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THE ELUTION WITH CARBONATE SOLUTION OF AN ION EXCHANGE RESIN LOADED WITH URANYL SULPHATE

by

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RADIOACTIVITY DIVISION

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ABSTRACT

A practical method has been developed by which sodium carbonate and sodium bicarbonate solutions can be employed to elute anion exchange resins which have been loaded with uranium from acid sulphate solutions.

Carbon dioxide evolution on elution was prevented by the passage of 1.0N Na_2CO_3 solution until the eluate pH reached 4.5, followed by 1.0N $NaHCO_3$ solution to accomplish the bulk of the actual elution.

A retention time of 30 minutes for the Na_2CO_3 solution is recommended. The optimum range of retention time for the $NaHCO_3$ solution was 15 to 30 minutes. A shorter time resulted in a considerable increase in bed volumes of eluate required.

CO_2 gas formation in the column during loading was prevented by rinsing the eluted resin thoroughly with water, followed by three bed volumes of 2% Na_2SO_4 solution.

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(17 pages, 7 tables, 2 figures)

INTRODUCTION

From time to time there has been some interest in using sodium carbonate or bicarbonate solutions for the elution of uranium from anion-exchange resins which have been loaded from acid solutions. These carbonate eluting solutions might be expected to reduce the amounts of poisons such as silica, polythionates and phosphate that may accumulate on the resin. When acid eluting systems are used these poisons may reduce the uranium capacity of the resin.

While solutions of sodium bicarbonate will elute uranium quite effectively, one immediate operating difficulty has been that evolution of carbon dioxide occurs when such solutions are passed directly through a resin bed that has been used to extract uranium from an acid solution.

It was thought that if the loaded resin could be contacted first with a sodium carbonate solution of sufficient concentration to neutralize the acidity of the resin by a reaction similar to

$$H_2SO_4 + 2Na_2CO_3 \longrightarrow 2NaHCO_3 + Na_2SO_4,$$

rather than

$$H_2SO_4 + Na_2CO_3 \longrightarrow H_2O + CO_2 + Na_2SO_4,$$

then evolution of gas would not occur.

Also, it was thought that elution with combinations of carbonate and bicarbonate solutions would yield eluates with higher uranium concentrations which would, in turn, yield higher grade precipitates.

GENERAL SUMMARY

Since the use of a bicarbonate solution to elute resin which has been loaded from acid solution will cause considerable gas formation, an elution procedure[1] consisting of two steps was developed. In the first step, sodium carbonate was passed through the column until the effluent reached a pH of 4.5. In the second step, elution was continued with sodium bicarbonate solution until all the uranium was stripped from the resin.

A study of the efficiency of carbonate elution of uranium-loaded IRA 400 resin was performed in columns which contained 50 ml of resin (tapped down volume). One bed volume (1 b.v.) is, therefore, 50 ml. The resin was saturated with uranium by passing, 100% in excess, a synthetic solution containing 2 g U_3O_8/l and 30 g SO_4/l. The uranium was added as UO_2SO_4, the SO_4 was added as Mg SO_4, and the pH was adjusted to 1.75 with sulphuric acid. A retention time of 4 minutes was maintained. The uranium loading on the resin averaged 100.3 grams per litre of resin.

The variables under study in this work were the concentrations of the carbonate and bicarbonate solutions used for elution, and the retention times of these eluting solutions within the resin bed.

By choosing a suitable concentration and retention time for the sodium carbonate solution, the gas formation which ordinarily occurred during the initial phase of bicarbonate elution could be completely eliminated.

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(1) This reference has been placed at the end of the report (page 15).

It was also found that a resin rinse, comprising a water flush followed by dilute sodium sulphate solution, was required after the completion of elution. This rinse converted the resin to the sulphate form in preparation for the subsequent loading operation, thus avoiding gas formation at this point in the overall recovery cycle.

PROCEDURE

The operating steps followed were:

1. Resin loading with synthetic uranium liquor at 4 minutes retention time.
2. Water displacement rinse at 4 minutes retention time.
3. Sodium carbonate flow until the eluate leaving the column attained pH 4.5. Retention time was a variable.
4. Sodium bicarbonate elution until the resin was stripped of all the uranium. Retention time was a variable.
5. Thorough water rinse (4 b.v.) at a retention time of 4 minutes.
6. Flow of Na_2SO_4 solution through the column to strip $[HCO_3]^-$ and $CO_3^=$ and thus prevent gas formation on the subsequent resin-loading operation. Retention time was 5 minutes. This step converted the resin to the sulphate form.

The eluate pH was read continuously by allowing the solution to pass into the bottom of a small vial which contained the pH electrodes (Figure 1). The solution moved upward around the electrodes and out through the overflow tube into sample bottles.

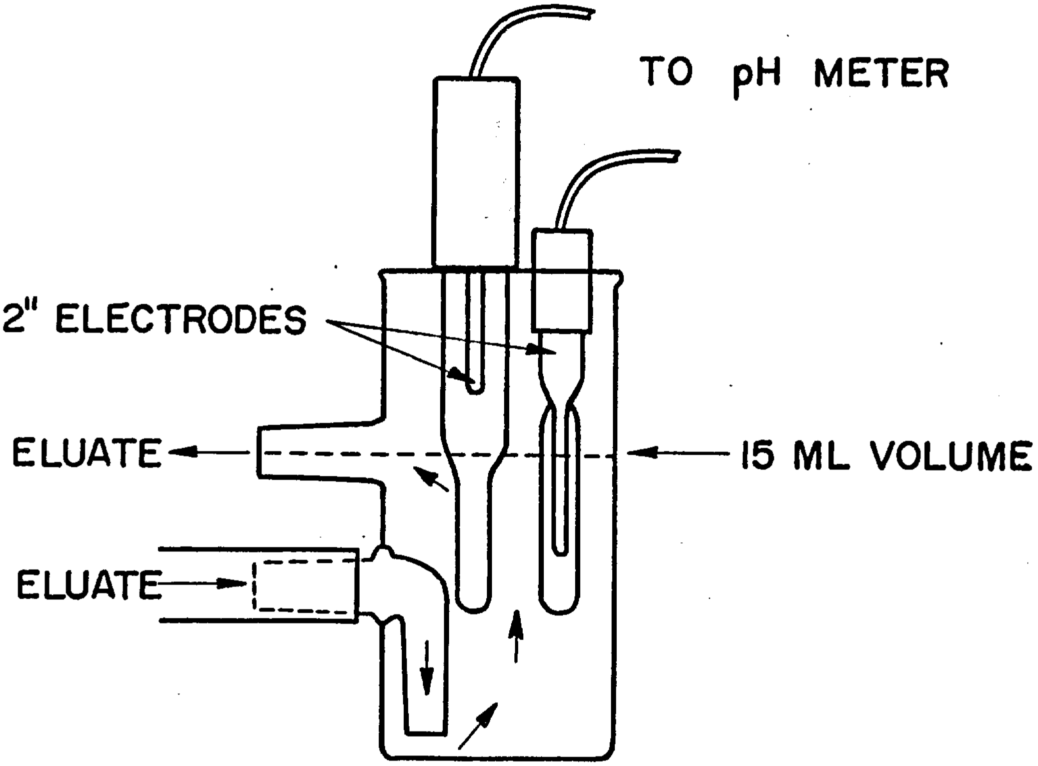

FIGURE I

ASSEMBLY FOR CONTINUOUS pH READING

RESULTS AND DISCUSSION

Tables 1 to 4 and Figure 2 show the elution data obtained during the several runs. The pH values shown in Tables 1 and 2 are readings taken on the eluate samples. All of the eluate was collected as samples for analysis.

In tests 1 to 4 (Tables 1 and 3), similarly loaded resins were eluted, at 30 minutes retention time, using a carbonate solution followed by a bicarbonate solution. In each test the normalities of the two eluting solutions were the same. The normalities investigated were 0.50, 0.75, 1.0 and 1.25.

Although elution with 1.25N sodium bicarbonate solution appears to be faster, the preparation of this nearly-saturated solution is time-consuming. Consequently, it is thought that 1.0N bicarbonate solution would be preferable in an operating plant. The use of 0.75N Na_2CO_3 for the first stage of elution, until the eluate pH reached 4.5, resulted in some subsequent gas formation. Therefore, the combination of 1.0N Na_2CO_3 followed by 1.0N $NaHCO_3$ appears to be the most satisfactory.

For elution with 1.0N Na_2CO_3 followed by 1.0N $NaHCO_3$, plots of pH, sulphate concentration, and uranium concentration in the eluate, versus bed volumes passed, are shown in Figure 2. It will be noted that the peak U_3O_8 concentration in the eluate exceeded 30 grams per litre (for a 1/2 b.v. sample).

TABLE 1

Eluate Assays in Na_2CO_3-$NaHCO_3$ Normality Study

(Solution Retention Time = 30 min.)

		U_3O_8 (g/l)				SO_4 (g/l)				pH			
Test No.		1	2	3	4	1	2	3	4	1	2	3	4
Normality ***		0.50	0.75	1.0	1.25	0.50	0.75	1.0	1.25	0.50	0.75	1.0	1.25
Operation	Vol. (b.v.)												
Rinse	1.5		1.23				3.5				1.6		
	2.0				1.04				2.8				1.7
	2.5	0.74											
	2.7			1.07				3.0				1.6	
	3.0		0.96		0.87		2.3		2.4		1.7		1.9
	3.8		0.83				2.0				1.8		
Elution	0.5	1.74			2.49	18.0			44.0	2.2			2.7
	1.0	1.89	1.20	2.04		24.8	32.4	31.4		2.3	2.6	2.4	
(Double	1.3				14.48				63.0				*6.4
underline	1.4		1.55				39.0				2.9		
designates	1.6			6.48				50.4				*5.3	
change	1.8				23.59				41.9				10.0
from	2.0	2.07				27.8				2.8			
carbonate	2.1			10.47				45.2				*7.3	
to	2.2		4.15				36.4				*5.5		
bicarbonate	2.3				38.07				24.0				9.3
eluting	2.6			16.60				31.3				9.8	
solution)	2.8				36.04				2.6				9.1
	3.0	3.25				26.1				*5.9			
	3.1			27.49				18.6				8.9	
	3.2		11.91				26.9				7.4		
	3.4				23.95				1.2				9.0
	3.6			31.33				2.9				8.3	
	4.0				14.03				0.9				9.0
	4.1	7.92				25.4				7.2			
	4.2		17.00				9.4				8.1		
	4.6			19.66				0.7				8.5	
	5.0				7.13				0.2				8.9
	5.1	11.10				9.9				8.1			
	5.6			10.61				0.4				8.7	
	5.7		14.35				1.0				8.1		
	5.8				4.61				0.2				
	6.1	13.70				3.1				8.6			
	6.6			6.82				0.2				8.5	
	6.7		10.98				0.2				8.6		
	6.8				0.85				0.1				
	7.1	13.36				0.3				8.4			
	7.6			4.41				0.1				8.6	
	7.7		8.24				0.1				8.4		
	7.8				0.28								8.8
	8.1	7.90				0.2				8.6			
	8.6			2.58				0.1				8.6	
	8.8				**0.07								
	9.1	5.19				0.2				8.7			
	9.6			1.77								8.6	
	9.7		4.24				0.1				8.5		
	9.8				0.04								
	10.1	3.98				0.2				8.6			
	10.8				0.01								
	11.1	3.08		1.19		0.2				8.7		8.6	
	11.7		2.62								9.1		
	12.1	2.38		0.69								8.6	
	13.1	2.34		0.43								8.6	
	13.7		1.38								8.8		
	14.1	1.86		0.38									
	15.1			**0.12								8.7	
	15.7		0.86								8.7		
	16.1	1.54											
	16.3			0.06									
	17.6			0.03									
	17.7		0.64								8.6		
	18.1	1.28											
	18.6			0.02									
	19.6			0.01									
	19.7		0.62								8.6		
	20.1	1.04											
	21.7		0.52								8.7		
	22.1	0.95											
	23.7		0.39								8.7		
	25.1	0.79											
	25.7		0.33										
	27.7		0.28										
	28.7		0.21										
	29.1	0.55											
	29.7		0.20										
	30.7		0.15										
	31.7		0.12										
	32.7		0.12										
	33.1	0.41											
	33.7		**0.10										
	34.9		0.09										
	36.1	0.34											
	39.1	0.27											
	41.1	0.15											
	42.1	**0.09											
	44.1	0.04											

* White precipitate in samples.
** Elution considered complete at U_3O_8 = 0.10 g/l.
*** Normality of eluting solution in sodium carbonate or sodium bicarbonate.

Notes: Each value in table represents the assay of the volume collected since the preceding assay. The total bed volumes of rinse for each test are indicated by the position in the table of the final rinse assays.

TABLE 2

Eluate Assays in Retention Time Study
(1.0N Na_2CO_3 followed by 1.0N $NaHCO_3$)

		U_3O_8 (g/l)				SO_4 (g/l)		pH			
Test No.		3	5	6	7	3	7	3	5	6	7
Retention Time (Min.)		30	15	10	*5	30	*5	30	15	10	*5
Operation	Vol. (b.v.)										
Rinse	2.5		0.79						1.7		
	2.7	1.07				3.0		1.6			
	3.0			0.96						1.8	
	3.4				-		-				1.7-1.9
Elution (Double underline designates change from carbonate to bicarbonate eluting solution)	0.6		2.08	3.69					2.2	4.7	
	1.0	2.04			2.30	31.4	36.5	2.4			2.9
	1.1		3.06						5.0		
	1.6	6.48				50.4		**5.3			
	1.8			8.47						**6.8	
	1.9				9.05		40.2				10.7
	2.0		6.05						**5.3		
	2.1	10.47				45.2		**7.3			
	2.6	16.60	9.28			31.3		9.8	**7.1		
	2.8			8.78						8.1	
	2.9				13.50		23.8				9.4
	3.1	27.49				18.6		8.9			
	3.4		14.24						7.5		
	3.6	31.33				2.9		8.3			
	3.8			10.98						8.1	
	3.9				16.18		6.8				8.9
	4.2		22.46						7.9		
	4.6	19.66				0.7		8.5			
	4.8			14.86						8.5	
	4.9				11.95		2.4				9.0
	5.0		18.98						8.4		
	5.6	10.61				0.4		8.7			
	5.8			12.18						8.8	
	6.1		11.56						8.5		
	6.6	6.82				0.2		8.5			
	6.8			8.68						8.7	
	6.9				7.41		1.0				9.0
	7.0		7.69						8.4		
	7.6	4.41				0.1		8.6			
	7.8			6.60						8.9	
	8.0		3.79								
	8.6	2.58				0.1		8.6			
	8.9				4.74		0.6				9.0
	9.6	1.77						8.6			
	9.8			3.84						9.0	
	10.0		2.92								
	10.9				2.92		0.3				
	11.0		1.76								
	11.1	1.19						8.6			
	12.1	0.69						8.6			
	12.8			2.15						9.0	
	12.9				1.42		0.1				
	13.0		1.14								
	13.1	0.43						8.6			
	14.1	0.38						8.7			
	14.8			1.78						8.8	
	15.0		0.58								
	15.1	***0.12									
	15.9				1.16						
	16.3	0.06									
	16.8			1.40						8.8	
	17.0		0.31								
	17.6	0.03									
	18.0		0.19								
	18.5		0.15								
	18.6	0.02									
	18.9				0.78						
	19.0		***0.12								
	19.5		0.09								
	19.6	0.01									
	19.8			0.84							
	20.0		0.08								
	21.0		0.06								
	21.8			0.58							
	21.9				0.50						9.1
	22.0		0.03								
	23.8			0.35							
	24.9				0.32						
	25.8			0.22							
	26.8			0.16							
	27.8			0.14							
	27.9				0.16						
	28.8			0.12							
	29.8			***0.10							
	29.9				0.14						
	30.8			0.07							
	31.9				0.12						
	33.9				***0.10						

* Retention time for Na_2CO_3 = 30 min.
** White precipitate in samples.
*** Elution considered complete at U_3O_8 = 0.10 g/l.

Notes: Each value in table represents the assay of the volume collected since the preceding assay. The total bed volumes of rinse for each test are indicated by the position in the table of the final rinse assays.

TABLE 3

Effect of Carbonate Concentration on Eluting Solution Volume Required

(Solution Retention Time* ≑ 30 min.)

Test	First Stage Na_2CO_3 eluting solution		Second Stage $NaHCO_3$ eluting solution		Observed Evolution of Gas
	Normality	Bed Volumes Passed	Normality	Bed Volumes to Nilspot**	
1	0.50	3.0	0.50	39.1	Considerable
2	0.75	2.2	0.75	31.5	Slight
3	1.0	1.6	1.0	13.5	None
4	1.25	1.3	1.25	7.5	None

* Solution Retention Time = $\frac{\text{Void Volume}}{\text{Flow Rate}} = \frac{\text{Bed Volume} \times 0.4}{\text{Flow Rate}}$

** Nilspot = point at which assay of eluate had dropped to 0.1 g U_3O_8/litre.

TABLE 4

Effect of Retention Time on Eluting Solution Volume Required

Test	First Stage 1.0N Na_2CO_3 eluting solution		Second Stage 1.0N $NaHCO_3$ eluting solution		Observed Evolution of Gas
	Retention Time (Min.)	Bed Volumes Passed	Retention Time (Min.)	Bed Volumes to Nilspot*	
3	30	1.6	30	13.5	None
5	15	2.0	15	17.0	Slight
6	10	1.8	10	28.0	Considerable
7	30	1.9	5	32.0	None

* Nilspot = point at which assay of eluate had dropped to 0.1 g U_3O_8/litre.

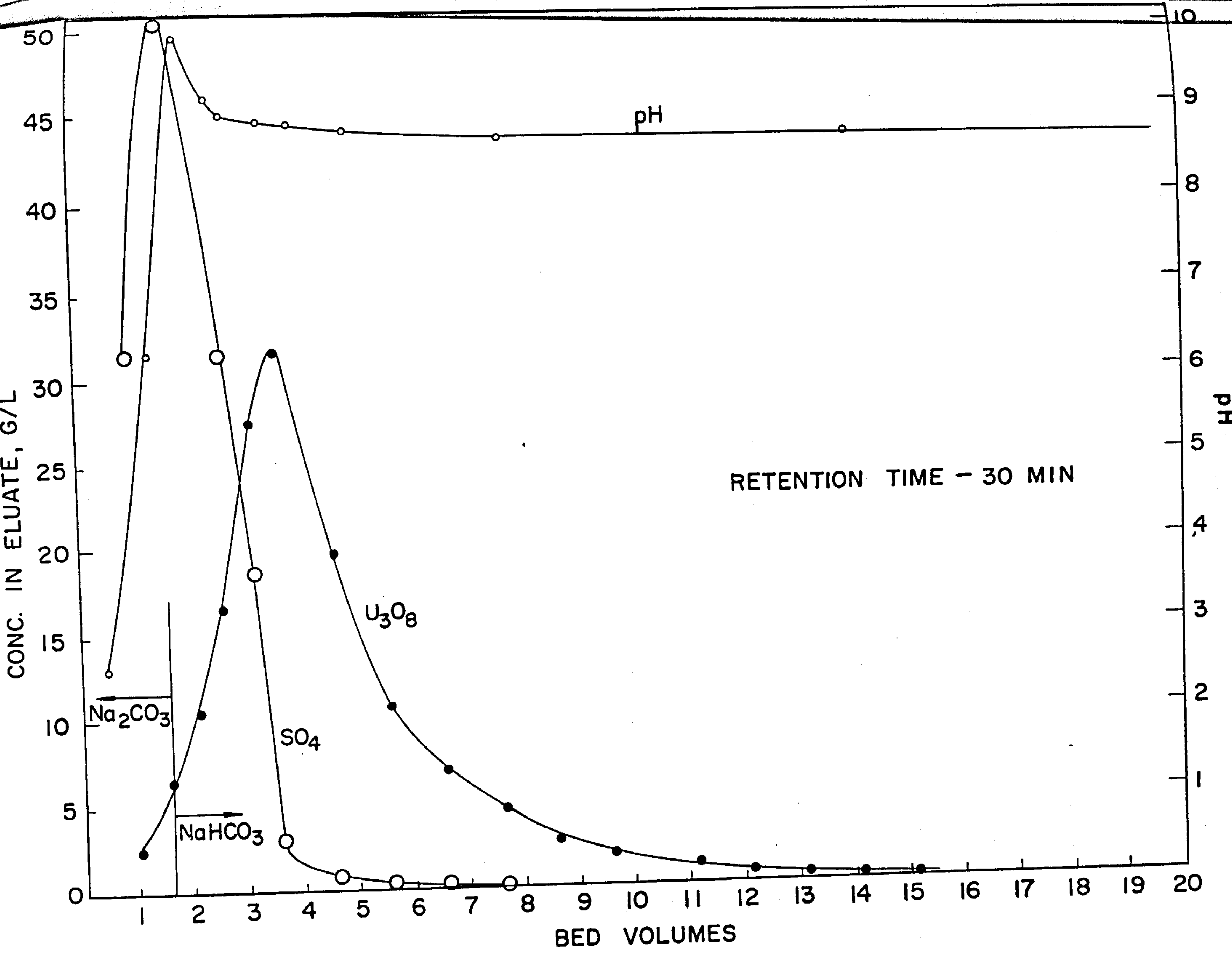

FIGURE 2

TWO-STAGE ELUTION OF URANIUM-LOADED RESIN USING 1·0 N Na_2CO_3 FOLLOWED BY 1·0 N $NaHCO_3$

Tests 3, 5, 6 and 7 (Tables 2 and 4) show the effect of flow rate on elution efficiency. The retention times studied were 30, 15, 10 and 5 minutes. Both eluting solutions were 1.0N. The retention times for the Na_2CO_3 and $NaHCO_3$ solutions were the same in each of the tests except number 7. Since 10 minutes was obviously much too short for efficient preliminary stripping of the $[HSO_4]^-$, there was no point in trying a 5-minute retention time. Therefore, in test 7, the Na_2CO_3 retention time was increased to 30 minutes. No gas formation was observed during the test. The retention time for $NaHCO_3$ elution should be within the range of 15-30 minutes in order to achieve complete elution in less than 20 bed volumes of eluate. Sodium carbonate retention time must be of the order of 30 minutes, to avoid gas formation.

Bisulphate ion is present in the synthetic acid pregnant, even at pH 1.75, and is very strongly adsorbed on the resin even in competition with $[UO_2(SO_4)_3]^{-4}$ and $SO_4^{=}$. The following equations illustrate the reactions in the process of elution:

$$RHSO_4 + Na_2CO_3 \longrightarrow RHCO_3 + Na_2SO_4 \quad \ldots\ldots (1)$$

(The bisulphate will not exist in solution when the pH is greater than 2.)

$$2RHCO_3 + Na_2CO_3 \longrightarrow R_2CO_3 + 2NaHCO_3 \quad \ldots\ldots (2)$$

Below pH 4.5, $NaHCO_3$ is decomposed, resulting in CO_2 production.

The uranium will first be converted to the uranyl tricarbonate complex on the resin, and will then be eluted in this form by bicarbonate ion, as follows:

$$R_4\,UO_2(SO_4)_3 + 3\,Na_2CO_3 \longrightarrow R_4\,UO_2(CO_3)_3 + 3\,Na_2SO_4 \ldots\ldots (3)$$

$$R_4\,UO_2(CO_3)_3 + 4\,NaHCO_3 \longrightarrow Na_4\,UO_2(CO_3)_3 + 4\,RHCO_3 \ldots\ldots (4)$$

The assay results in Table 1 show that the sulphate moves off first, while carbonate elution is proceeding. The bulk of the uranium moves off after bicarbonate elution starts. In these solutions the uranyl tricarbonate complex is more stable than the trisulphate complex. The uranium elution during the carbonate step probably results from the sodium bicarbonate formed (equation 2).

In tests 1 and 6, where considerable gas evolution was experienced, elution data would be affected to some extent since a backwash was required to clear the column of CO_2 gas early in the second part of the elution.

Table 5 shows the total amount of uranium which was on each column at the start of the test indicated. The variation in the loadings is not considered to be great enough to affect the elution data appreciably.

TABLE 5

Saturation Uranium Loadings

Test	1	2	3	4	5	6	7
g U_3O_8/1 resin	100.7	103.5	101.2	99.5	95.9	103.4	97.9

TABLE 6

Resin Treatment After Elution

(Solution Retention Time = 5 min.)

Test	Method	Observation
A.	Very thorough water rinse and backwash.	Gas formation on re-entry of acid synthetic solution.
B.	Water rinse followed by 1.2 b.v. of 0.75$\underline{N}$ Na_2CO_3; effluent pH rose from 6.0 to 9.0. Rinse and backwash with water.	Gas formation much reduced, mainly in top 2/3 of column. Possibly further Na_2CO_3 treatment would be advantageous.
C.	Water rinse* plus 6 b.v. 10% Na_2SO_4 solution.	No gas formation on re-entry of acid synthetic solution.
D.	Water rinse* plus 6 b.v. 5% Na_2SO_4 solution.	No gas formation on re-entry of acid synthetic solution.
E.	Water rinse* plus 6 b.v. 2% Na_2SO_4 solution.	No gas formation on re-entry of acid synthetic solution.
F.	Water rinse* plus 3 b.v. 2% Na_2SO_4 solution.	No gas formation. Treatment is recommended.
G.	Water rinse* plus 3 b.v. 1% Na_2SO_4; effluent pH rose from 6.0 - 8.4.	Very slight gas formation on re-entry of acid synthetic solution.

* Water rinse = 4 bed volumes

Table 6 summarizes a series of tests that were carried out in conjunction with the elution study in order to determine the simplest treatment that would satisfactorily allow re-entry of acid synthetic solution into the column after elution, without the formation of gas. It is apparent that 3 bed volumes of 2% Na_2SO_4 solution, preceded by a water rinse, was successful in preventing the formation of CO_2 by converting the resin to the sulphate form. A retention time of 5 minutes for this solution was chosen. The water rinse was 4 bed volumes. A backwash would be advantageous.

For two of the tests, an analysis of the collected effluent from this Na_2SO_4 treatment showed the quantities of carbonate and bicarbonate ions which were on the resin, and the quantity of sulphate which replaced these ions (Table 7). The total quantity of $CO_3^{=}$ and $[HCO_3]^-$ stripped from the resin was approximately twice the equivalent of the sulphate ion adsorbed. This may be due to the difficulty involved in water-rinsing carbonate (and bicarbonate) solution from the resin particles.

Some minor observations were made during this work. The Na_2CO_3 solution causes the resin to turn dark in colour. The resin was almost black when 1.25$\underline{N}$ Na_2CO_3 was used. However, by the time the eluate has reached a pH of approximately 8 on $NaHCO_3$ elution, the resin colour lightens to become just slightly darker than the shade of the sulphate form of the resin. The carbonate eluate always has a strong odour of amine.

At the point in the elution when the $NaHCO_3$ eluate combines with the previously collected Na_2CO_3 eluate, white precipitate forms. In the samples in which this precipitate remained, the pH range was 5.3-7.3. A small quantity of sodium bicarbonate was added to these samples to dissolve the precipitate.

TABLE 7

Displacement of Carbonate Ions From Resin by Sodium Sulphate Treatment

Test Number		1	2
Normality of Carbonate and Bicarbonate Solutions Used for Elution		0.50	0.75
Na_2SO_4 solution passed through column	% w/v	5	10
	b.v.	6	6
$SO_4^=$ adsorbed	(g)	3.59	3.74
$CO_3^=$ eluted	(g)	2.51	0.99
$[HCO_3]^-$ eluted	(g)	4.80	7.63
$SO_4^=$ equivalent to carbonates eluted	(g)	7.80	7.58

WORK IN PROGRESS

Using the measures developed in the course of this work to avoid the difficulty caused by the evolution of gas, a more extensive study is in progress. It involves continuous single-column ion exchange operation, employing the standard split-elution technique.

Solution obtained from the acid leaching of a uranium ore is fed to the column in order to load the resin with uranium. Precipitation of the uranium from the eluate will yield a product for analysis, in order to establish whether the use of carbonate-bicarbonate systems for elution does, in fact, result in a higher grade product.

REFERENCE

1. Brown, E.A., et al, "Some Variations of Uranium-Ore Treatment Procedures", reported at the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, September, 1958. Prepared by the Department of Mines and Technical Surveys, Ottawa, Canada, May, 1958.

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THE QUEEN'S PRINTER AND CONTROLLER OF STATIONERY
OTTAWA, 1959