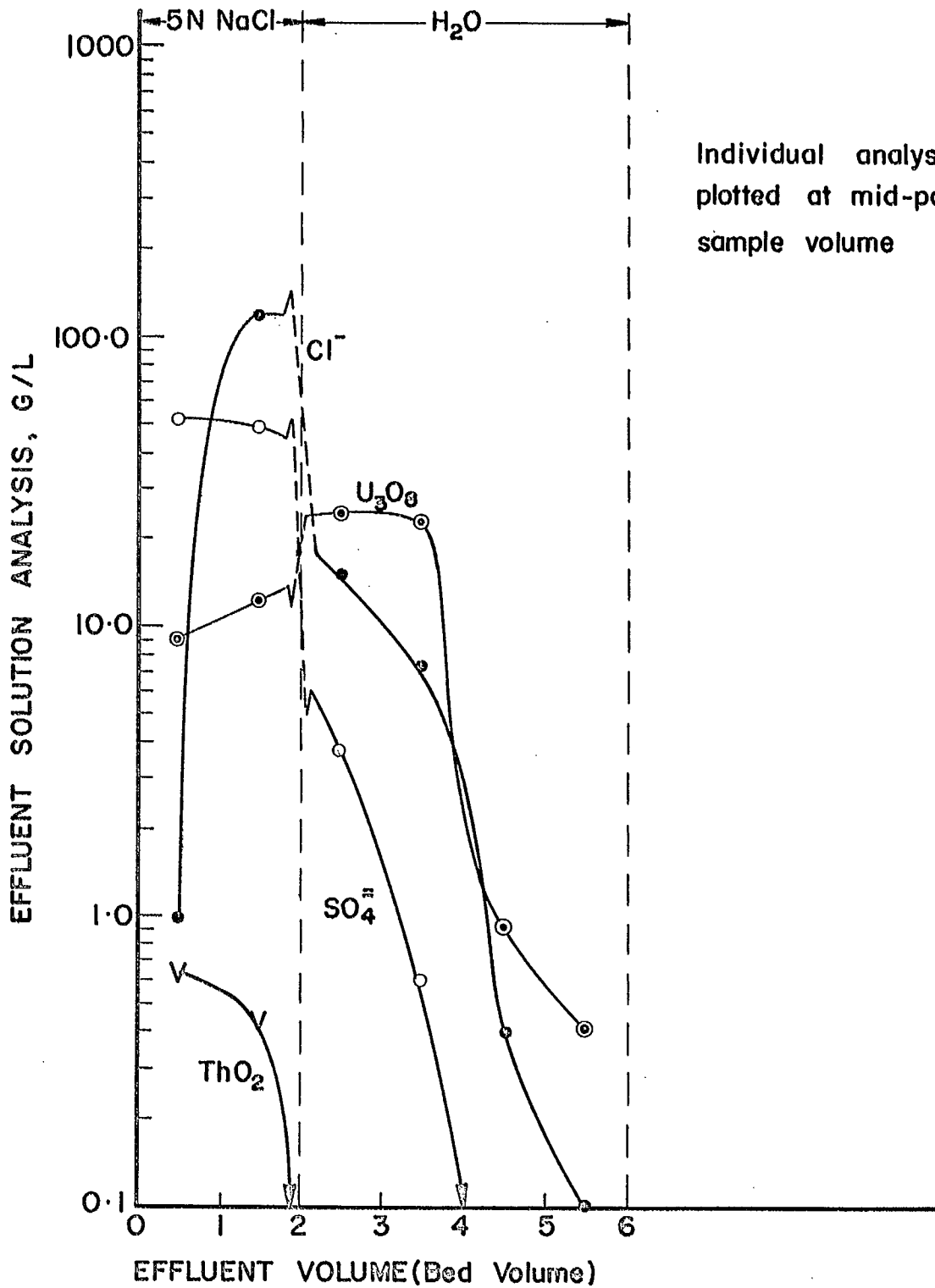


FIGURE 13
 ELUTION CURVES FOR NEUTRAL 5N CHLORIDE SOLUTION
 SERIES 3 (See Table 17)

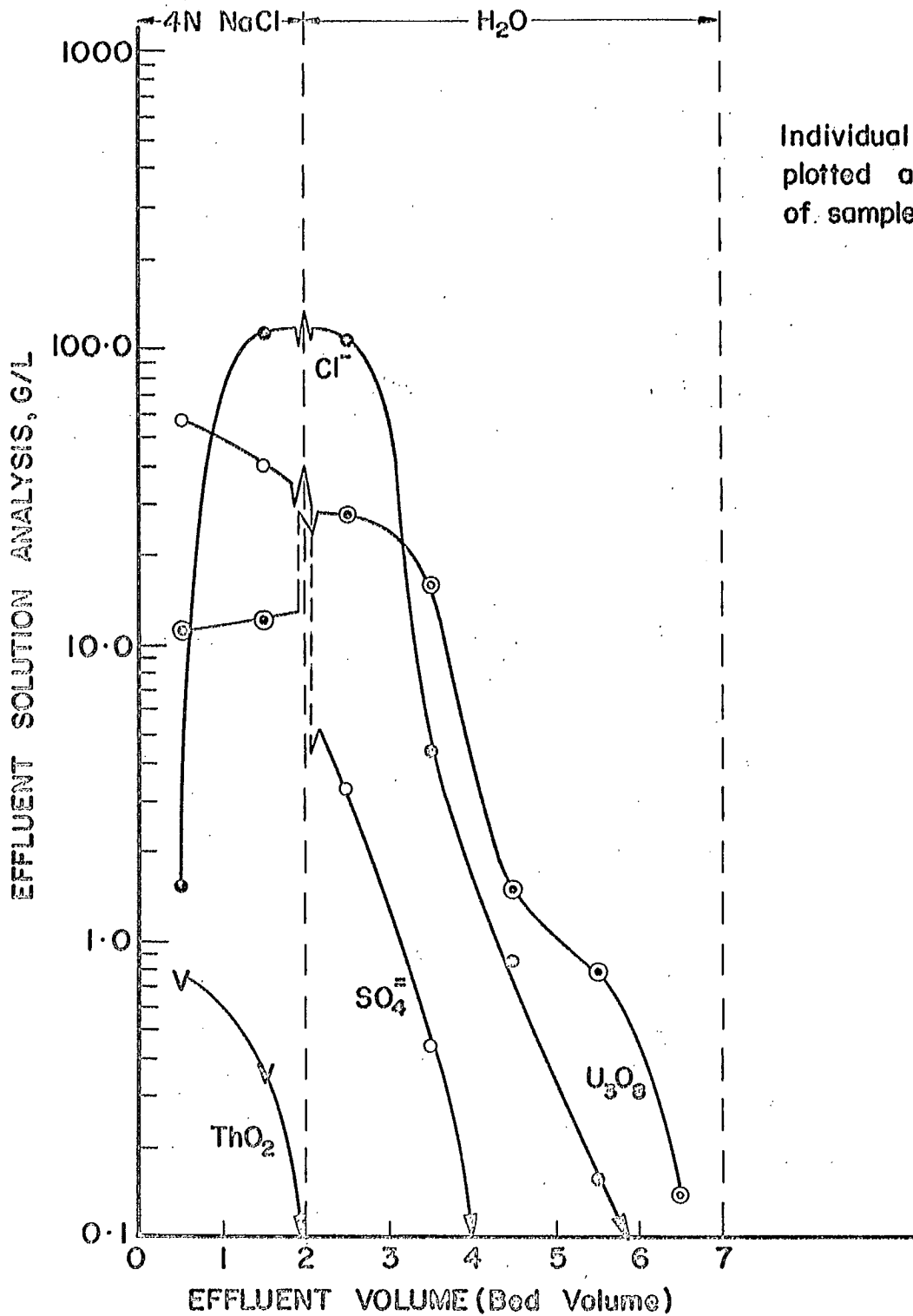


FIGURE 14

ELUTION CURVES FOR NEUTRAL 4N CHLORIDE SOLUTION
 SERIES 3 (See Table 18)

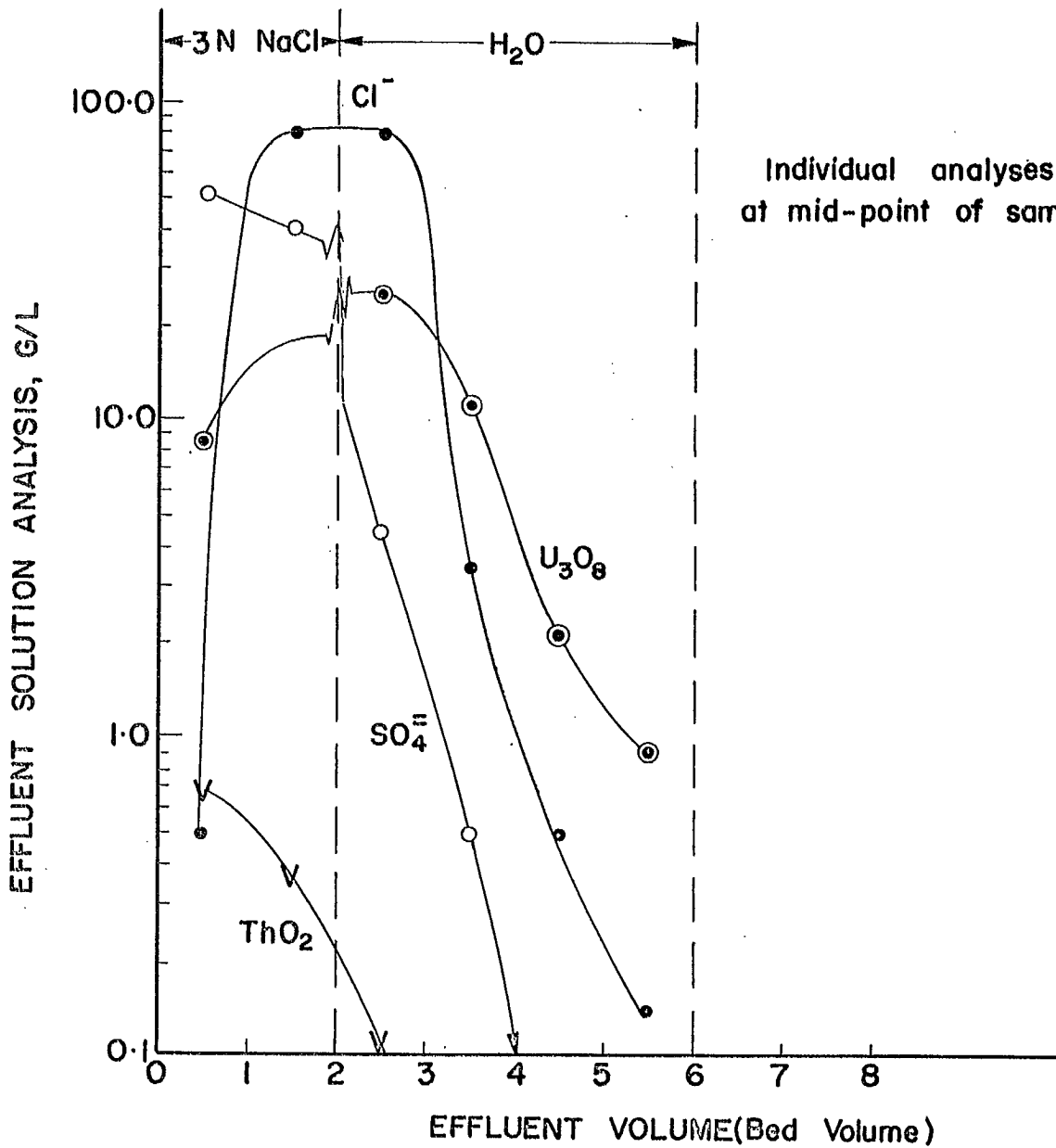


FIGURE 15

ELUTION CURVES FOR NEUTRAL 3N CHLORIDE SOLUTION
 SERIES 3 (See Table 19)

B. Recovery Process

1. Previous Work

(a) Conventional Precipitation

In a pilot plant scale study carried out in 1952 (6) using leach liquor obtained from an ore from the Beaverlodge area, strong chloride elution was employed using 3N sodium chloride: 0.1N sulphuric acid (5.2 bed volumes) followed by a water wash of 3.1 bed volumes.

The precipitate obtained by conventional two stage precipitation of the strong chloride solution, using ammonia, analyzed 84.8% U_3O_8 and contained 3.0% Na, 0.25% Fe and 1.95% SO_4 .

The precipitate obtained by direct precipitation of the wash solution with ammonia analyzed 86.4% U_3O_8 , 0.2% Na and 0.41% Fe. The strong chloride solution contained 65% of the total uranium eluted and the water wash solution contained the remaining 35%.

(b) Sodium Peroxide Precipitation

The use of hydrogen peroxide to precipitate uranium from relatively pure uranium solutions has been employed in the industry on many occasions.

Precipitation occurs over a relatively narrow pH range around pH 3.4 and, since the precipitation step liberates

hydrogen ion, a stoichiometric amount of sodium hydroxide must be added (to maintain this pH). Use of sodium peroxide as the precipitating agent in place of hydrogen peroxide, which does not appear to have been investigated elsewhere, suggested itself. Sodium peroxide would have the advantage of providing a cheaper reagent and eliminating the necessity for separate addition of caustic. However due to the excess free caustic in commercial sodium peroxide, a small amount of acid (or hydrogen peroxide) must be added to maintain pH.

The procedure was tested here (7) as a means of providing a pure product from the first stage of the concentrated chloride elution, to eliminate the necessity for recycle. The application is particularly appropriate since the procedure works best with a relatively concentrated uranium solution. Iron and sulphate should preferably be absent, so for this reason the peroxide treatment was applied as the second stage of a two-stage treatment, the iron cake (gypsum and iron) being removed as in the conventional two-stage procedure.

A two litre quantity of eluate, containing 13.4g/l

U_3O_8 , and 4.4 g/l iron, (from the same test as described on page 32) was adjusted to pH 3.7 with lime and the iron cake filtered off. The cold filtrate was then treated with 7.0 grams of sodium peroxide (90%) and 2.0 ml of hydrogen peroxide solution (30%) at a pH of 3.4 maintained by the addition of 0.15 ml of hydrochloric acid (36%). Reagent consumption was thus 0.27 lb Na_2O_2 (90%) and 0.08 lb H_2O_2 (36%) per lb of U_3O_8 . The dried precipitate had a uranium content of about 83%, and after ignition analyzed 98.4% U_3O_8 .

2. Solvent Extraction

As a further possibility for treating the uranium-bearing solutions from the strong chloride process, it was decided to investigate a solvent extraction method: such a treatment might offer the most practical way of achieving a high purity product. Accordingly, some tests were carried out using di-2-ethylhexyl phosphoric acid in varsol, which has already been shown (8) to extract uranium from chloride solutions.

Synthetic solutions, simulating the expected composition of the concentrated chloride eluate and the water wash, respectively, were extracted twice with equal volumes of solutions of di-2-ethylhexyl phosphoric acid in varsol, and the uranium concentrations of the two phases were determined to

establish the extraction coefficients. The results are given in Tables 21 and 22, and show that, if found desirable, the solutions could be treated by a solvent extraction procedure. The tests were of an exploratory nature to illustrate the feasibility of this approach, but no attempt was made to determine what advantages such treatment might have over the suggested precipitation procedures.

TABLE 21

Extraction Coefficients for the Separation of Uranium from a Solution Approximating Strong Chloride Eluate, using Di-(2-ethylhexyl) Phosphoric Acid in Varsol

Phase Ratio 1:1

Aqueous Solution Composition:

50 g/l U_3O_8 4M NaCl; 0.86M SO_4
initial pH, 1.51

EHPA Conc'n %	Extraction	Final pH	U_3O_8 g/l		E_d^o
			in aq.	in organic	
20 *	1st	--	2.40	45.0	18
	2nd	.25	.05	2.35	47
40	1st	--	.10	49.1	491
	2nd	.30	.003	.10	33
60	1st	--	.03	48.7	1600
	2nd	.30	.005	.03	6

* 10% primary decyl alcohol added to improve phase separation.

TABLE 22

Extraction Coefficients for the Separation of Uranium from a Solution Approximating the Water Wash Effluent, using Di-(2-ethylhexyl) Phosphoric Acid in Varsol

Phase Ratio 1:1

Aqueous Solution Composition:

100 g/l U_3O_8 as UO_2Cl_2 in water, pH adjusted to 3.6

EHPA Conc'n %	Extraction	Final pH	U_3O_8 g/l		E_d^o
			in aq.	in organic	
20	1st	--	6.9	87.5	12.7
	2nd	.43	.005	6.9	1380
40	1st	--	.12	97.5	810
	2nd	.43	.003	.12	40
60	1st	--	.05	92.5	1850
	2nd	.43	.001	.05	50

DISCUSSION AND CONCLUSIONS

The results summarized in Table 20 show that a large portion of the uranium loaded on the anion exchange resin IRA 400 can be made to report in an aqueous solution almost free of thorium and sulphate ions. The earlier studies indicate that the bulk of the iron can also be eliminated. This aqueous solution is suitable as a feed to precipitation processes for the production of a high-purity product.

There appears to be no advantage in using an acidified sodium chloride solution instead of neutral sodium chloride, the chloride concentration serving to prevent hydrolysis by complexing

action. The optimum conditions, insofar as rejection of thorium, iron and sulphate, and concentration of uranium in the water wash, were obtained in test 2 of series 1 (see Table 7 and Figure 3) and test 1 of series 3 (Table 17 and Figure 13). These conditions were 2 bed volumes of 5N sodium chloride solution followed by a water wash to nil spot (about 5 bed volumes) at a retention time of 10 minutes. Since no work was done in which retention time was varied, there may be scope for further investigation to determine an optimum value for this variable as well.

In all the tests, about one-third or more of the uranium was in the concentrated chloride solution which contained the impurities. It would be necessary to recycle this solution for economic reasons, due to its high chloride content. To make this feasible, as much of the impurity content as possible must be eliminated, to prevent build-up of sulphate, for example, which would reduce the effectiveness of the elution, and of thorium and iron which might then appear in the water wash. It has been shown that the uranium can be precipitated from this solution by the conventional two-stage precipitation to give an acceptable product, and in all probability enough sulphate will be removed to maintain the efficiency of the strong chloride eluant after chloride make-up.

Alternatively, iron, thorium and sulphate can be removed by the first stage precipitation with lime to pH 3.2 as in the

conventional procedure. To provide additional sulphate decontamination it would be desirable to carry out the chloride make-up with calcium chloride, prior to filtration of the gypsum (iron) cake. The filtrate could then be recycled directly without removing the uranium, thus building up its uranium content. The absence of sulphate, coupled with the high uranium concentration of the recycle solution, would probably lead to higher uranium loading on the resin during the concentrated chloride treatment. This would give a higher uranium concentration in the water wash effluent, until at equilibrium, all the uranium loaded in one cycle would appear in this solution.

Investigational work will be necessary to determine how effectively thorium can be eliminated in the first stage treatment, since present knowledge indicates that the lime treatment is not entirely satisfactory. Supplementary treatment of the first stage barren with phosphate or some other thorium precipitant may be required at intervals and may provide an economical method of obtaining a by-product thorium concentrate.

As regards the water wash solution, direct precipitation with ammonia or caustic would give a pure product of the sodium diuranate type, due to the relatively high concentration of sodium chloride. The sodium peroxide treatment, producing $\text{UO}_4 \cdot 2\text{H}_2\text{O}$, would give a product which could be converted directly to U_3O_8 or UO_2 .

The cost of the reagents in most of these alternatives will be greater than in conventional elution. Calcium chloride for make-up, costs about 2¢ per lb (100% basis), against about 1¢ per lb for salt. On an equivalent chloride basis, the amount of calcium chloride equivalent to 1 lb of salt costs 2.3¢. In addition, the amount of chloride in the water wash represents a loss (Tables 17 and 20 can be used as guides in estimating this). The increase in the cost of elution might be as much as 10¢ per lb U_3O_8 .

If conventional precipitation is used, there will no change in the cost here. Sodium peroxide precipitation, on the other hand, would cost about 7¢ per lb of U_3O_8 , as against 2-3¢ per lb for caustic, MgO or ammonia precipitation.

Thus the increased purity of the product must be balanced against a possible increased cost of 15¢ per lb U_3O_8 for reagents.

The above economic discussion is highly hypothetical and is merely presented to put the process in perspective as an aid in deciding its potential value. Any further serious study would involve use of a typical leach liquor, probably from the Bancroft area, under conditions simulating plant operation, and with the appropriate solution treatment and recycle.

The results of the very brief solvent extraction study show that the product streams are amenable to upgrading by this technique. The strong chloride elution has the advantage that the

solutions produced by recycling would be very high grade. This, coupled with the corresponding high solvent loadings, would mean that a very small plant would suffice. Use of concentrated aqueous solutions would permit loading the organic solvent to saturation in very few stages, and thus promote rejection of impurities by the solvent. It is thus conceivable that it would be more economical to base processes for purifying eluates to refinery grade material on the strong chloride system, than on current nitrate elution procedures.

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