CANADA

RECOVERY OF URANIUM FROM AN ACID LEACH LIQUOR, USING AN ANION EXCHANGE RESIN AND SODIUM CARBONATE AND BICARBONATE AS ELUTING AGENTS

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EXTRACTION METALLURGY DIVISION

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ABSTRACT

It has been shown that it is possible, using both sodium carbonate solution and sodium bicarbonate solution as eluting agents, to remove uranium completely from Amberlite IRA-400 anion exchange resin loaded from an acid leach liquor. During 51 cycles of loading and elution, the resin sample used showed only slight deterioration.

The uranium was precipitated from the eluate by means of sodium hydroxide. The precipitate assayed 82.7% U_3O_8, but was over specification in thorium content.

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Direction des Mines

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RÉCUPÉRATION DE L'URANIUM À PARTIR D'UNE LIQUEUR DE LESSIVAGE À L'ACIDE, À L'AIDE D'UNE RÉSINE FAVORISANT L'ÉCHANGE D'ANIONS AINSI QUE DE CARBONATE ET DE BICARBONATE DE SOUDE EN TANT QU'AGENTS D'ÉLUTION

par

MM. E. Kornelsen[*], V.M. McNamara[*] et J.C. Ingles[**]

RÉSUMÉ

On a établi qu'il est possible, en utilisant une solution de carbonate de soude et une solution de bicarbonate de soude comme agents d'élution, d'extraire complètement l'uranium à l'aide d'une résine favorisant l'échange d'anions Amberlite IRA-400 enrichie, à partir d'une liqueur de lessivage à l'acide. Après 51 cycles d'enrichissement et d'élution, l'échantillon de résine utilisé ne s'était détérioré que très légèrement.

L'uranium a été précipité de l'éluat à l'aide de l'hydroxyde de sodium. A l'analyse, le précipité titrait 82.7 p. 100 d'U_3O_8, mais la teneur en thorium était supérieure à la limite admissible.

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INTRODUCTION

A system for the elution of uranium-bearing anion exchange resins (loaded from acid leach solutions) by means of sodium bicarbonate was proposed in a recent report of the Mines Branch.[1]   Such a system has a number of potential advantages: 1) it reduces or eliminates many ions which would otherwise accumulate on the resin and reduce its efficiency; 2) it provides a precipitation feed solution from which uranium can be precipitated in a somewhat purer form, using conventional precipitation techniques; 3) it provides a feed solution which may be amenable to selective precipitation of a reactor-grade product, by virtue of the differences in stability of the metal-carbonate complexes; 4) it provides a feed solution which can be treated by a recently developed electrolytic process (the Excer process), to produce reactor grade UO_2.

The previous work was aimed at evolving a system for eluting uranium loaded on the resin from acid solutions, in such a way as to avoid gas evolution. This was accomplished by a two-stage process, using carbonate solution first to reduce gas evolution, followed by a bicarbonate solution to remove the bulk of the uranium. These studies were carried out batch-wise, using synthetic solutions.

The experiments reported here were designed 1) to test the proposed system under conditions simulating actual plant operation, using authentic leach liquor obtained by acid leaching an ore particularly high in undesirable impurities, and recycling the final low-grade eluates (the experimental arrangement did not permit make-up and recycle of the

precipitation barren solution); 2) to establish the operating conditions that would make a typical plant cycle operable with the proposed system of elution; 3) to subject the anion exchange resin to the alkaline carbonate solution, and by carrying out a sufficient number of alternations from sulphate to carbonate forms of the resin, to establish the long-term effect of the system on resin properties; and 4) to obtain sufficient precipitation feed solution to evaluate the product obtained by standard treatment procedures for its suitability as a refinery feed material, and in particular to compare it to a similar product obtained from the same ore by conventional ion exchange treatment. No attempt was made, however, to evaluate the process from the economic point of view.

EXPERIMENTAL

In essence, the experimental procedure was to carry out the complete ion exchange procedure repeatedly by means of automatic equipment (examining the resin at intervals to determine whether any deterioration had occurred), to treat the collected precipitation feed solution by the usual caustic precipitation procedure used for carbonate leach solutions, and then to analyze the product for the impurities of interest. This experimental work is described under two headings, Section A- Ion Exchange Studies, and Section B- Precipitation Studies.

Section A - Ion Exchange Studies

The operating schedule for the ion exchange cycle is given in Table 1 and can be summarized briefly as follows. Leach liquor, prepared by acid leaching a flotation concentrate of ore from the Bancroft area, Ref. No. 7/57-7, was passed on the resin for a period of 8 hours and 20 minutes. The effluent (barren solution) was discharged to waste. After a 2 bed volume water displacement of leach liquor (to waste), elution with a carbonate: hydroxide solution was started, the first 0.4 bed volume (which represented displacement of water) being discarded. This portion of the elution cycle was continued to give a total period of 1 hour, and all of the eluate, except the displacement solutions, was collected for precipitation feed. Bicarbonate elution was then started using bicarbonate solution that had been used for the last half of the preceding elution and this eluate also was collected as precipitation feed. This portion of the cycle took six hours. Then elution was continued for 5 1/2 hours using barren (fresh) bicarbonate solution, the eluate being collected for recycle during the next cycle. A water displacement, followed by sulphate treatment to remove carbonate from the resin, completed the cycle, which occupied a total time of 22 hours and 10 minutes.

Apparatus

The equipment used consisted essentially of a glass column holding the resin, a Sigmamotor pump for passing the various solutions through the resin, a splitter to separate the effluent from the ion exchange column into desired fractions, and a timer to control the cycle of loading, washing and elution.

The rate of flow of liquids pumped by the Sigmamotor pump was controlled by varying the speed of rotation of the pump, and by using two different internal diameters of rubber tubing passing through the pump. A variable speed motor was used to drive the pump and the speed of rotation was altered as required, using controls actuated by the automatic timer. The choice of the desired piece of rubber tubing was made by means of solenoid valves, again controlled by the automatic timer. These solenoid valves also were used to select the type of solution flowing through the resin.

The effluent-splitter divided the effluent from the resin column into four parts, as follows:

1. Waste
2. Precipitation feed
3. Recycle eluate
4. Storage

Two timers were used to control the speed of the motor, the solenoid valves and the effluent splitter: A Robotron Control, Type B 680, and a cam-type timer. The cam-type timer had to be used in addition to the Robotron Control because the latter could not control a sufficient number of functions.

Reagents

The resin used was Amberlite IRA-400 (Lot No. 1904) anion exchange resin.

For the standard loading and elution tests, the following two solutions were used (enough of each was prepared at the beginning to permit completion of three standard tests):

  i. Synthetic pregnant solution containing uranyl sulphate,

   magnesium sulphate and sulphuric acid.

  ii. Standard eluting solution which was 1 N in sodium chloride

   and 0.1 N in sulphuric acid.

   The leach liquor used to load the resin was prepared by acid leaching of a uranium-bearing ore.

   The combination of solutions used to remove uranium that had been adsorbed from the leach liquor consisted initially of 1 N sodium carbonate followed by 1 N sodium bicarbonate. Later, the sodium carbonate solution was made 0.5 N in sodium hydroxide as well, and the concentration of the bicarbonate solution was increased to about 1.1 N.

   To remove the bicarbonate ion from the resin after elution, a solution of 2% sodium sulphate was tried initially. This concentration was later increased to 10%. The displacement of bicarbonate was essential to prevent the formation of CO_2 during subsequent loading from an acid leach liquor.

Procedure

   After conditioning the resin to be used by contacting it with 1 N NaCl- 0.1 N H_2SO_4, a volume of the conditioned resin consisting of approximately 100 ml was placed in the column. The resin bed volume was obtained by fluidizing it (backwash) and then pumping water through it (downwash) at 10 ml/min. The minimum volume resulting was taken as the resin bed volume. The average of several trials was 102 ml.

Since it was intended to test the effect, on the resin, of repeated loading and elution with carbonate solutions, the work was started with a standard loading test. A second such test was done during the course of the work, and a third at its completion. These tests were done in the following manner:

The resin was loaded using synthetic pregnant solution. The first 4450 ml of barren effluent was collected, mixed, and analysed for U_3O_8. The next 50 ml portion of barren solution was analysed for U_3O_8 and, following this, a 50 ml sample of barren was taken after every 450 ml throughput until enough synthetic pregnant solution had been passed through the column to saturate the resin. Each 50 ml sample was assayed for uranium. The 450 ml portions were combined, mixed, and also assayed for uranium.

Following saturation of the resin, it was washed with water at the same flow rate as that of the synthetic pregnant solution.

Eluting solution was then passed through the resin. The eluate was collected in 100 ml volumetric flasks for the first 500 ml throughput, and in 250 ml flasks afterwards. In the case of the first standard elution, the total volume of eluate collected was 2000 ml, and in the case of the second and third, 2500 ml. A larger volume of eluate was collected in the later elutions, to ensure removal of all uranium from the resin even if its elution rate had dropped as a result of deterioration.

For each standard elution, a composite eluate sample, consisting of 10 ml from each 100 ml fraction and 25 ml from each 250 ml

fraction, was prepared and assayed for uranium. The individual fractions were also analysed for U_3O_8.

A standard test was done at the beginning, after 17 cycles, and after 51 cycles of loading from leach liquor. Prior to the second and third standard loading tests, 1 N NaCl - 0.1 N H_2SO_4 solution was pumped through the resin to assure the removal of all uranium.

Following completion of the first standard loading and elution test, loading with leach liquor was started. With a few exceptions, a retention time of 4 min was used throughout for adsorption. However, a number of cycles had to be run before satisfactory eluting conditions were established. In Mines Branch Research Report R 41,[1] it is reported that the eluate pH had to reach 4.5 before bicarbonate solution could enter the resin bed without causing gassing. Therefore, pH readings of eluate from Cycle 1 were taken, and the course of uranium and sulphate removal from the resin was followed.

During Cycle 2, it was intended to pass only 80 ml of 1 N Na_2CO_3 solution through the resin. Because of timer trouble, the actual volume was 100 ml, and even this was not sufficient to prevent gas formation. As a result, it was decided to pump a greater volume of carbonate solution, prior to the final elution with 1 N sodium bicarbonate.

After the loading portion of Cycle 3 had been completed, the pH of the 1 N sodium carbonate effluent was once more measured, as a check on measurements made during Cycle 1. This time, a volume of 500 ml of 1 N Na_2CO_3 solution was pumped, followed by 1 N $NaHCO_3$ solution, to complete elution.

Elution of Cycle 4 was attempted, using 120 ml of 1 N Na_2CO_3 solution, but gas formation was again troublesome, and consequently the amount of sodium carbonate solution pumped before completing elution with 1 N $NaHCO_3$ was again increased. Accordingly, elution of Cycle 5 was started, using a mixed solution of 1 N Na_2CO_3 and 1 N NaOH. A 120 ml volume of this solution was pumped, followed by 1 N $NaHCO_3$ solution. Although gas formed, it was absorbed before the resin bed broke up. Elution was completed as usual, with 1 N $NaHCO_3$.

In Cycle 6, elution was started with 1.5 N Na_2CO_3, 120 ml being used. However, when 1 N $NaHCO_3$ followed this solution, heavy gas formation again occurred.

In Cycle 7, 1 N Na_2CO_3 solution was again used but the volume was increased to 160 ml. Once more, gassing was a problem.

So far, the eluting solution retention time had been about 20 min. In Cycle 8, this was increased to about 28 min and 1 N Na_2CO_3 solution was pumped initially for 80 min. Again, the resin bed was broken up by gas formation.

For Cycle 9, the elution solution retention time was decreased to about 20 min, but the time during which 1 N Na_2CO_3 was pumped was increased to 2 hr 20 min. During this cycle, gas still continued to form.

The addition of NaOH to the Na_2CO_3 solution was once more tried in Cycle 10. This time, the solution was 1 N Na_2CO_3 and 0.5 N NaOH. This was pumped for 80 min at a retention time of 20 min. Gas formed but was later absorbed, leaving no sizable bubbles in the resin bed.

In Cycle 11, eluting conditions were the same as in Cycle 10 except that the duration of Na_2CO_3-NaOH elution was reduced to 1 hr. Gas formed, but was still absorbed as elution progressed.

As satisfactory eluting conditions had now been established, the recycling of eluate to increase the uranium content of precipitation feed was started with Cycle 12.

The time schedule of the cycle used, starting with Cycle 11 and continuing to the end of the test work, is shown in Table 1.

Values shown in Table 1 are nominal, and small deviations from the values shown occurred.

During the first 23 cycles of operation, sodium bicarbonate solution of nominally 1 N concentration was used. Analysis of this solution showed it to contain 80.0 g $NaHCO_3/l$. The recycle eluate collected during Cycle 20 assayed 67.9 g $NaHCO_3/l$. As may be seen in Table 1, there is dilution of the bicarbonate solution in the recycle eluate by the final water wash. Therefore, to compensate for both the low bicarbonate content of the sodium bicarbonate used (USP) and its dilution, a stronger solution, containing 97 g/l of the USP salt, was used for Cycle 24 and following cycles. This solution assayed 92.8 g $NaHCO_3/l$ and 9.25 g Na_2CO_3/l.

When gas formation was observed in the resin bed at the beginning of loading, Cycle 3, the concentration of the sodium sulphate solution used to convert the resin to the sulphate form was increased to 10%, from 2%. This concentration was used for the remainder of

TABLE 1

Time Schedule of Over-all Cycle

Influent Solution	Retention time * (min)	Flow rate (ml/min)	Volume throughput		Duration (hr: min)	Column effluent to:
			litres	Bed volumes		
Leach liquor	4	10.2	5.1	50	8:20	Waste
Water	8	5	0.2	2	0:40	Waste
1 N Na_2CO_3- 0.5 N NaOH	20	2	0.04	0.4	0:20	Waste
1 N Na_2CO_3- 0.5 N NaOH	20	2	0.08	0.8	0:40	Precipitation feed
Recycle eluate	20	2	0.72	7.1	6:00	Precipitation feed
$NaHCO_3$	20	2	0.62	6.1	5:10	Recycle eluate
Water	8	5	0.10	1	0:20	Recycle eluate
10% Na_2SO_4	5	8	0.32	3.1	0:40	Waste

$$* \text{ Retention time (min)} = \frac{\text{Void volume (ml)}}{\text{Flow rate (ml/min)}} = \frac{0.4 \times \text{Bed volume (ml)}}{\text{Flow rate (ml/min)}}$$

the work, although it is possible that a lower concentration of sulphate would have been as effective.

From time to time, samples of precipitation feed were assayed for uranium, and the resin loading was calculated. A precipitate which formed regularly in the precipitation feed was analysed spectrographically. Before analysis, the precipitate was washed with a little 1 N Na_2CO_3 solution. The filter paper and the precipitate were ignited in a platinum crucible. The fused mass which resulted was treated with 1:1 HNO_3 and ignited.

Data and Results

Conditions and results of the three standard loading tests are shown in Tables 2 and 3. The standard loading curves are shown in Figure 1.

The calculation of the uranium capacity to breakthrough of the resin is shown in Table 4. The calculation of the uranium capacity to saturation of the resin, based on the standard loadings, is shown in Table 5.

The results of elution of the resin loaded from synthetic pregnant solution are shown in Table 6 and the elution curve is shown in Figure 2. (Only one curve has been drawn, because in most cases the three corresponding points are close together.)

The calculation of the uranium (saturation) capacity of the

TABLE 2

Conditions of Standard Loadings

Particulars	Unused resin	Resin after 17 cycles	Resin after 51 cycles
Synthetic pregnant solution:			
U_3O_8 assay (g/l)	1.00	1.00	1.00
Volume pumped (l)	11.0	11.0	11.0
U_3O_8 content (g)	11.0	11.0	11.0
pH	1.5	1.5	1.5
$SO_4^=$ assay (g/l)	33.5	33.5	33.5
Resin bed volume (ml)	102	102	102
Average flow rate (ml/min)	13.4	13.3	13.4
Average retention time (min)	3.04	3.07	3.04
Barren effluent composite:			
Volume (l)	5.85	5.85	5.85
U_3O_8 assay (g/l)	0.63	0.64	0.66
U_3O_8 content (g)	3.69	3.74	3.86
Water wash:			
Volume (l)	0.20	0.20	0.20
U_3O_8 assay (g/l)	0.66	0.80	0.62
U_3O_8 content (g)	0.13	0.16	0.12

TABLE 3

Results of Standard Loadings

Fraction of barren effluent		Barren effluent from					
		Unused resin		Resin after 17 cycles		Resin after 51 cycles	
ml	Bed volumes*	U_3O_8 assay (g/l)	U_3O_8 content (g)	U_3O_8 assay (g/l)	U_3O_8 content (g)	U_3O_8 assay (g/l)	U_3O_8 content (g)
0-4,450	-	0.0007	0.0031	0.0002	0.0009	0.0006	0.0027
4,450-4,500	43.9	0.0007	0.0000	0.0006	0.0000	0.015	0.0008
4,950-5,000	48.8	0.006	0.0003	0.006	0.0003	0.077	0.0038
5,450-5,500	53.7	0.049	0.0024	0.054	0.0027	0.22	0.0110
5,950-6,000	58.6	0.21	0.0105	0.27	0.0135	0.41	0.0205
6,450-6,500	63.5	0.44	0.022	0.55	0.0275	0.58	0.029
6,950-7,000	68.4	0.64	0.032	0.73	0.0365	0.70	0.035
7,450-7,500	73.3	0.7	0.035	0.84	0.042	0.75	0.0375
7,950-8,000	78.2	0.97	0.0485	0.87	0.0435	0.84	0.042
8,450-8,500	83.1	1.0	0.050	1.01	0.0505	0.75	0.0375
8,950-9,000	88.0	1.0	0.050	1.00	0.050	0.80	0.040
9,450-9,500	92.9	1.0	0.050	0.97	0.0485	0.79	0.0395
9,950-10,000	97.8	0.93	0.0465	1.01	0.0505	0.92	0.046
10,450-10,500	102.7	0.92	0.046	0.96	0.048	0.92	0.046
10,950-11,000	107.6	0.96	0.048	1.07	0.0535	0.80	0.040
Total U_3O_8 content of leakage samples (g)			0.4443		0.4679		0.4313

* Bed volumes have been calculated to the "mid-point" of the sample, e.g., to 4,475 ml for the 4450-4500 ml fraction
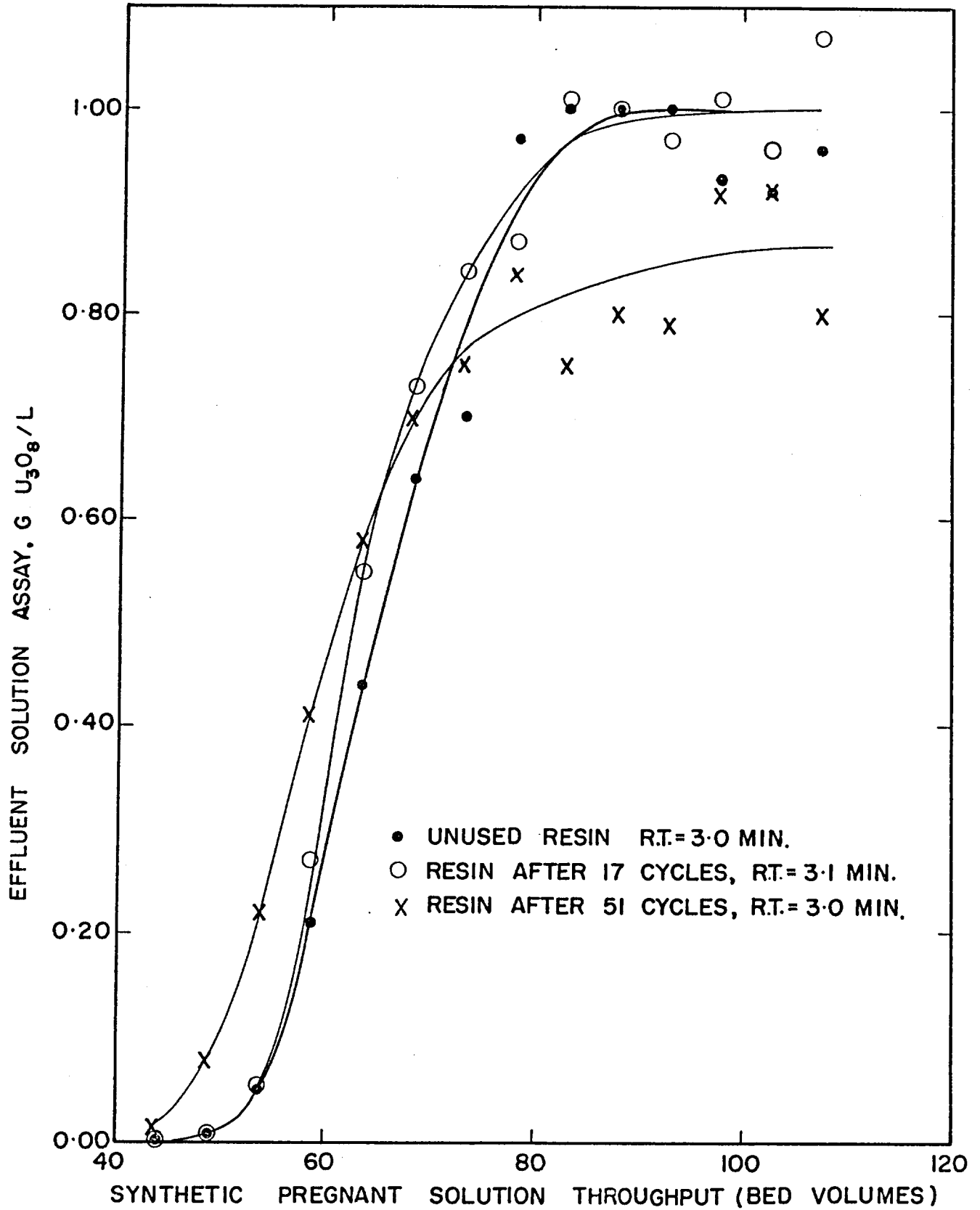
FIGURE I

LOADING CURVES, STANDARD LOADING TESTS

TABLE 4

Calculation of Uranium Capacity to
Breakthrough*

Particulars	Unused resin	Resin after 17 cycles	Resin after 51 cycles
Bed volumes of synthetic pregnant solution to breakthrough**	54	54	47
Volume of synthetic pregnant solution to breakthrough (1)	5.5	5.5	4.8
U_3O_8 content of synthetic pregnant solution to breakthrough (g)	5.5	5.5	4.8
U_3O_8 capacity of resin to breakthrough (g U_3O_8/l resin)	54	54	47

*Breakthrough is taken as the point at which the U_3O_8 concentration of the barren effluent reaches 0.05 g/l.

**These values are taken from Figure 1.

TABLE 5

Calculation of U_3O_8 Capacity of Resin,

Loading Stage

Particulars	Unused resin U_3O_8 (g)		Resin after 17 cycles U_3O_8 (g)		Resin after 51 cycles U_3O_8 (g)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
Synthetic pregnant solution (see Table 2)	11.0		11.0		11.0	
Barren effluent composite (see Table 2)		3.69		3.74		3.86
Leakage samples (see Table 3)		0.44		0.47		0.43
Water Wash (see Table 2)		0.13		0.16		0.12
Total U_3O_8 effluent		4.26		4.37		4.41
U_3O_8 held on resin (g)	6.7		6.6		6.6	
U_3O_8 capacity of resin (g/1 resin)	66		65		65	

TABLE 6

Results of Elution of Resin Loaded from
Synthetic Pregnant Solution

Fraction of eluate		U_3O_8 assay of eluate fractions (g/l)		
ml	Bed volumes	Unused resin (Av.R.T.= 10.4 min)	Resin after 17 cycles (Av.R.T.= 10.1 min)	Resin after 51 cycles (Av.R.T. = 10.1 min)
0-100	0.49	0.50	0.59	0.57
100-200	1.47	15.09	17.06	16.78
200-300	2.45	19.40 ·	19.06	17.92
300-400	3.43	13.07	12.69	11.82
400-500	4.41	8.05	7.87	7.35
500-750	6.13	3.44	3.30	3.26
750-1000	8.58	0.87	0.87	0.99
1000-1250	11.03	0.23	0.25	0.29
1250-1500	13.48	0.060	0.090	0.12
1500-1750	15.93	0.017	0.045	0.082
1750-2000	18.38	0.003	0.014	0.026
2000-2250	20.83	-	0.005	0.012
2250-2500	23.28	-	0.003	0.007

R.T. = Retention Time
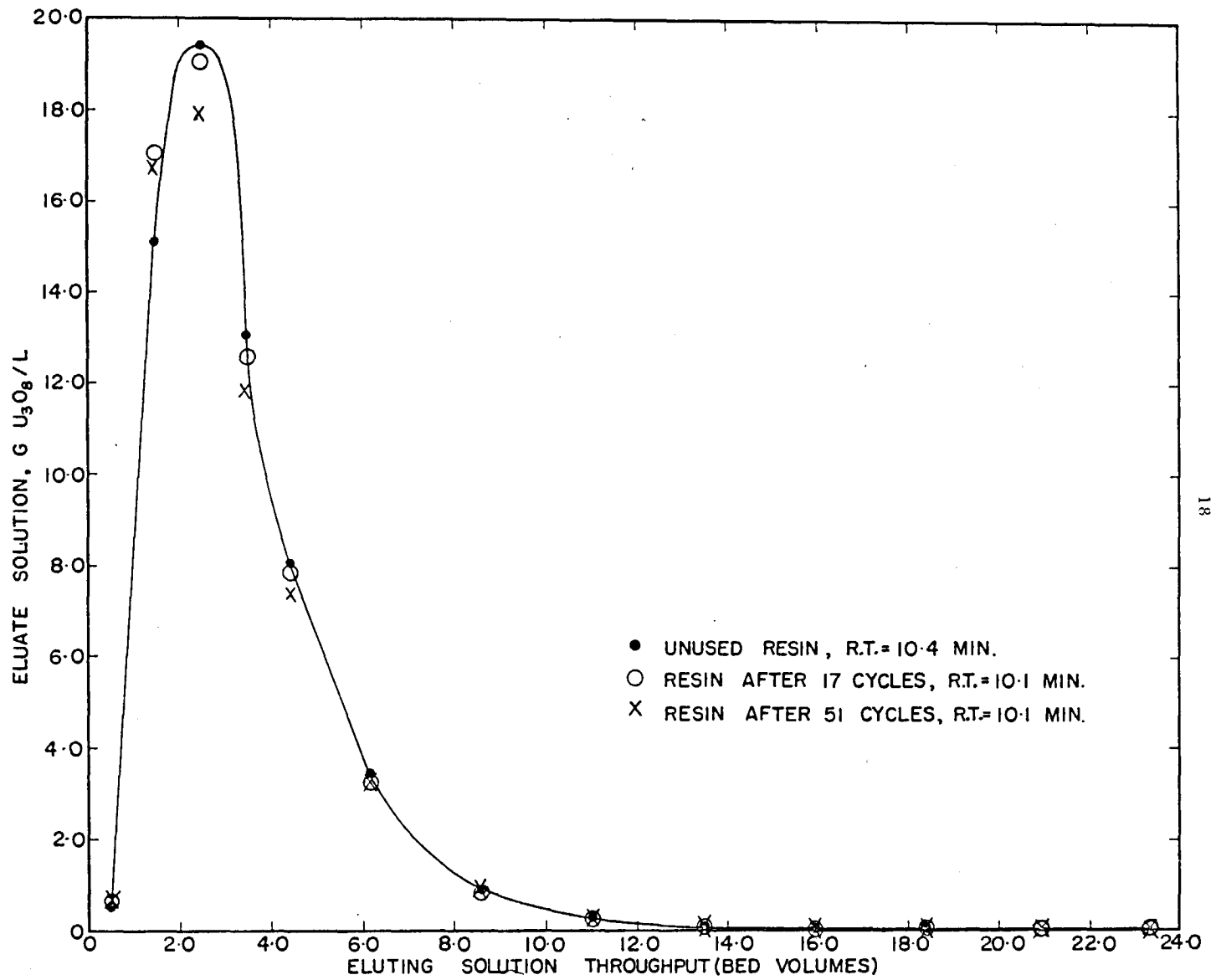
FIGURE 2

ELUTION CURVE, STANDARD LOADING TESTS

resin based on the standard elution stage is shown in Table 7.

TABLE 7

Calculation of U_3O_8 Capacity, Elution Stage

	Unused resin	Resin after 17 cycles	Resin after 51 cycles
U_3O_8 assay of eluate composite (g/l)	3.37	2.75	2.62
Total volume of eluate (l)	2.00	2.50	2.50
U_3O_8 content of eluate (calculated from eluate composite assay) (g)	6.74	6.88	6.55
U_3O_8 capacity of resin (g U_3O_8/l resin)	66	67	64

Assays of the two batches of leach liquor used are given in Table 8.

Table 9 shows the amount of uranium collected in the precipitation feeds of several cycles, and from this the uranium loading has been calculated. This loading value does not represent the complete capacity of the resin bed, because elution was not carried to completion during the cycles in which leach liquor was used for loading the resin.

TABLE 8

Leach Liquor Assays

Batch No. ⟶	1	2
Used in Cycles ⟶	1-17 inc	18-51 inc
pH	1.75	1.74
U_3O_8 (g/l)	2.66	2.81
ThO_2 (g/l)	1.83	2.10
Fe^{+++} (g/l)	-	2.52
Tot Fe (g/l)	1.90	2.84
$Na_2S_4O_6$ (g/l)	0.06	0.057
V_2O_5 (g/l)	-	0.009
Mo (g/l)	-	<0.001
$(R.E.)_2O_3$* (g/l)	0.89	2.63
F (g/l)	-	0.14
SiO_2 (g/l)	-	1.78
As + P_2O_5 (g/l)	-	0.03
Cl (g/l)	-	0.47
SO_4 (g/l)	18.12	26.8

* Rare earth oxides

TABLE 9

Uranium Loading of Resin Calculated from Uranium
Content of Precipitation Feed

Cycle number	Precipitation feed volume (l)	U_3O_8		U_3O_8 loading of resin (g U_3O_8/l resin)
		Assay (g/l)	Content (g)	
12	0.78	10.95	8.54	84
20	0.78	10.73	8.37	82
26	0.79	11.28	8.91	87
40	0.78	10.90	8.50	83

Note: The operating uranium loading is higher than the standard
loading because of the higher uranium concentration of the
leach liquor as compared with that of the standard synthetic
head solution used in the standard loading tests.

The precipitation feeds of Cycles 13, 14 and 15 were combined and assayed, with the following results:

U_3O_8:   11.24 g/l

ThO_2:   0.37 g/l

F: 0.01 g/l

$NaHCO_3$:   34.8 g/l

Na_2CO_3:   6.98 g/l

In Table 10 are shown the results of semi-quantitative spectrographic analysis of the precipitate that formed in the precipitation feed.

Tables 11 to 16 show the results of studies made on the properties of the various eluting solutions during the course of the elution process.

Iron and uranium assays of the effluent collected while removing residual uranium from the resin prior to the second and third standard loading tests are shown in Table 17.

The results of the analysis of the used resin are shown in Tables 18 and 19. To permit comparison, all analyses were performed on unused resin as well.

TABLE 10

Results of Spectrographic Analysis of Precipitate Removed from Precipitation Feed of Cycle No. 12 and Ignited

Element	Assay (%)
Sodium	Principal constituent
Iron	10
Thorium	8
Silicon	2
Uranium	1.5
Cerium	1
Lanthanum	1.5
Aluminum	0.6
Calcium	0.2
Magnesium	0.15
Titanium ?	0.09
Lead	0.03
Manganese	0.02
Yttrium ?	0.04
Zirconium ?	0.009
Copper ?	0.008

Note: ? indicates that identification is not positive.

TABLE 11

Results of Elution of Resin, Cycle 1

| Fraction of eluate* | | pH | U_3O_8 | | $SO_4 =$ |
ml	Bed volumes		Assay (g/l)	Content (g)	(g/l)
0-75	0.37	---	0.88	0.066	5.79
75-78	0.75	2.4	---	---	---
87-90	0.86	2.5	---	---	---
97-100	0.96	2.5	---	---	---
75-125	0.98	---	3.59	0.180	38.16
122-125	1.22	3.8	---	---	---
147-150	1.45	5.1	---	---	---
125-175	1.47	---	10.67	0.534	44.46
172-175	1.71	5.4	---	---	---
175-225	1.96	---	15.06	0.753	41.52
225-325	2.70	---	14.97	1.497	---
325-375	3.43	---	28.31	1.416	9.66
375-475	4.17	---	23.16	2.316	---
475-525	4.90	---	14.78	0.739	0.042
525-625	5.64	---	8.62	0.862	---
625-675	6.37	---	5.37	0.268	0.033
675-775	7.11	---	3.58	0.358	---
775-825	7.84	---	2.49	0.124	0.030
925-975	9.31	---	1.10	0.055	0.042
1075-1125	10.78	---	0.49	0.024	0.027
1225-1275	12.25	---	0.22	0.011	---
1375-1425	13.72	---	0.086	0.004	---
1525-1575	15.19	---	0.034	0.002	0.024
				TOTAL = 9.21 g	

*One normal sodium carbonate solution was pumped while the 0-175 ml portion of eluate was collected, and one normal sodium bicarbonate solution thereafter.

NOTE: All portions of eluate not listed above were combined. This combined sample had a volume of 500 ml and assayed 0.58 g U_3O_8/l.

TABLE 12

pH of Eluate*, Cycle 3

Fraction of eluate		pH
ml	Bed volumes	
25-28	0.25	1.7
50-53	0.51	1.7
75-78	0.75	2.0
100-103	1.00	2.3
125-128	1.24	2.4
150-153	1.49	2.5
178-181	1.76	5.0
200-203	1.98	5.3
225-228	2.22	5.6
250-253	2.47	6.5
275-278	2.71	8.3
300-303	2.96	10.4
325-328	3.20	10.7
350-353	3.45	10.8
375-378	3.69	11.2
400-403	3.94	11.3
425-428	4.18	11.3
450-453	4.43	11.3
475-478	4.67	11.3

* 1 N Na_2CO_3 was pumped until 500 ml of eluate had been collected. This was followed by 1 N $NaHCO_3$. After about 225 ml of eluate had been collected, most of the gas which had formed in the resin bed either had been absorbed or had gathered in a glass fitting at the bottom of the ion exchange column. By the time 265 ml of Na_2CO_3 had passed through the resin, most of the gas had disappeared. The

TABLE 13

pH of Eluate*, Cycle 10

Eluate Volume		pH (indicating paper)	Remarks
ml	Bed volumes		
60	0.6	1	Some gas observed in resin bed.
70	0.7	1+	-
90	0.9	2	-
110	1.1	2	-
120	1.2	2	-
130	1.3	2+	-
140	1.4	4	Gas still present.
150	1.5	4+	Gas still present but decreasing.
160	1.6	5	-
180	1.8	6	Still some gas in column.
190	1.9	6	-
210	2.1	8+	Most of the gas out of resin.
230	2.3	9	Only a few isolated bubbles of gas left in resin.
260	2.5	10	-
290	2.8	11	-
350	3.4	11	Precipitate in eluate line leading from column.
550	5.4	8	Precipitate disappeared.

* The pH of the eluate coming from the column was measured only approximately, using indicating paper. The eluate volume is approximate, also, having been calculated from the flow rate (2 ml/min) and the length of time of pumping. 1N Na_2CO_3 - 0.5 N NaOH was pumped for 1 hr 20 min, giving about 160 ml of throughput. Following this, 1 N $NaHCO_3$ was pumped.

TABLE 14

Changes Caused by Increasing the Concentration of NaHCO$_3$ Eluting Solution*

	U$_3$O$_8$ assay (g/1)		NaHCO$_3$
	Final 25 ml portion of NaHCO$_3$ eluate	10% Na$_2$SO$_4$ effluent	assay of recycle eluate (g/1)
Cycle 19 using 0.95 N NaHCO$_3$	1.22	0.28	--
Cycle 20 using 0.95 N NaHCO$_3$	--	0.27	67.9
Cycle 25 using 1.1 N NaHCO$_3$	0.31	--	--
Cycle 26 using 1.1 N NaHCO$_3$	--	0.020	--
Cycle 32 using 1.1 N NaHCO$_3$	--	--	72

* Starting with Cycle 24, the stronger NaHCO$_3$ solution was used.

TABLE 15

Analysis of Eluate*, Cycle 41

Eluate Fraction		U_3O_8	$SO_4^=$	$NaHCO_3$	Na_2CO_3	ThO_2	pH (indicating paper)
ml	Bed volumes	(g/l)	(g/l)	(g/l)	(g/l)	(g/l)	
0-100	0.49	2.35	28.38	--	nil	0.51	2
100-200	1.47	11.70	48.27	6.5	2.9	--	8
200-300	2.45	25.11	17.28	10.3	15.7	0.46	9
300-400	3.43	20.50	3.09	44	7.3	0.49	8
400-500	4.41	9.90	1.32	53	11.0	0.38	8
500-600	5.39	5.14	0.69	58	11.6	0.21	8
600-700	6.37	3.15	0.51	57	14.4	0.15	8
700-800	7.35	2.51	0.66	58	13.4	0.26	8
800-900	8.33	1.66	0.27	67	10.8	0.20	8
900-1000	9.31	1.15	0.036	70	nil	0.03	8
1000-1100	10.29	0.94	0.003	74	6.7	0.01	8
1100-1200	11.27	0.59	--	74	8.3	0.01	8
1200-1300	12.25	0.36	--	75	6.7	0.02	--
1300-1400	13.23	0.21	--	74	7.1	0.01	7+
1400-1500	14.21	0.12	--	76	5.5	--	7+
1500-1536	14.88	0.035	--	--	--	--	8

*Average retention time was 20 min.

TABLE 16

Calculation of Mole Ratio of $SO_4^=$ to UO_2^{++} in Eluate, Cycle 41

Eluate fraction (ml)	U_3O_8 (g/l)	Equivalent UO_2^{++}		$SO_4^=$		Ratio: $\dfrac{SO_4^= \text{ (millimoles)}}{UO_2^{++} \text{ (millimoles)}}$
		g/l	millimoles/l	g/l	millimoles/l	
0-100	2.35	2.26	8.37	28.38	295.72	35.33
100-200	11.70	11.26	41.71	48.27	502.97	12.06
200-300	25.11	24.16	89.49	17.28	180.06	2.01
300-400	20.50	19.72	73.04	3.09	32.20	0.44
400-500	9.90	9.52	35.26	1.32	13.75	0.39
500-600	5.14	4.94	18.30	0.69	7.19	0.39
600-700	3.15	3.03	11.22	0.51	5.31	0.47
700-800	2.51	2.41	8.93	0.66	6.88	0.77
800-900	1.66	1.60	5.93	0.27	2.81	0.47
900-1000	1.15	1.11	4.11	0.036	0.38	0.09
1000-1100	0.94	0.90	3.33	0.003	0.03	0.01

Conversion factor: U_3O_8 to UO_2 = 0.962

Ionic weight of UO_2^{++} = 270
Ionic weight of $SO_4^=$ = 96

TABLE 17

Analysis of 1 N NaCl - 0.1 N H_2SO_4 Effluent Collected
While Preparing Resin for Standard Loading Tests

Following cycle	Effluent volume (1)	U_3O_8		Fe	
		Assay (g/1)	Content (g)	Assay (g/1)	Content (g)
17	2.64	0.029	0.077	<0.04	-
51	3.65	0.004	0.015	0.07	0.26

TABLE 18

Results of Resin Analyses

Type of analysis	Unused resin	Resin after 51 cycles	Resin after 52 cycles of salt-sulphuric elution ***
Salt-splitting anion exchange capacity (meq/g*)	3.57	2.90	2.78
Weak-base anion exchange capacity (meq/g*)	0.66	0.78	0.77
Moisture (%**)	48.6	46.5	43.8
Polythionate sulphur as S (%*)	<0.002	<0.004	-
Sulphated ash (%*)	0.37	1.10	0.35
SiO_2 (%*)	<0.02	<0.03	0.19

meq = milliequivalent
* Based on dry weight of resin.
** Based on wet weight of resin.
*** Previous work

TABLE 19

Results of Semi-Quantitative Spectrographic
Analysis of Resin Ash

Element	Assay (%)			
	Unused resin ash		Resin ash after 51 cycles	
Iron	1.5	(1)	P.C.	(2.5)
Aluminum	P.C.	(10)	1	(10)
Silicon	0.3	(0.1)	1.5	(10)
Niobium	N.D.	(N.D.)	1	(0.8)
Thorium	N.D.	-	1.5	-
Tungsten	N.D.	-	0.7	-
Magnesium	0.25	(0.2)	0.25	(1)
Calcium	0.08	(0.05)	0.15	(0.15)
Zirconium	N.D.	(N.D.)	0.3	(10)
Zinc	0.4	(0.2)	0.4 (?)	(N.D.)
Sodium	0.3 (?)	(N.D.)	N.D.	(3)
Titanium	0.005	(0.001)	0.25	(0.1)
Arsenic	N.D.	-	0.3 (?)	-
Manganese	0.006	(0.003)	0.1	(0.007)
Lead	0.04	(0.009)	0.1	(0.09)
Molybdenum	N.D.	(N.D.)	0.1	(3)
Barium	N.D.	-	0.02	-
Chromium	0.006	(0.006)	0.02	(0.009)
Vanadium	N.D.	-	0.02	-
Tin	N.D.	-	0.03 (?)	-
Copper	0.02	(0.05)	0.07	(0.03)
Silver	N.D.	-	0.006	-
Lanthanum	N.D.	-	0.02 (?)	-
Cobalt	N.D.	(N.D.)	0.007	(0.02)
Nickel	0.009	(0.01)	0.02 (?)	(N.D.)
Boron	0.003	(0.001)	0.003	(0.002)

P.C. = Principal constituent
N.D. = None detected

Note: The values in brackets are corresponding resin ash
analysis results obtained during a test with leach liquor
from the same ore and which differed from this test chiefly
in the use of sodium chloride-sulphuric acid eluting solution
instead of the sodium carbonate-sodium bicarbonate system.
The number of cycles involved (52) was about the same as in
the present work.

Section B - Precipitation Studies

The combined eluate (23 litres) obtained from the carbonate-bicarbonate elution study gradually settled out a small quantity of fine, brown precipitate. This precipitate was filtered out, dried (wt = 7 grams), and ignited at 1500° F (wt = 4 grams). Table 20 shows the results of a semi-quantitative analysis of this material. The dry weight amounted to 2.5% of the total weight of dry solids which was subsequently precipitated from the eluate.

The filtered eluate was divided into two portions for the purpose of precipitating the uranium. Precipitation was done by the addition of sodium hydroxide.

The bulk of the precipitation was carried out at room temperature and with constant stirring. The caustic was added slowly as dilute (20 to 30% w/v) NaOH solution. The uranium concentration in the barren eluate was lowered to 0.4 g/l under these conditions. In order to recover all the uranium for the composite precipitate, the filtrate was heated to 135° F and precipitation continued with solid sodium hydroxide to give a final barren solution assaying 0.06g U_3O_8/l. The conditions of the two batch precipitations are outlined in Table 21.

Table 22 shows the results obtained from the assay of samples withdrawn as the precipitation progressed. Figure 3 shows these results graphically. Corrections to make allowance for sampling volumes were not applied to these assay values.

The results show that sulphate would rapidly build up in

TABLE 20

Semi-Quantitative Spectrographic Analysis of Precipitate*
Filtered from Eluate Prior to Caustic Addition

(Assays in %)

Ignited at 1500° F

Fe -	P.C.	Ti -	0.3
Na -	12	As(?)-	0.3
Si -	7	Mg -	Trace
Ce -	5	Y -	"
Th -	4	Mn -	"
La -	3	Cu -	"
U(?) -	2.5	Ba -	"
Al -	1.5	Gd -	"
Ca -	0.4		

* Weight, dried 100° C = 7 grams

Weight, ignited 1500° F= 4 grams

(?) - Identification not positive

P.C.- Principal Constituent

TABLE 21

Precipitation Test Data

Test	1	2
Eluate		
Volume (1)	12	11
pH	8.75	8.85
U_3O_8 (g/1)	10.7	10.8
Precipitant		
A. Caustic, solution		
Volume (1)	1.65	0.95
NaOH (% w/v)	20	30
S.G. (78° F)	1.186	1.260
Barren solution		
U_3O_8 (g/1)	0.41	0.49
U_3O_8 recovery (%)	95.6	95.2
B. Caustic, solid *		
NaOH (g)	240	220
Barren solution		
U_3O_8 (g/1)	0.06	0.056
U_3O_8 recovery (%)	99.4	99.4
NaOH consumption (lb/lb U_3O_8) Basis: Caustic solution and U_3O_8 precipitated from eluate (see Table 22).	2.69	2.66
Precipitate		
Weight (g)		
Wet	290	240
Dry	150	127
U_3O_8 (%)	82.68	
NaOH consumption (lb/lb U_3O_8) Basis: Caustic solution and uranium precipitate.	2.69	

* Added to barren from caustic solution precipitation in order to increase U_3O_8 recovery from 95% to 99% (Precipitation temperature = 135° F).

TABLE 22

Precipitation Test Results

Test	Description	Solution Volume (1)	U₃O₈ Assay (g/l)	U₃O₈ Quantity in sol'n (g)	Na₂CO₃ assay (g/l)	NaHCO₃ assay (g/l)	SO₄ assay (g/l)	NaOH Quantity added (g)	NaOH Cumulative quantity (g)	NaOH Solution assay (g/l)	Pptd U₃O₈* Cumulative quantity (g)	Solution pH
1.	Eluate	12	10.71	128.5	10.2	25.9	12.6	-	-	-	-	8.75
	20% w/v NaOH (78°F)	1.50	3.32	44.8	66.8	Nil	-	300	300	<0.05	83.7	12.35
		0.15	0.41	5.6	67.9	Nil	11.1	30	330	3.1	122.6**	12.50
	120 g NaOH 135°F	-	0.15	1.8	-	-	-	120	450	-	126.4	-
	120 g NaOH 135°F	-	0.06	0.7	-.	-	-	120	570	-	127.5 (Max 128.2)	-
2.	Eluate	11	10.81	118.9	10.0	29.7	12.6	-	-	-	-	8.85
	30% w/v NaOH (78°F)	.25	10.57	118.9	27.9	19.3	-	75	75	-	Nil	9.55
	"	.20	10.38	117.8	41.4	5.5	-	60	135	-	Nil	9.95
	"	.15	10.16	115.8	49.4	2.4	-	45	180	-	1.0	10.40
	"	.10	10.14	115.6	56.3	1.3	-	30	210	-	0.2	11.35
	"	.05	9.85	111.8	60.0	1.6	-	15	225	-	3.0	11.95
	"	.05	7.07	79.9	62.6	0.7	-	15	240	-	33.9	12.15
	"	.05	3.99	44.9	65.9	Nil	-	15	255	0.3	68.2	12.25
	"	.05	1.77	19.8	67.7	Nil	-	15	270	0.6	92.9	12.40
	"	.05	0.61	6.8	68.2	Nil	-	15	285	3.1	105.7	12.55
	Final volume	11.1	0.49	5.4	69.2	Nil	11.1	-	-	-	107.0 **	12.55
	110 g NaOH 135°F	-	0.16	1.8	-	-	-	110	395	-	110.6	-
	55 g " "	-	0.09	1.0	-	-	-	55	450	-	111.4	-
	55 g " "	-	0.056	0.6	-	-	-	55	505	19.8	111.8 (Max 112.4)	-

* Corrected for loss to sampling (sample volume = 100 ml).

** Quantity of uranium from which NaOH consumption values are calculated (Table 21).
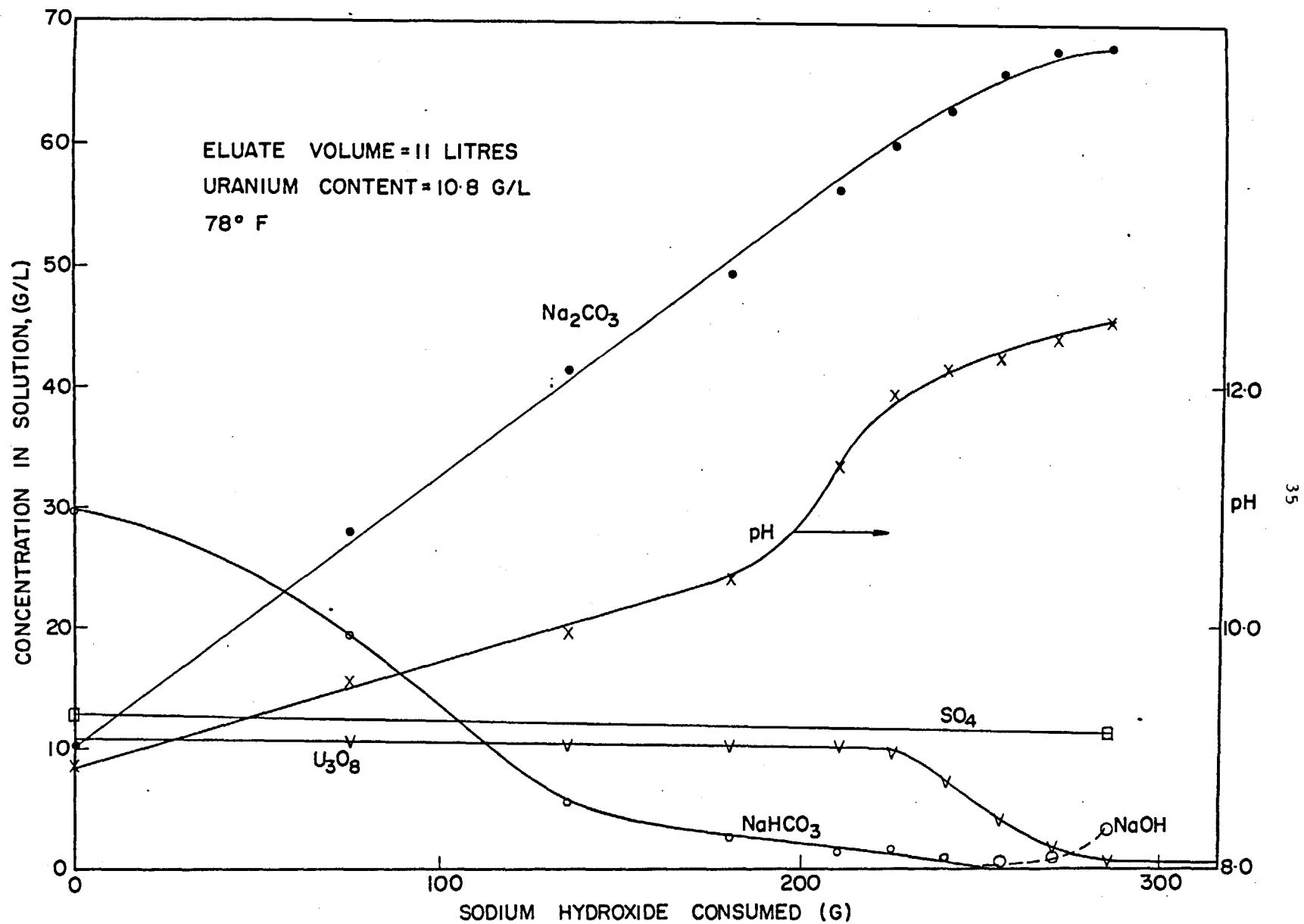
34

FIGURE 3

BATCH PRECIPITATION OF URANIUM FROM CARBONATE ELUATE WITH 30% W/V NaOH

the eluting solution when recycling is employed. A barren filtrate bleed would be required to control the sulphate level and the solution volume. In this work, the effect of recycling the re-carbonated barren eluate was not studied. If a portion of the sodium carbonate filtrate were used for the initial part of the elution, the effect of the sulphate in solution should also be observed. Sodium carbonate make-up would be required.

Figure 4 shows the result of plotting the quantity of NaOH consumed versus the quantity of uranium precipitated. The plotted values have been corrected for the quantity of U_3O_8 in the samples which were withdrawn from the batch precipitation.

It is difficult to obtain a satisfactory barren filtrate from a caustic solution precipitation of carbonate eluate, especially at ambient temperature. Forty-four percent of the total sodium hydroxide consumed was required to reduce the uranium in the filtrate from 0.49 g U_3O_8/l to 0.056 g U_3O_8/l (at 135° F). However, the sodium hydroxide consumption (Table 21) has been calculated from a barren filtrate assaying approximately 0.45 g U_3O_8/l. If the batch precipitation, using caustic solution, had been carried out at a higher temperature (120-140° F), a more satisfactory barren filtrate would possibly have been obtained with a reagent consumption of 2.7 lb NaOH per lb U_3O_8.

The uranium cake obtained from the precipitation at 78° F (containing 95.5% of the total U_3O_8) was combined with the quantity of uranium cake (containing approximately 4% of the total uranium) obtained from precipitation at 135° F. A complete analysis of the dried precipitate is given in Table 23.
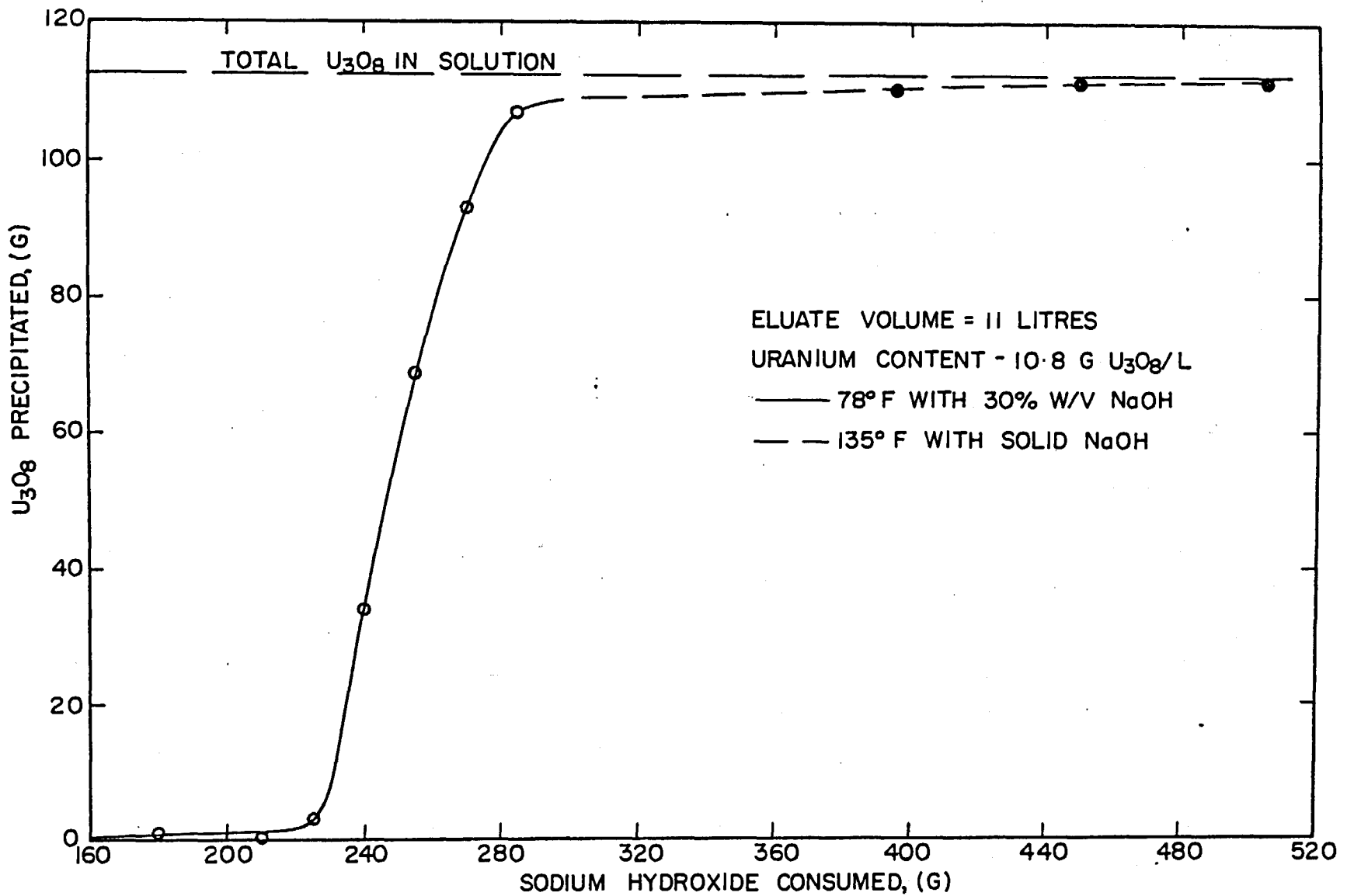
FIGURE 4

BATCH PRECIPITATION OF URANIUM FROM CARBONATE ELUATE

TABLE 23

Product Grade and Purity (%)

Element	Process	
	Salt-sulphuric elution; 2-stage precipitation with MgO *	Bicarbonate elution; single precipitation with NaOH
U_3O_8	74.74	82.68
Na	1.2	6.9
ThO_2	2.0	2.2
Fe	0.50	0.01
CO_2	0.36	1.83
CaO	2.31	0.11
MgO	7.44	-
SiO_2	1.07	0.20
Cl, Br, I,	0.03	0.017
F	0.025	0.003
SO_4	0.39	0.03
$(R.E.)_2O_3$ **	0.09	0.01
B	0.003	<0.001
Mo	<0.001	<0.001
V_2O_5	<0.02	0.02
As	<0.01	<0.002
P_2O_5	0.03	0.03
Ti	<0.10	0.02
Acid insoluble	1.40	0.29
Ni	0.002	0.003
Cu	0.002	<0.0005

* From previous work
** Rare earths oxides

DISCUSSION

1. Mechanism of the Elution Process

It is not possible, with the data obtained in this work, to do more than speculate on the mechanism of the elution process. It may be of value, however, to point out that the reactions are in fact somewhat more complicated than a simple displacement of the uranyl trisulphate complex by carbonate and bicarbonate.

It has been shown by Sutton (2) that, as the pH of an acid solution of uranyl ion is raised above a value of 2, condensed hydrolytic species, viz., $U_2O_5^{++}$, $U_3O_8^{++}$, $U_3O_8(OH)^+$, etc., are formed, with the simultaneous liberation of hydrogen ion. It is therefore postulated that the formation of gas, when resin loaded from an acid sulphate solution is eluted with a solution containing only carbonate or bicarbonate, results primarily from these hydrolysis reactions, although in the case of very acidic leach liquors, adsorption of bisulphate ions during the loading cycle may also play a part. Thus, in the initial steps of the elution, carbonate ion will diffuse into the resin matrix. Since its concentration in the inner resin phase will be low at first, there will be no question of formation of the anionic uranyl tricarbonate complex. Rather, the carbonate will probably displace sulphate ions in the internal solution and so raise its pH. This will be followed by displacement of some of the uranyl trisulphate complex adsorbed at the active sites of the resin. This complex, now in a medium low in excess sulphate, would be expected to dissociate. The liberated uranyl ions, as a result of the high pH, would hydrolyze to give

TABLE 23

Product Grade and Purity (%)

Element	Process	
	Salt-sulphuric elution; 2-stage precipitation with MgO *	Bicarbonate elution; single precipitation with NaOH
U_3O_8	74.74	82.68
Na	1.2	6.9
ThO_2	2.0	2.2
Fe	0.50	0.01
CO_2	0.36	1.83
CaO	2.31	0.11
MgO	7.44	-
SiO_2	1.07	0.20
Cl, Br, I,	0.03	0.017
F	0.025	0.003
SO_4	0.39	0.03
$(R.E.)_2O_3$ **	0.09	0.01
B	0.003	<0.001
Mo	<0.001	<0.001
V_2O_5	<0.02	0.02
As	<0.01	<0.002
P_2O_5	0.03	0.03
Ti	<0.10	0.02
Acid insoluble	1.40	0.29
Ni	0.002	0.003
Cu	0.002	<0.0005

* From previous work
** Rare earths oxides

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the condensed hydrolytic species, and the liberated hydrogen ion, diffusing out of the resin, would then react with the carbonate ion in the external solution to produce the gassing observed.

The diffusion of the hydrolyzed cationic uranium species into the external solution puts them into a medium of high carbonate-bicarbonate concentration and results in the establishment of the uranyl tricarbonate complex. The reaction consumes both carbonate and bicarbonate $\left(UO_2(CO_3)_3^{4-}\right.$ is not included in the assay values for CO_3^{2-} and $HCO_3^{-}\left.\right)$.

$$U_3O_8^{++} + 4\ HCO_3^{-} + 5\ CO_3^{=} \longrightarrow 3\ UO_2(CO_3)_3^{4-} + 2\ H_2O \quad\text{---1}$$

When carbonate eluant is being used, the necessary bicarbonate may be in the solution in advance as a result of the hydrolysis reaction noted above. If it is not present in sufficient amounts, complete conversion of the hydrolytic species will not occur. If bicarbonate eluant is being used, on the other hand, further gas production can be anticipated.

$$U_3O_8^{++} + 14\ HCO_3^{-} \longrightarrow 3\ UO_2(CO_3)_3^{4-} + 7\ H_2O + 5\ CO_2 \quad\text{---2}$$
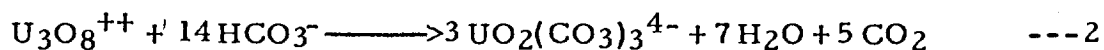
It is therefore evident that if an attempt is made to use a bicarbonate solution alone for the elution, continuous and violent gas evolution will ensue throughout the course of the elution. If carbonate solution is used, gas evolution will occur until the pH of the contents of the resin column have been raised above pH 8 or thereabouts. After this point, further introduction of hydrogen ion will lead to the production of bicarbonate ion, and the carbon dioxide gas in the column will be absorbed slowly to produce more of the same ion.

This mechanism has been confirmed in a series of experiments (not reported here), in which concentrated uranyl sulphate solutions were titrated with normal carbonate and bicarbonate solutions while measuring the volume of gas evolved, and the pH of the uranyl sulphate solution. However, the addition of sodium hydroxide to the sodium carbonate solution should effect complete elimination of gassing and its attendant inconvenience.

The experimental work amply confirms this. It was found possible to start elution with a solution containing carbonate alone and maintain gas formation within controllable amounts, but an excessive volume of the solution was required. The addition of sodium hydroxide permitted keeping the volume of solution used in this stage of elution at a minimum. A concentration of 0.5 NaOH in 1 N Na_2CO_3 gave good results, and it is possible that an even smaller amount would have worked as well.

As has been seen, a carbonate solution is in itself likely to be a poor eluant, if for no other reason than that it will not convert all the uranium species to the carbonate complex, and any uranium not in the form of the complex will precipitate as a uranate at these pH values. Bicarbonate, on the other hand, is capable of accomplishing the complete conversion and is known to be effective in preventing readsorption of the anionic uranyl tricarbonate complex. Table 14 illustrates the improvement in completeness of elution which results from increasing the bicarbonate concentration. The solution used in the latter part of the test work (1.1 N in bicarbonate) approaches the limit of solubility of the sodium salt.

2. Effectiveness of Carbonate Elution as Compared with Conventional Treatment

From an operating standpoint, carbonate elution offers a number of advantages over conventional methods. It provides a precipitation feed solution, of adequate uranium concentration, from which a relatively high purity product can be precipitated (Table 23). The principal impurities are sodium, thorium, and rare earths. It is believed that further study would make possible a substantial elimination of the two latter elements during the precipitation step. This is suggested by the nature of the precipitate which settled out of the eluate on standing (Table 20), indicating that by proper adjustment of the solution, hydrolytic break-down of the carbonate complexes of most of the undesirable elements could be induced. This precipitate caused no difficulty in either elution or precipitation steps.

The time required for carbonate elution (14 hours in this work) is only slightly longer than conventional elution (10-14 hours). The resin is left in the sulphate form, eliminating one of the major causes of uranium loss, namely royal barren at the start of elution. It should be pointed out, however, that this does involve one extra step (displacement of carbonate by sulphate) and a slight extra cost.

The principal point that remains to be investigated is the effect of sulphate build-up in the recycled barren eluate on elution and precipitation. From general considerations, it is extremely likely that moderate sulphate concentrations would be beneficial in both cases.

Another subject for investigation would be improved methods for recovery of uranium from the eluate, particularly with a view to eliminating thorium and the rare earths, but also with the ultimate goal of producing refinery-grade oxide.

3. Effect of Carbonate Elution on Resin Life

Since alkaline solutions are, in general, known to be deleterious to quaternary-ammonium type anion exchange resin, some anxiety was felt as to the effect of the proposed elution cycle on the stability of the resin. This concern was somewhat heightened by the observation that the alkaline eluates had a noticeable amine odour. For this reason, the bulk of the work was carried on in the form of a life test, even though all the operating data had not been established. In this way it was possible to obtain a reasonable number of cycles to permit comparison of the condition of the resin used for the test work, with the condition of similar resin used on liquor from the same ore in a conventional elution procedure.

In so far as the standard uranium loadings are concerned, resin capacity to breakthrough showed a slight drop as compared with unused resin (47 g/l and 54 g/l resin, respectively), while the saturation capacity remained approximately the same (65 g/l resin). This behaviour, indicative of a decrease in the rate of exchange, can be observed as a decrease in the slope of the final loading curve in Figure 1. It is symptomatic of degradation of the strong-base quaternary exchange sites of the resin, an interpretation which is confirmed by the results of the resin analyses given in Table 18 (specifically, the determinations of salt-splitting and weak-base exchange capacities of the new and used resins).

The changes in these two capacities, however, are remarkably similar to those observed in the case of salt-sulphuric acid elution. Indeed, the curves shown in Figure 1 are nearly superimposable on the same curves found during life tests using the same liquor and salt-sulphuric acid elution.

Incidentally, despite the slight deterioration noted, operating loadings did not decrease significantly (Table 9), and approximately the same weight of uranium was contained in the precipitation feed solution throughout the test work. (The fact that the operating uranium loading is higher than the standard loading is due to the higher uranium concentration of the leach liquor as compared with that of the standard synthetic head solution used in the standard loading tests.) The standard acid elution (Figure 2) was scarcely affected at all.

The similarity of the moisture values between used and unused resin provides a good indication that the resin has undergone no physical breakdown or depolymerization, and that no significant blocking of the resin structure by deposition of insoluble material has occurred.

Silica build-up is less that is the case with conventional acid eluants (Table 18), but the resin ash content, although low (1.10%), is somewhat higher. This higher ash content results from what is, in effect, one of the major advantages of this method of elution, i.e., exclusion of iron from the precipitation feed, due to its insolubilization in the resin by carbonate. The precipitated iron is substantially stripped from the resin during the loading cycle and is discarded with

the barren solution. Nevertheless, some of the iron seems to be firmly attached to the resin, since it was not completely removed by an intervening standard loading test and a treatment with 3-4 litres of salt-sulphuric acid eluant (Table 17).

To summarize, therefore, it is not expected that use of the carbonate elution procedure will result in any significant reduction in resin life.

CONCLUSIONS

It has been shown that anion exchange columns that have been loaded with uranium from acid sulphate leach liquors can be eluted successfully, using a bicarbonate solution. Prior treatment with a solution containing both sodium hydroxide and sodium carbonate is necessary to neutralize acid liberated by the hydrolysis of the uranyl (UO_2^{++}) cation, and by the subsequent reaction of the hydrolysed cations with carbonate and bicarbonate to form the uranyl tricarbonate complex. If no prior treatment is given, this acid will react with the carbonate and bicarbonate ions to liberate CO_2 gas, disrupting the resin bed and blocking the flow of solutions.

This elution method produces a precipitation feed solution of adequate uranium concentration. The precipitate obtained by treatment of this solution with sodium hydroxide is of higher grade than is that obtained by the use of salt-sulphuric acid elution followed by MgO precipitation. The purity of the product with respect to many important impurities is also better than that of the product from the conventional

elution procedure. It does not, unfortunately, approach refinery grade, the high thorium and rare-earth contents being still objectionable. It should be pointed out, however, that in this work we have been dealing with a leach liquor containing exceptional amounts of these two elements. The procedure described here might well produce a substantially purer (and possibly more saleable) product from a low-thorium ore, e.g. from the Beaverlodge, Sask. area. Another possibility to be borne in mind is that the eluate (precipitation feed solution) from this process may prove to be particularly advantageous as feed for a second up-grading step, made with the aim of producing reactor grade material at the mine-site. In particular, the differences in stability of the uranium, thorium and rare earth complex carbonates make it quite likely that the latter elements can be eliminated by more sophisticated treatment than that undertaken in the work described in this report.

No evaluation of the costs of the process is given, since considerably more extensive work would be required to establish the relative importance of the various factors. The reagent costs are undoubtedly in the proper range, but the amount of recycling possible has not been studied. Another important factor is the increase in capital costs necessitated by the more complex cycle. Examination of the resin showed no serious deterioration; but further tests to verify this would be desirable, since there appears to be no literature data on the long-term stability of quaternary-base anion-exchange resin in this type of service.

REFERENCES

1. V.M. McNamara and W.A. Gow, The Elution with Carbonate Solution of an Ion Exchange Resin Loaded with Uranyl Sulphate.

   Research Report R 41, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada, January 1959.

2. J. Sutton, The Hydrolysis of the Uranyl Ion; Part 1.

   J. Chem. Soc., Supplementary Issue, No. 2,   S275-S286 (1949).

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EK:VM:JCI:dm-im.