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TOPICAL REPORT WIN-88

LABORATORY STUDIES IN CARBONATE ION EXCHANGE
FOR URANIUM RECOVERY

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FOR URANIUM RECOVERY

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ABSTRACT

The results of laboratory studies on sodium carbonate ion exchange are shown. The effect of salt concentration, uranium concentration, and possible interference with ion exchange from vanadium, molybdenum, sulfate and chloride are discussed. Various elution systems and the effect of residual uranium are described. A short discussion of ammonium carbonate ion exchange is also presented.

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INTRODUCTION

This report is a summary of work done at the Winchester Laboratory and the Grand Junction Pilot Plant on one phase of the sodium carbonate leaching process, namely the recovery of dissolved uranium from leach pulps and leach liquors by the use of ion exchange resins. A section is also included on the ion exchange of ammonium carbonate solutions.

In general, the carbonate leaching process involves the oxidation of contained uranium and the subsequent dissolution of the uranium into solution as a sodium uranyl tricarbonate.

Some installations which use sodium carbonate leaching circuits effect a recovery of the uranium from solution by precipitation with excess sodium hydroxide. The uranium precipitate is removed from the barren liquor by filtration and the liquor is then recarbonated and recycled back to the leaching section. The process has some deficiencies with one inherent difficulty being to obtain complete precipitation of the uranium values. Obviously, if complete uranium precipitation is not obtained there is a loss of dissolved values. Recycle of the barren is practiced but there is always some loss of solution with the leached residue and bleeding of barren solution directly to tails is sometimes required.

If vanadium is present in solution it will co-precipitate with the uranium, thereby contaminating the yellow cake. The use of ion exchange for uranium recovery from carbonate liquors offers the possibility of rejecting most of the vanadium to obtain a higher grade product. The problem of uranium losses in the bleed may be minimized by control of the ion exchange effluent to a uranium value much lower than that obtained by caustic precipitation.

These facts were recognized in earlier laboratory work which was reported by Abrams¹ in 1951. Unfortunately, an efficient method for the removal of adsorbed uranium was not developed at that time and as a result the work was discontinued.

The program was reopened in the summer of 1954 with the result that the elution difficulties were overcome and the process made applicable to either the ion exchange of clear solution or the ion exchange of pulps.

The Grand Junction Pilot Plant has tested two flowsheets; one for the RIP process^{2,3,4,5} (Figure 1) and one for a conventional column ion exchange² (Figure 2). The salient feature of the flowsheets is that each has a reagent recovery system such that

about two thirds of the leaching reagents are recovered and recycled. Complete recovery of reagents, by recycling of the ion exchange tails is not practical due to the buildup of ions which are introduced during the elution step. When considered on an overall cost plus tails basis these methods could in many instances compete favorably with the conventional process employing caustic precipitation.

Conversion of existing acid RIP or column ion exchange plants to one of the carbonate processes shown in Figures 1, and 2 is also possible without extensive revision: such conversion could result in considerable saving in treating high lime ores.

CHEMISTRY OF CARBONATE ION EXCHANGE

The leach liquor or leach pulp used in the carbonate ion exchange system is obtained by leaching an ore with a mixture of sodium carbonate and sodium bicarbonate.

Uranium must be in the hexavalent state if it is to be soluble in carbonate solution. If the uranium is oxidized the reaction may be considered to be:

In other instances where uranous uranium is present in the ore, oxidation is necessary for dissolution. The dissolution may be expressed as:

In addition to the complex uranyl tricarbonate anion, both reactions produce hydroxyl ion which must be neutralized with bicarbonate in order to prevent precipitation of the uranium as sodium uranate.

The anion exchange process by which uranium is recovered from carbonate leach solution or leach pulps may be compared to that from an acid system. When the resin and solution are contacted the reaction may be considered to be of the following type:

where R is a strong base anion resin.

The removal of the adsorbed uranium is effected by the use of neutral salts, the most efficient of which are sodium chloride and sodium nitrate. The presence of free HCO_3^- or $\text{CO}_3^{=}$ in the eluant is generally beneficial.

In some cases it has been difficult to remove all of the adsorbed uranium from the resin using normal volumes of eluant. It has been determined that the cause of the elution difficulty is the result of hydrolysis of the uranyl tricarbonate within the resin beads while in contact with solutions low in free carbonate or bicarbonate. This reaction which can occur in either the loading, washing, or elution cycle is discussed more fully in Appendix A, Studies of Residual Uranium in Carbonate Ion Exchange.

URANIUM EXHAUSTION FROM SODIUM CARBONATE SOLUTIONS

Leaching of uranium ores with solutions of sodium carbonate and sodium bicarbonate results in the production of relatively few anions to interfere with the exhaustion of uranium with strong base anion exchangers. In addition to the leaching reagents, CO_3^{2-} and HCO_3^- , the leach liquors often contain vanadate, molybdate, and sulfate and the effect of each of these constituents will be discussed under appropriate headings in this section. Soluble organics also act as resin foulants. These constituents may be controlled by adding an adsorbent such as MgO to the leaching circuit, or by other methods of treatment before ion exchange. Consequently the effect of carbonate soluble organics on ion exchange will not be discussed in this report.

Effects of Concentration of CO_3^{2-} , HCO_3^- , U_3O_8 , Contact Time and Resin Form

Factorial tests were conducted in a batchwise manner by contacting resin and solution in four ounce bottles on laboratory rolls for predetermined times. The resin used was XE-123 and the solution to resin ratio was six to one. The six to one ratio was chosen since it was a common ratio in use in acid resin-in-pulp processes.

The first factorial experiment considered four levels of carbonate, four levels of bicarbonate concentration and three levels of contact time. This necessitated $4 \times 4 \times 3$ or 48 batch tests. In these tests, the carbonate and bicarbonate concentrations were made up to be 0.5, 0.2, 0.1, and 0.0M, but because of the presence of about seven per cent carbonate in the bicarbonate stock solution, the carbonate concentrations were slightly high while the bicarbonate concentrations were correspondingly low. The contact times were 10, 15 and 20 minutes. The U_3O_8 concentration at the beginning of each batch contact was 0.97 gram per liter (0.0035M) added as sodium uranyl tricarboxylate. The resin was in the chloride form. After each batch contact, the liquor was submitted for uranium analysis. In order to illustrate how the experiment was designed the results of the tests at the 15 minute contact time are presented in Table 1.

Table 1

Uranium Concentrations After 15 Minute Contact With XE-123
in the Chloride Form (grams U₃O₈ per liter)

NaHCO ₃	Na ₂ CO ₃			
	0.5M	0.2M	0.1M	0.0M
0.5M	0.55	0.35	0.26	0.14
0.2M	0.30	0.11	0.043	0.0067
0.1M	0.21	0.050	0.016	0.0011
0.0M	0.16	0.024	0.0056	0.22

To conveniently analyze the effect of each variable, the data are arranged in two-way tables as in Table 2. These are formed by averaging the results for all conditions of one variable at each combination of the remaining two variables.

Table 2
Two-Way Tables for Terminal U_3O_8 Concentration (g/l)

	Na_2CO_3 , <u>M</u>	<u>Contact Time, Minutes</u>		
		<u>10</u>	<u>15</u>	<u>20</u>
Average of four	0.5	0.34	0.31	0.28
analyses, four	0.2	0.15	0.13	0.13
bicarbonate levels	0.1	0.096	0.081	0.078
combined.	0.0	0.11	0.092	0.084
Avg.		0.17	0.15	0.14

	<u>Contact Time, Min.</u>	<u>$NaHCO_3$ Molarity</u>			
		<u>0.5</u>	<u>0.2</u>	<u>0.1</u>	<u>0.0</u>
Average of four	10	0.37	0.13	0.087	0.12
analyses, four	15	0.33	0.11	0.069	0.10
carbonate levels	20	0.32	0.10	0.062	0.089
Avg.		0.34	0.11	0.073	0.10

	$NaHCO_3$, <u>M</u>	<u>Na_2CO_3 Molarity</u>			
		<u>0.5</u>	<u>0.2</u>	<u>0.1</u>	<u>0.0</u>
Average of three	0.5	0.56	0.37	0.27	0.15
analyses, three	0.2	0.31	0.11	0.044	0.0078
contact times	0.1	0.22	0.052	0.017	0.0020
combined.	0.0	0.15	0.027	0.0062	0.23
Avg.		0.31	0.14	0.084	0.097

This tabulation shows clearly that the uranium loading increases with increasing contact time and that the improvement in loading between 10 and 15 minutes is more pronounced than that between 15 and 20 minutes. The adverse effect of high concentrations of either carbonate or bicarbonate is also quite obvious. The optimum concentration of carbonate or bicarbonate seems to be some-

what less than 0.1 molar. With absolutely no excess carbonate or bicarbonate loadings become poorer, possibly because of adsorption of carbonate initially combined in the uranium complex, thereby destroying the complex and allowing the uranium to remain in solution unadsorbed, or possibly because the four moles of chloride released per mole of uranium adsorbed prevents further uranium adsorption in the absence of excess carbonate or bicarbonate.

The second factorial experiment employed all the conditions of the first experiment except that the U_3O_8 concentration at the beginning of each batch contact was 0.10 gram per liter (added as sodium uranyl tricarbonate). The test data showed the same trends as were observed earlier. The results of the tests at the 15 minute contact time are presented in Table 3.

Table 3

Uranium Concentrations after 15 Minute Contact with
XE-123 in the Chloride Form (grams U_3O_8 per liter)

<div> <div>NaHCO₃</div> <div>Na₂CO₃</div> </div>				
	0.5M	0.2M	0.1M	0.0M
0.5M	0.053	0.033	0.023	0.012
0.2M	0.025	0.0069	0.0032	0.0006
0.1M	0.017	0.0037	0.0013	0.0005
0.0M	0.011	0.0022	0.0014	0.035

The third and fourth factorial experiments were performed to evaluate the effect of resin form. These experiments were simplified by eliminating the time variable (all tests at 15 minutes contact time) and removing the 0.5 molar levels of carbonate and bicarbonate concentration from consideration thus reducing the number of tests per experiment from 48 to 9. As in the first experiment, the U_3O_8 concentration at the beginning of each batch contact was 0.97 gram per liter (added as sodium uranyl tricarbonate). The resin forms studied were bicarbonate and carbonate. The test data are presented in Tables 4 and 5.

Table 4

Uranium Concentrations after 15 Minute Contact with
XE-123 in the Bicarbonate Form (grams U_3O_8 per liter)

$\begin{array}{c} \text{Na}_2\text{CO}_3 \\ \diagdown \\ \text{NaHCO}_3 \end{array}$	0.2M	0.1M	0.0M
	<u>U_3O_8 g/l</u>		
0.2M	0.044	0.020	0.0039
0.1M	0.023	0.0075	0.0007
0.0M	0.0087	0.0023	0.015

Table 5

Uranium Concentrations after 15 Minute Contact with
XE-123 in the Carbonate Form (grams U_3O_8 per liter)

$\begin{array}{c} \text{Na}_2\text{CO}_3 \\ \diagdown \\ \text{NaHCO}_3 \end{array}$	0.2M	0.1M	0.0M
	<u>U_3O_8 g/l</u>		
0.2M	0.035	0.013	0.0041
0.1M	0.016	0.0056	0.0014
0.0M	0.0081	0.015	0.22

The results of these tests indicate that in very dilute solutions, the $UO_2(CO_3)_3^{4-}$ ion is more readily adsorbed by a carbonate form resin than by a bicarbonate form resin, probably because of the inherent difference between monovalent-tetravalent exchange and divalent-tetravalent exchange. This difference would be expected to become less pronounced as the solutions become more con-

centrated in carbonate or bicarbonate, and indeed, this is the case. A detailed technical discussion illustrating this phenomenon may be found in ACCO-61, pp. 10-16.

Effect of Vanadium

Many carbonate leach liquors contain vanadium. The adsorption of this vanadium by anion exchange resin leads to an impure uranium product as well as lowering the capacity of the resin for uranium.

Laboratory studies were made to evaluate the variables involved in the adsorption of vanadium by anion resin. The variables studied were uranium concentration, vanadium concentration, carbonate concentration, and the pH of the system. As will be shown later, especially in the work performed at the Grand Junction Pilot Plant, probably the most important variable subject to control is that of pH.

The first experiment was concerned with the adsorption of pentavalent vanadium from pure carbonate solutions. Test solutions were prepared from two stock solutions; one containing 125 grams Na_2CO_3 per liter, and the other 10 grams V_2O_5 (added as Na_3VO_4) per liter and 13.8 grams Na_2CO_3 per liter.

The laboratory tests were run batchwise at a ratio of 20 ml of resin to 100 ml of solution. The resin volume (IRA-400 in the carbonate form) was obtained by tapping wet settled resin in graduated cylinders. The contact time selected was 15 minutes. Table 6 lists the vanadium barren assays (grams V_2O_5 per liter) at each vanadium and salt concentration.

Table 6

Vanadium Adsorption from Pure Carbonate Solutions

Vanadium Concentration after 15 Minutes Contact with IRA-400 in the Carbonate form (grams V_2O_5 per liter)

V_2O_5 g/l (V^{+5})	Na_2CO_3 g/l					
	100	75	50	20	10	0
	V_2O_5 g/l					
2	0.86	0.71	0.57	0.25	0.14	0.042
1	0.47	0.42	0.32	0.17	0.092	0.014
.5	0.25	0.22	0.18	0.10	0.058	0.005
.1	0.053	0.049	0.042	0.042	0.016	0.002

Table 6 shows that vanadium, at all concentrations considered, was more strongly adsorbed at lower carbonate concentrations.

The next experiment substituted NaHCO_3 for Na_2CO_3 as one of the variables. Table 7 is a tabulation of the results obtained.

Table 7

Vanadium Adsorption from Pure Bicarbonate Solutions

V_2O_5 g/l (V^{+5})	NaHCO_3 g/l	75	50	20	10
		V_2O_5 g/l			
2		0.35	0.14	0.054	0.036
1		0.17	0.077	0.036	0.027
.5		0.086	0.039	0.023	0.019
.1		0.017	0.068	0.006	0.006

Again, we find that the higher the salt concentration, the lower the vanadium adsorption. However, the effect of bicarbonate is less than that of the carbonate. This is shown more clearly in Figure 3 which is a comparative plot of the per cent vanadium adsorption versus the salt molarity of both carbonate and bicarbonate.

Figure 3

Adsorption of a 2g V₂O₅/l Solution by IRA-400

In the next experiment five stock solutions containing five different ratios of carbonate to bicarbonate were prepared. Each of these five solutions was then diluted with water to five different concentrations. The effect of dilution on pH was observed to be negligible. The vanadium concentration was maintained constant in all tests at 1 gram V₂O₅ per liter. Table 8 presents the salt concentrations and pH used in each test, and the vanadium solution assays at the end of the contact period.

Table 8

Vanadium Assays of Carbonate and Bicarbonate Solutions

Na ₂ CO ₃ plus NaHCO ₃ Concentration, g/l	CO ₃ ⁼ : HCO ₃ ⁻ ratio			
	9/1 (pH 10.3)	3/1 (pH 9.9)	1/1 (pH 9.5)	1/3 (pH 9.1)
100	0.39	0.28	0.20	0.22
75	0.34	0.25	0.17	0.15
50	0.26	0.20	0.13	0.093
25	0.17	0.13	0.091	0.063
10	0.078	0.067	0.051	0.038

The data in Table 8 indicate that the adsorption of vanadium decreases with increasing carbonate to bicarbonate ratio, which is to be expected considering the data determined for vanadium adsorption from carbonate and bicarbonate solution.

When liquors containing both vanadium and uranium are ion exchanged, the values for uranium adsorption from pure uranium carbonate solutions will be needed for comparative purposes. These are shown in Table 9 which is a compilation of the uranium assays after 15-minute contacts with carbonate-bicarbonate solutions. The initial uranium concentration in the pregnant solution was 1 gram U₃O₈ per liter, added as Na₄UO₂(CO₃)₃. As in the vanadium experiments, the resin to solution ratio was 1 to 5, 20 ml of resin being taken for each 100 ml of pregnant liquor.

Table 9

Uranium Concentration (grams U₃O₈/l) in Carbonate Solutions After 15 Minutes Contact with IRA-400

NaHCO ₃ g/l	Na ₂ CO ₃ g/l						
	50	40	30	20	10	5	0
50	0.15	0.13	0.089	0.076	0.059	0.045	0.031
40	0.086	0.073	0.048	0.034	0.023	0.017	0.0096
30	0.047	0.034	0.022	0.014	0.0094	0.0055	0.0028
20	0.023	0.017	0.010	0.0059	0.0028	0.0018	0.0026
10	0.011	0.0076	0.0039	0.0032	0.0009	0.0006	0.0002
5	0.0076	0.0060	0.0029	0.0014	0.0012	0.0005	0.0005
0	0.0056	0.0044	0.0027	0.0015	0.0017	0.0013	--

Conditions for the most favorable uranium-vanadium separation were chosen on the basis of the equilibrium data for uranium and vanadium ion exchange from carbonate solutions presented in Tables 6 and 9. The data indicate that the most favorable separation could be attained from a solution containing little or no bicarbonate. Furthermore, the data indicate that the uranium-vanadium separation would be virtually independent of the total carbonate concentration. Thus, both at 20 grams Na_2CO_3 per liter and at 50 grams Na_2CO_3 per liter, and for solutions containing equal quantities of uranium and vanadium, it can be predicted that the vanadium loading will be about 1 per cent of the uranium loading.

In order to substantiate this prediction, 20-ml samples of IRA-400 were loaded columnwise from a solution containing 1 gram U_3O_8 per liter and 1 gram V_2O_5 per liter. One liquor contained 20 grams Na_2CO_3 per liter, and the other contained 50 grams Na_2CO_3 per liter. The resin loaded from the higher carbonate liquor was found to contain 69.5 grams U_3O_8 per liter WSR and 0.69 gram V_2O_5 per liter at uranium saturation. The equilibrium data predicted a vanadium contamination of 1.2 per cent. The resin loaded from the lower carbonate solution contained 83.8 grams U_3O_8 per liter WSR and 0.83 gram V_2O_5 per liter WSR. The equilibrium data predicted 0.8 per cent vanadium contamination.

A test simulating an RIP circuit was made in the laboratory at the Grand Junction Pilot Plant to study the loading of uranium and vanadium at pH 10.8. Six bottles were contacted on the rolls, each bottle containing 25 ml WSR from the Alkaline RIP circuit and 100 ml clarified IXF from the Utex run. One hour contact time per bottle was used. The effluent from the feed bottle was transferred to the No. 2 bottle, effluent from the No. 2 bottle was transferred to the No. 3 bottle, etc. Effluent from No. 6 bottle was tails solution. Loaded resin was removed from the feed bottle, eluted resin added, and the bottle placed in the No. 6 position. Fresh feed was then introduced into the new No. 1 bottle.

Plant eluted resin was used in all bottles at the beginning of the test and five complete cycles or 30 contacts were required to establish steady state conditions. Under these conditions the vanadium content of the tails solution was approximately the same as the feed solution. Uranium tails varied from 0.002 to 0.008 g $\text{U}_3\text{O}_8/\text{l}$.

Assay of the feed solution is tabulated below:

<u>Feed Solution</u>				
<u>g $\text{U}_3\text{O}_8/\text{L}$</u>	<u>pH</u>	<u>g $\text{V}_2\text{O}_5/\text{L}$</u>	<u>g $\text{Na}_2\text{CO}_3/\text{L}$</u>	<u>g NaHCO_3/L</u>
1.53	10.8	1.17	7.7	1.5

After approximately three liters of uranium tails solution had been produced, resin from each bottle was eluted with 1M NaHCO_3 , the eluate assayed, and a loading gradient for both uranium and vanadium on the resin was obtained. This is shown in Figure 4.

Resin Loading Gradient

Alkaline RIP Circuit Utex Liquor XE-123 Resin

pH-10.8, U_3O_8 1.53 g/l, V_2O_5 1.17 g/l

Figure 4

Results of the test indicate that it should be possible to operate an RIP circuit with seven or more banks on exhaustion at a calculated loading of 4 lb U_3O_8 /cu ft WSR by adjusting the IXF within a pH range of 10.7 - 11.0 with caustic. Furthermore, it is essential to carry the uranium loading to saturation if vanadium contamination is to be minimized.

Effect of Molybdenum

Molybdenum has a very deleterious effect on the exchange of leach liquors obtained by the acid leaching process. In order to evaluate the effect of molybdenum in a carbonate system on ion exchange, tests were made both on single and multiple column systems.

Two resins, XE-123 and IRA-400, were loaded in single columns with pregnant solution containing 5.4 grams Na_2CO_3 , 2.4 grams $NaHCO_3$, 1.0 gram U_3O_8 , and 0.102 gram Mo per liter added as Na_2MoO_4 . Figure 5 shows the loading curves for uranium and molybdenum. Retention times were three minutes for IRA-400 and six minutes for XE-123 respectively.

The data show that molybdenum continued to adsorb almost to the point of uranium breakthrough. Thereafter, the molybdenum was displaced from the resin as evidenced by the rise in molybdenum content of the effluent to a value four to five times that of the feed grade. At the point of saturation, with respect to uranium, the molybdenum content of the effluent had decreased to approximately feed grade, and rejection of molybdenum from the resin was essentially complete.

In a second test, carbonate-bicarbonate solution containing uranium and molybdenum was ion exchanged using a multi-column system; that is, two columns of resin in series on exhaustion and one column on elution. The object of this study was to investigate the behavior of molybdenum in a multi-column system.

The conditions of the test were:

Resin - IRA-400

Retention Time - Three minutes on exhaustion and 10 minutes on elution.

Head Solution - Five grams per liter of carbonate as sodium carbonate.
Two grams per liter of bicarbonate as sodium bicarbonate.
0.1 gram per liter of molybdenum as sodium molybdate.
One gram per liter of U_3O_8 as $Na_4UO_2(CO_3)_3$

Eluant - 1M sodium chloride.

Figure 5

Exhaustion of Resin with Molybdenum Spiked Pregnant Solution

Figures 6 and 7 show typical exhaustion and elution curves of the uranium and molybdenum during these studies. As will be noted, the molybdenum is adsorbed by the eluted resin in the second or tail column and as the uranium loads on the resin the molybdenum is displaced. At uranium breakthrough, in the second column, the molybdenum is coming off in the effluent at a much higher concentration than feed grade. Very little molybdenum was held on the resin. Less than 0.4 gram of molybdenum per liter was reported in the richest eluate fraction. The resins were ashed after the testing was finished and analyzed for molybdenum. Less than 0.005 gram molybdenum per liter of resin remained on the resin after eluting the uranium.

At the concentrations tested, the separation of uranium from molybdenum was excellent without sacrificing uranium loading on the resin.

Figure 6. Exhaustion Curves - Carbonate System Illustrating
Self Elution of Mo

Figure 7

Bed Volumes of 1M NaCl EluateTypical Elution of Uranium and Molybdenum
from Carbonate - Loaded IRA-400

Effect of Sulfate

Most uranium ores contain carbonate soluble sulfates and/or sulfides. Consequently, the effect of sulfate on the adsorption of uranium from solutions of varying sulfate, carbonate and bicarbonate concentrations was investigated. In the first or batch tests, all distributions were determined by contacting 20 ml of carbonate-form IRA-400 with 100 ml of solution containing 2.0 grams of U_3O_8 per liter. The data in Table 10 indicate the amount of uranium remaining in the aqueous phase after a 15-minute contact of resin and solution.

As can be seen from the data, sulfate concentrations of a few grams per liter have a serious effect on the adsorption of uranium. A sulfate concentration of 5 grams per liter with carbonate and bicarbonate concentration held at 10 grams per liter results in a 50 per cent reduction in the value of the uranium distribution coefficient.

Table 10

Uranium Concentration (grams U_3O_8 /l) in Carbonate Solutions
Containing Varying Amounts of Sulfate After 15 Minutes
Contact with IRA-400

		<u>Na_2CO_3 g/l</u>					
		0	10	20	30	40	50
<u>$NaHCO_3$</u>	<u>SO_4</u>						
<u>g/l</u>	<u>g/l</u>						
0	0	0.0010	0.0006	0.0020	0.0050	0.0088	0.013
10	0	0.004	0.0027	0.0058	0.011	0.019	0.026
20	0	0.0021	0.0057	0.014	0.029	0.037	0.056
30	0	0.0069	0.018	0.032	0.062	0.083	0.11
0	1	0.019	0.0011	0.0020	0.0045	0.0082	0.015
10	1	0.0013	0.0024	0.0061	0.010	0.017	0.027
20	1	0.0044	0.0077	0.018	0.028	0.043	0.053
30	1	0.013	0.022	0.039	0.060	0.075	0.11
0	3	0.0010	0.0039	0.0028	0.0059	0.012	0.017
10	3	0.0025	0.0039	0.0087	0.015	0.024	0.034
20	3	0.0033	0.011	0.020	0.035	0.050	0.070
30	3	0.013	0.029	0.045	0.073	0.096	0.14
0	5	0.004	0.0017	0.0057	0.011	0.018	0.025
10	5	0.0016	0.0056	0.012	0.019	0.031	0.043
20	5	0.0061	0.016	0.031	0.043	0.066	0.084
30	5	0.0069	0.041	0.058	0.090	0.13	0.15
0	10	0.0024	0.0063	0.011	0.020	0.029	0.044
10	10	0.0059	0.015	0.022	0.039	0.054	0.075
20	10	0.016	0.034	0.055	0.071	0.097	0.13
30	10	0.039	0.069	0.093	0.14	0.17	0.19
0	20	0.018	0.031	0.043	0.055	0.073	0.091
20	20	0.069	0.20	0.12	0.15	0.19	0.21
30	20	0.12	0.17	0.19	0.25	0.30	0.32

Two series of tests were then conducted with columns to determine the effect of sulfate concentration on the uranium ion exchange characteristics of carbonate-bicarbonate liquors. One series was run using a synthetic leach liquor which contained 1.0 gram U_3O_8 per liter, and a total concentration of Na_2CO_3 plus $NaHCO_3$ of about 10 grams per liter. A second set of similar liquors was prepared, in which the carbonate plus bicarbonate additions were increased to about 20 grams per liter.

Single column tests were run using 25 ml of wet settled XE-123 (plus 20-mesh) resin. Retention times were six minutes for exhaustion and ten minutes for elution. The eluant was a 1M NaCl solution.

The data in Table 11 indicate that the presence of sulfate in the liquor causes a sharp drop in the rate of uranium adsorption, as evidenced by the breakthrough volumes. The uranium saturation loadings were also adversely affected, especially at the higher sulfate levels. In the last test given in Table 11 analyses of the eluate revealed a sulfate loading of about 41 grams per liter of resin and a U_3O_8 saturation loading of only 10.1 grams per liter.

Effect of Chloride

The effect of chloride on uranium adsorption from carbonate leach liquor was first reported in this laboratory by Abrams.¹ It is unfortunate that in the test work reported, hydrochloric acid was used as an eluant and a 100 per cent recycle of barren carbonate liquor was attempted. Continued recycle resulted in a buildup of chloride ion and a sharp drop in uranium loading on the resin. Subsequent laboratory studies and pilot plant testwork demonstrated the value of sodium chloride as an eluant as well as the necessity of avoiding chloride buildup in the carbonate leach liquor.

Normally, after resin has been eluted, it is rinsed with water which displaces eluant from the resin bed but leaves the active resin sites occupied by the eluting anion. In the case of sodium chloride elution the active sites would be taken up by chloride ion. A subsequent exhaustion cycle results in chloride ion being displaced by the uranium complex with the chloride leaving the column with the effluent.

In the preparation of feed for carbonate column ion exchange, as depicted in Figure 2 in the introduction, the leached pulp is treated in a countercurrent decantation process which effects about a two-thirds recovery of the leaching reagents and allows the effluent from the ion exchange circuit to be sent to waste. The desorbed chloride values from the resin are thus removed from the circuit. The feed

Table 11

Effect of Sulfate Concentration on Carbonate Ion Exchange
With XE-123 Resin

<u>Head Assay, Grams/Liter</u>			<u>pH</u>	<u>Bed Volumes To:</u>			<u>Loading g U₃O₈/l WSR</u>
<u>Na₂CO₃</u>	<u>NaHCO₃</u>	<u>SO₄</u>		<u>Breakthru</u>	<u>Saturation</u>	<u>Elution</u>	
6.7	2.9	0.0	10.1	54	86	7	64.7
6.0	4.6	6.3	10.1	43	76	6	56.9
6.6	3.2	11.0	9.9	36	64	6	46.4
6.5	3.5	51.4	9.6	0	28	5	11.7
11.7	8.2	0.0	9.8	46	85	6	57.2
10.9	10.3	5.1	9.8	37	66	6	50.4
11.4	8.8	10.2	9.7	29	68	6	41.0
11.6	8.6	25.9	9.6	11	48	6	21.3
11.7	8.6	51.4	9.4	0	26	5	10.1

prepared for the carbonate resin-in-pulp process (Figure 1) is treated in much the same manner except that no effort is made to obtain a clear, pregnant solution.

Six single column exhaustion tests with IRA-400 resin in the chloride form were made to investigate the effect of chloride on uranium adsorption from carbonate solution. A second objective was to determine the chloride gradient of the effluent to assess the possibility of recycling a portion of the barren solution in a CCD washing circuit. The stock pregnant solution assayed as follows:

U_3O_8 1.0 g/l, $\text{CO}_3^{=}$ 6.1 g/l, HCO_3^- 2.15 g/l, $\text{SO}_4^{=}$ 1.15 g/l

Chloride concentration was varied in the range of zero to four grams per liter.

Table 12 shows the effect of chloride concentration on the number of bed volumes of solution to breakthrough and the total uranium capacity of the resin. Saturation loadings were determined by eluate assays. The U_3O_8 and chloride content of the effluents are plotted in Figures 8 and 9 respectively.

Satisfactory uranium breakthrough and saturation loadings were obtained from these solutions at chloride levels up to about two grams per liter although a deleterious effect is apparent at lower concentrations. The results also indicate that deleterious chloride buildup could be prevented by discarding the first 20 to 25 bed volumes of uranium barren solution and recycling the remainder.

Table 12
Effect of Chloride on Exhaustion of
Uranium from Carbonate Solutions

<u>Test No.</u>	<u>g Cl/l</u>	<u>Volumes to Breakthrough</u>	<u>Uranium Loading g/l</u>
1	0.00	76	81
2	0.25	76	79
3	0.50	72	81
4	1.0	72	75
5	2.0	64	65
6	4.0	48	50

Figure 8

Effluent U_3O_8 Concentration During Exhaustion of IRA-400 with Chloride
Spiked Carbonate-Bicarbonate Pregnant Solution

Figure 9

Effluent Chloride Concentration During Exhaustion of IRA-400 with Chloride Spiked
Uranium Carbonate-Bicarbonate Pregnant Solution

Exhaustion with Various Coarse Bead Resins

A comparison was made of the uranium capacities of competitive coarse bead ion exchange resins at different carbonate and bicarbonate concentrations. From the results listed in Table 13, the highest uranium capacities were obtained with a head solution containing 1.0 gram U_3O_8 , 3.0 gram Na_2CO_3 , and 1.0 gram $NaHCO_3$ per liter. The data also show that a decrease in uranium capacity is obtained when the total salt strength is increased and that the effect of salt concentration is not the same for all resins. However, at the carbonate and bicarbonate concentrations commonly encountered in alkaline RIP operations all of the resins had essentially the same capacity.

Table 13Effect of Carbonate and Bicarbonate Concentrations on the Uranium Capacity of Various Coarse Bead Resins

	Capacity, g U_3O_8 /l WSR		
	<u>Dowex 11</u>	<u>XE-123</u>	<u>SKB</u>
Head 1 g U_3O_8 , 3 Na_2CO_3 , 1 g $NaHCO_3$ /l	80	80	74
Head 1 g U_3O_8 , 5 g Na_2CO_3 ^{1/} , 2 g $NaHCO_3$ /l	78	78	76
Head 1 g U_3O_8 /l, 10 g Na_2CO_3 , 10 g $NaHCO_3$ /l	70	66	55
Head 1 g U_3O_8 /l, 25 g Na_2CO_3 , 10 g $NaHCO_3$ /l	56	57	42

^{1/} Approximately the $CO_3^{=}$ and HCO_3^- concentration encountered in alkaline RIP.

ELUTION STUDIES

One of the most important considerations in ion exchange is the removal of the adsorbed uranium as efficiently as possible. For this reason a number of reagents and reagent combinations were studied.

Sodium chloride was found to be the most efficient eluant under the test conditions used. Two molar NaCl was more effective than 1 Molar. Sodium nitrate is also an excellent eluant but on the basis of cost, sodium chloride is much more economical. Saturated NaHCO_3 at 50°C was also effective.

Elution with Neutral Salts

In the first tests, XE-123 resin, which had been converted to the carbonate form, was contacted with carbonate leach liquor in a bottle on rolls for 12 hours. The resin was removed from the liquor, water washed, and air dried. The air dried resin was then weighed into charges for future use.

The elution tests were done in single columns with equal weights of resin in each column. The retention time used was 10 minutes in all tests. The per cent elution was calculated by adding all fractions from the tests and comparing with the total obtained from the acid elution. The test data shown in Table 14 indicate that NaCl and NaNO_3 were the most effective eluants. The introduction of acid into the sodium sulfate system produced gassing, probably from the adsorbed uranium complex. The gassing effect was not noticed when acid was used in a chloride system probably because about 90% of the uranium had been removed by the time acid was introduced.

Table 14
Elution Data
Neutral Salt

% Elution						
Col Vol of Eluate	1M NaCl + H_2O	1M NaCl 1N H_2SO_4	2M NaCl	2M NaCl + 1N H_2SO_4	1M NaNO_3	1M Na_2SO_4 + HCl
1	18.5	30.3	68.3	51.4	30.6	21.3
2	88.5	86.6-	97.8	95.6-	93.1	37.6
3	98.9	97.9	99.5	99.3	98.1	52.2-
4	100	99.6	100	99.8	99.5	59.1
5		100		99.9	99.9	65.3
6				100.0	100.0	79.4
7						91.1
8						97.3
9						100.0

- Indicates where H_2O or acid introduced.

The elution of the uranyl tricarbonate complex from Amberlite IRA-400 with sodium sulfate was also investigated. The elution was performed with a $1M$ Na_2SO_4 - $0.1M$ Na_2CO_3 solution at a 10-minute retention time. One elution was performed at room temperature, and the other at $40^\circ C$. The two elution curves are shown in Figure 10. Sulfate, while not nearly as effective an eluant as nitrate or chloride, is suitable for elution.

Figure 10. Elution of Uranyltricarbonate with Sodium Sulfate, Sodium Carbonate So-

Elution with Bicarbonate and Bicarbonate-Chloride Solutions

The third series of tests on carbonate loaded XE-123 resin used the following eluants:

1. a. $1M$ $NaHCO_3$ - $0.025M$ $NaCl$
 b. $1M$ $NaHCO_3$ - $0.05M$ $NaCl$
 c. $1M$ $NaHCO_3$ - $0.1M$ $NaCl$
2. a. $1M$ $NaHCO_3$ - Ambient Temperature
 b. $1M$ $NaHCO_3$ - $50^\circ C$
 c. $1.29M$ $NaHCO_3$ - $50^\circ C$

The resin was loaded from pregnant solution containing 10 grams of Na_2CO_3 , 10 grams of $NaHCO_3$, and one gram of U_3O_8 per liter. U_3O_8 loading was 68 grams per liter. Data from the tests are presented in Table 15 and in Figures 11 and 12.

Table 15

Elution Tests on XE-123 Resin

Eluants	Column Volumes to Complete Elution	Per Cent U_3O_8 Eluted Column Volumes			
		4	6	8	10
1M $NaHCO_3$ 0.025M $NaCl$	14.8	72	88	94	98
1M $NaHCO_3$ 0.05M $NaCl$	14.4	77	90	96	98
1M $NaHCO_3$ 0.1M $NaCl$	13.2	81	93	97	99
1M $NaHCO_3$ Ambient	14.0	78	90	96	98
1M $NaHCO_3$ 50°C	12.8	88	96	98	99
1.29M $NaHCO_3$ 50°C	6.8	97	99.8	-	-

The data show that the addition of up to 0.1M $NaCl$ to a 1.0M solution of $NaHCO_3$ or increasing the temperature from about 25°C to 50°C had little effect on the volume of eluant required for complete elution. Some improvement in the initial rate of elution was obtained, however, by the addition of $NaCl$ or increasing the temperature. The most effective eluant tested in this series was a saturated (1.29M) solution of $NaHCO_3$ at 50°C, which resulted in complete elution in 6.8 bed volumes

Figure 11

Elution of Carbonate Loaded Resin with Sodium Bicarbonate and Sodium Chloride

Figure 12. Elution of Carbonate Loaded Resin with Sodium Bicarbonate at Ambient Temperature and at 50°C

Pilot Plant Elution with Sodium Chloride

A study of the resin-in-pulp process as applied to the recovery of uranium, by carbonate ion exchange, from a sample of LaSal ore and a sample of Utex ore is given in WIN-393. In this work 1.0M NaCl was used as an Eluant with excellent results.

A separate test run of Todilto, Mesa Top, and LaSal ore is reported in WIN-774. The initial eluant was 1.0M NaCl but it was found that the use of 2.0M NaCl as an eluant cleaned the resin of foulants much more readily than did 1.0M NaCl.

Column ion exchange tests were also made in which 2.0M NaCl was used as an eluant. The data are shown in Table 16. Using an ion exchange feed liquor averaging 0.95 g. U_3O_8 /l, column loadings of 4.3 lb U_3O_8 /cu ft WSR were realized. Recovery averaged 99.9 per cent. When the first column was saturated the second column was partially loaded. The loaded column was removed from the feed cycle, backwashed, and drained. Then barren eluate was fed in series through the stand-by column (partially eluted) and on through the loaded column. This procedure partially eluted the loaded column and completed the elution of the stand-by column. Only two columns were on exhaustion during elution; however, due to the short elution time, three columns were on exhaustion 70 per cent of the time and excellent recovery was obtained. Several cycles were run at each barren eluate volume of 172, 150, 103, 52, 41, and 33 gallons. Final eluate assays were satisfactory in all instances with the possible exception of that at the end of the 33-gallon test volume. Eluate to precipitation increased from 17.7 to 72.5 g U_3O_8 /l and final eluates ranged from 0.075 to 0.176 g U_3O_8 /l. Sodium chloride consumption was reduced to less than two pounds per pound of U_3O_8 eluted.

A series of samples was taken during elution of the second column in series to determine the U_3O_8 and chloride gradient in the eluate. Fifty-two gallons of barren eluate was used for the elution. Figure 13 is a graph showing U_3O_8 and Cl contents of the column effluent during this elution scheme.

Table 16
Column Ion Exchange Data
Alkaline Leach - CCD - Column IX Pilot Plant
Holly Blend Ore

Resin: IRA 400, 5 cu ft WSR/column
Eluant: 2 M NaCl

<u>Run Time, days</u> <u>Cycles</u>	2	9	4	2	8	2	4
	3.13	11.4	5.6	2.8	11.8	4.5	10.5
<u>Feed</u>							
gpm	4.3	3.0	3.0	3.0	3.0	4.0	4.0
g U ₃ O ₈ /l	0.942	0.875	0.894	0.946	0.882	0.933	1.05
g V ₂ O ₅ /l	0.018	0.013	0.014	0.015	0.013	0.015	0.13
g SO ₄ /l	1.77	1.50	1.50	1.59	1.51	1.70	1.82
<u>Tails, g/l</u>							
U ₃ O ₈	0.001	0.001	0.001	nil	0.001	0.001	0.0015
V ₂ O ₅	0.016	0.010	0.009	0.007	0.013	0.013	0.010
Na ₂ CO ₃	4.02	3.59	3.50	3.60	4.41	4.73	5.50
NaHCO ₃	2.39	2.17	1.83	1.97	2.24	2.41	2.30
U ₃ O ₈ recovery, %	99.9	99.9	99.9	99.9	99.9	99.9	99.9
Changeover time, hr	15.3	19.0	17.1	17.3	16.2	10.6	9.1
Calculated loading, lb U ₃ O ₈ /cu ft WSR	4.64	5.75	4.48	4.58	4.31	4.02	3.35
<u>Elution</u>							
<u>Pregnant eluate to precipitation</u>							
Gallons	101	172	150	103	52	41	33
g U ₃ O ₈ /l	26.38	17.66	17.27	23.95	45.14	56.80	72.53
lb U ₃ O ₈	22.23	25.49	21.62	20.59	19.59	19.43	19.97
<u>Final Eluate</u>							
g U ₃ O ₈ /l	0.120	0.075	0.034	0.042	0.061	0.048	0.176
NaCl, lb/lb U ₃ O ₈	4.4	6.6	6.8	4.9	2.6	2.1	1.6

Figure 13

U_3O_8 and Cl Content in Column Effluent
Series Elution, 52 Gallons Eluant
Holly Uranium Company Blend

Elution of Residual Uranium with Carbonate-Bicarbonate Solutions

A cursory experiment was performed in order to determine whether a carbonate system could be used to elute the residual uranium which was found to resist the standard elution procedures of chloride and nitrate. Three columns of resin were loaded with a uranium solution known to be low enough in total uncomplexed CO_2 to produce residual uranium. After elution of the uranyl tricarbonate with concentrated chloride, the three columns were eluted with the various carbonate-bicarbonate solutions as indicated in Table 17. This was followed by an elution with three per cent HNO_3 to remove the remaining uranium, and the per cent uranium removed by each eluant was calculated. These data also appear in Table 17.

Table 17

Efficiency of Residual Uranium Elution With Carbonate and Bicarbonate

<u>Column</u>	<u>Eluant</u>	<u>Total Residual Uranium Mg</u>	<u>Eluted with Carbonates Mg</u>	<u>Per Cent</u>
1	0.0500M $\text{CO}_3^{=}$ 0.467M HCO_3^-	117	112	96
2	0.015M $\text{CO}_3^{=}$ 0.471M HCO_3^-	125	68	55
3	0.501M $\text{CO}_3^{=}$ 0 HCO_3^-	139	34	24

The above data suggest the possibility of eluting both the adsorbed uranium and the residual uranium with a single chloride or nitrate eluate containing carbonate and/or bicarbonate.

EXHAUSTION FROM AMMONIUM CARBONATE SOLUTIONS

Ammonium carbonate has been considered several times in the past as a lixiviant for uranium in ores^{6,7}. The difficulties encountered in leaching ores containing vanadium as well as the problems of reagent recovery have weighed against its use. Hence, only a cursory examination of the variables involved in the ion exchange of solutions obtained by ammonium carbonate leaching was made.

Comparison of Ammonium Carbonate with Sodium Carbonate

In these tests, as in the sodium carbonate tests, four levels of carbonate and bicarbonate concentration (0.5, 0.2, 0.1, and 0.0M) were investigated. The resin used was Amberlite XE-123 in the carbonate form, and the solution to resin ratio was six to one. The tests were conducted by contacting batchwise 10.1 ml of resin with 60 ml of solution in four-ounce bottles for 15 minutes on rolls. Prior to contact with resin, all solutions were 0.035 molar in sodium uranyl tricarbonate (0.97 gram U_3O_8 per liter).

A more rigorous investigation would have required the use of ammonium (rather than sodium) uranyl tricarbonate as the source of uranium. However, in the tests reported here, the use of sodium salt was not expected to appreciably affect the results since the sodium concentration was only 0.014 molar. The only test in which a significant error might occur would be that in which neither ammonium carbonate nor bicarbonate is present in the solution.

The test results are presented in Table 18. This tabulation clearly shows the adverse effect of high concentrations of either ammonium carbonate or ammonium bicarbonate on uranium loading. Similar effects also occur with sodium carbonate and bicarbonate systems, as illustrated in Table 19. A comparison of Tables 18 and 19 immediately reveals the improved uranium loadings obtained through the use of ammonium salts.

Table 18

Uranium Concentrations (grams U_3O_8 per liter) in Ammonium
Carbonate Solutions

<u>After 15 Minute Contact with XE-123 in the Carbonate Form</u>				
<u>$(NH_4)_2CO_3$</u>	<u>0.5M</u>	<u>0.2M</u>	<u>0.1M</u>	<u>0.0M</u>
NH_4HCO_3				
0.5M	0.45	0.28	0.17	0.079
0.2M	0.15	0.024	0.0082	0.0018
0.1M	0.075	0.0074	0.0023	0.0005
0.0M	0.050	0.0028	0.0007	0.22

Table 19

Uranium Concentrations (grams U_3O_8 per liter) in Sodium
Carbonate Solutions

After 15 Minute Contact with XE-123 in the Carbonate Form

	<u>Na_2CO_3</u>	<u>0.5M</u>	<u>0.2M</u>	<u>0.1M</u>	<u>0.0M</u>
$NaHCO_3$					
0.5M		-	-	-	-
0.2M		-	0.035	0.013	0.0041
0.1M		-	0.016	0.0056	0.0014
0.0M		-	0.0081	0.015	0.22

Effect of Heating

The effect of temperature on uranium loadings from ammonium carbonate liquors was also investigated. A solution containing 0.99 gram U_3O_8 per liter, (added as sodium uranyl tri-carbonate), 0.47M $(NH_4)_2CO_3$, and 0.35M NH_4HCO_3 was prepared. Aliquots were heated to different temperatures and immediately contacted with resin for 15 minutes at a solution to resin ratio of 6 to 1. Other aliquots were heated and allowed to cool prior to contact with resin. In both cases, as shown in Table 20, some benefit was realized by heating. Solution analyses after heating and cooling and prior to resin contact are presented in Table 21. These analyses indicate a slight decomposition on heating which may account for the improvement in uranium loadings.

Table 20

Uranium Concentrations (grams U₃O₈ per liter) after 15 Minute
Contact with XE-123 in the Carbonate Form

<u>Temperature</u>	<u>Heated Solution Contacted with Resin</u>	<u>Cooled Solution Contacted with Resin</u>
Ambient (Soln. not heated)	0.30	0.30
40°	0.25	0.26
50	0.25	0.26
60	0.25	0.26
70	0.23	0.27
80	0.19	0.23

Table 21

Analyses of Liquors After Heating and Cooling

<u>Solution History</u>	<u>g U₃O₈/l</u>	<u>M (NH₄)₂CO₃</u>	<u>M NH₄HCO₃</u>
Not heated	0.99	0.47	0.35
Heated to 40°C	1.02	0.42	0.38
Heated to 50°C	1.01	0.41	0.38
Heated to 60°C	0.99	0.40	0.38
Heated to 70°C	1.03	0.42	0.35
Heated to 80°C	1.04	0.38	0.34

Effect of Reagent Flashing by Boiling

Another series of tests was performed in which the ammonium carbonate liquor was heated to boiling for different time intervals and allowed to cool. Since on heating, the evolution of ammonia and carbon dioxide obscures the boiling point, boiling was considered to be vigorous ebullition. The cooled solutions were diluted to their former volumes and contacted with resin for 15 minutes at a solution to resin ratio of 6 to 1. The stock solution used contained 0.96 gram U₃O₈ per liter, (added as sodium uranyl tricarboxylate), 0.52M (NH₄)₂CO₃, and 0.44M NH₄HCO₃. The solution analyses at the end of each

test are presented in Table 22 which shows that only a few minutes of boiling are required to reduce the carbonate and bicarbonate concentrations to such low values that extremely efficient uranium loadings are possible.

Table 22

Solution Analyses of Boiled Liquors After 15 Minute Contact
with XE-123 in Carbonate Form

<u>Solution History</u>	<u>g U₃O₈/l</u>	<u>M (NH₄)₂CO₃</u>	<u>M NH₄HCO₃</u>	<u>M OH⁻</u>
Not heated	0.45	0.48	0.49	nil
Heated to boiling	0.12	0.59	nil	0.04
Boiled for 3 min.	0.0016	0.14	nil	0.28
Boiled for 6 min.	0.0009	0.081	nil	0.21
Boiled for 9 min.	0.009	0.072	nil	0.07

These results suggest that a fruitful field of investigation concerning ores that are amenable to ammonium carbonate leaching would be to recover the reagents by flashing and follow by either RIP or column ion exchange.

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A P P E N D I X

APPENDIX

Studies of Residual Uranium in Carbonate Ion Exchange

Hydrolysis of Sodium Carbonate

An experiment was performed in which several samples of resin, after being contacted with 1M NaCl, were washed with dilute chloride solutions up to 0.1M and separated by centrifugation. The total chloride associated with each resin was then measured and found to be identical with that for a resin sample washed free of adhering chloride with water. The effect of a water wash on carbonate loaded resin was demonstrated by loading four columns from a carbonate solution and washing with solutions varying from water to 0.1M carbonate. The columns were then centrifuged and eluted and the carbonate determined as a function of the resin weight. The data are shown in Table 23.

Table 23

Hydrolysis Upon Washing Carbonate-Loaded IRA-400

<u>Washing Solution</u> <u>M CO₃⁼</u>	<u>Resin</u> <u>CO₃⁼ Capacity, meq./g</u>
0.000	3.04
0.009	3.25
0.047	3.35
0.095	3.38

It is apparent that hydrolysis does occur to a certain extent with a water wash since previous experiments with chloride had indicated that saturation loadings are independent of the wash solution concentration in the range used.

Hydrolysis of Sodium Uranyl Tricarbonate

Two carbonate-bicarbonate ratios were investigated. In the first, a stock solution was prepared in which the carbonate to bicarbonate ratio was 7.65. Aliquots of this solution were then used to prepare the loading solutions. In all cases the uranium concentration was 0.01M. Six five-milliliter columns of resin were then loaded with these solution, and eluted with 1M NaCl.

The chloride was then eluted with 1M NaNO₃, and in this way both uranium and chloride capacities were determined for each resin sample. It was observed that the first two columns in this series, after elution with chloride and nitrate, were still strongly colored, indicating the presence of uranium. A subsequent wash with very dilute nitric acid removed the uranium and caused considerable gassing, indicating the presence of carbonate on the resin. When this residual uranium was added to the uranium eluted with chloride, the total uranium capacities were found to exceed the chloride capacities observed. The results of this test are presented in Table 24A.

In a third series of tests, the carbonate to bicarbonate ratio was approximately 0.13. The same procedure as described above was employed. However, all six columns were eluted with dilute nitric acid after chloride and nitrate elution. The results of this test appear in Table 24B. From these data it is apparent that residual uranium has been observed to occur most strongly with resins exhausted with solutions containing low concentrations of total free carbonate. It was suspected that the residual uranium was due to a solid species, as uranium is known to precipitate from solutions low in free carbonate. McClaine⁸ discusses the possibility of precipitating uranium as an uranate by hydrolysis.

In another series of tests, nine columns were loaded with five ml of wet settled Amberlite IRA-400 resin in the nitrate form which has been preconditioned with two uranium carbonate loading cycles. The columns were loaded with nine solutions of three different carbonate to bicarbonate ratios, with three different concentration levels in each. The effluent solutions were sampled at four-bed-volume intervals in order to determine loading curves.

The loaded resin columns were centrifuged and eluted with 1M NaCl. The resin was again eluted with 1M NaNO₃ to determine the total chloride capacity. Each resin column was then washed with dilute nitric acid to check on the completeness of elution. Analyses of the various eluates give the data shown

Table 24A

Analysis of Uranium Carbonate-Loaded IRA-400 Resin

High Carbonate to Bicarbonate Ratio

<u>Loading Solutions</u>			<u>Resin</u>					
<u>M UO₂⁺⁺</u>	<u>M Free CO₃⁼</u>	<u>M Free HCO₃⁻</u>	<u>Meq. UTC^{1/}</u>	<u>Meq. Free CO₃⁼</u>	<u>Meq. Free HCO₃⁻</u>	<u>Total^{2/}</u>	<u>Meq. Chloride</u>	<u>Residual U^{3/} As Meq. UTC</u>
0.0099	0.0106	0.0001	5.05	0.68	0.02	5.75	5.56	3.16
0.0100	0.0209	0.0026	5.75	0.64	0.20	6.59	6.84	1.40
0.0102	0.0409	0.0062	6.21	1.05	0.42	7.78	6.45	-
0.0107	0.0596	0.0087	6.16	0.72	0.24	7.12	6.50	-
0.0107	0.0809	0.0087	6.32	0.72	0.22	7.26	6.80	-
0.0101	0.100	0.0124	6.17	0.68	0.22	7.07	6.80	-

24B

High Carbonate to Carbonate Ratio

<u>Loading Solutions</u>			<u>Resin</u>					
<u>M UO₂⁺⁺</u>	<u>M Free CO₃⁼</u>	<u>M Free HCO₃⁻</u>	<u>Meq. UTC^{1/}</u>	<u>Meq. Free CO₃⁼</u>	<u>Meq. Free HCO₃⁻</u>	<u>Total^{2/}</u>	<u>Meq. Chloride</u>	<u>Residual U^{3/} As Meq. UTC</u>
0.0103	0.0041	0.0091	5.37	0.40	0.40	6.17	6.66	3.40
0.0102	0.0035	0.0239	5.75	0.36	0.32	6.43	6.14	1.86
0.0102	0.0070	0.0437	6.20	0.48	0.22	6.90	6.54	0.71
0.0099	0.0079	0.0687	6.28	0.44	0.22	6.94	6.62	0.32
0.0102	0.0111	0.0863	6.00	0.44	0.48	6.92	6.66	0.24
0.0102	0.0132	0.1070	6.12	0.44	0.60	7.16	6.62	0.21

1/ Uranyl tricarbonat complex, UO₂(CO₃)₃⁻⁴

2/ Equals meq. eluted by chloride

3/ Eluted with dilute HNO₃

in Table 25. It can be seen, on the following page, that in two instances a considerable amount of uranium remained on the resin after chloride elution and it required an acid eluant for removal. The uranium remaining after chloride elution, which is termed residual uranium is that caused by hydrolysis.

From the data in Table 25, page A-5, it appears that the occurrence of the residual uranium depends inversely on the total concentration of uncomplexed CO_2 . It appears to be independent of the carbonate to bicarbonate ratio.

It is also noteworthy to observe in Figure 14 on page A-6 that the effluent solutions from Columns 3 and 9, those found to contain the most residual uranium, never reached the uranium concentration of the influent solutions, despite the fact that 80 bed volumes were passed over Column 3, and 88 bed volumes were passed over Column 9. Instead, these solutions attained a concentration below that of the influent solution and remained relatively level, indicating the continued deposition of uranium.

An experiment was performed in which three five-milliliter columns of preconditioned IRA-400 resin were loaded with concentrated chloride, washed with dilute chloride, centrifuged, and eluted with nitrate. In this way, the chloride capacity, or total charge, of each column was determined. Each column was subsequently loaded with uranium in such a way that residual uranium would be deposited on the resin. The chloride capacity was now determined while residual uranium was present. A sample of resin was then submitted for carbon dioxide and uranium analysis. These data are presented in Table 26 on page A-7. From this table, it appears that the mole ratio of carbonate to uranium is slightly greater than one and that the capacity of the resin is decreased while residual uranium is present.

Table 25
Effect of Carbonate and Bicarbonate on Resin Capacities
and Residual Uranium

Loading Solutions			
Test No.	M UO_2^{++}	M Free $\text{CO}_3^{=}$	M Free HCO_3^-
1	0.0104	0.463	0.137
2	0.0103	0.100	0.013
3	0.0104	0.012	0.001
4	0.0106	0.515	0.487
5	0.0105	0.105	0.099
6	0.0104	0.011	0.012
7	0.0105	0.061	0.492
8	0.0104	0.008	0.120
9	0.0103	0.001	0.020

Resin Loading, Meq.						
Test No.	UTC ^{1/}	Free $\text{CO}_3^{=}$	Free HCO_3^-	Total ^{2/}	Chloride	Residual ^{3/} U
1	6.48	0.43	1.61	8.52	8.10	0.15
2	7.85	0	0.76	8.61	7.95	0.21
3	6.56	0.39	0.28	7.23	6.93	3.31
4	2.22	0.17	6.06	8.45	7.76	0.07
5	7.23	0	1.34	8.57	7.60	0.19
6	7.42	0	0.72	8.14	7.48	0.54
7	3.63	0.59	4.32	8.54	8.00	0.14
8	7.30	0.47	0.66	8.43	7.85	0.28
9	6.73	0.39	0.48	7.60	7.20	2.59

^{1/} Uranyl tricarboxylate complex, $\text{UO}_2(\text{CO}_3)_3^{-4}$

^{2/} Equals meq. eluted by chloride

^{3/} Eluted with dilute HNO_3 , calculated as UTC

Figure 14

Loading of Uranium on IRA-400 Resin from Several Carbonate
and Bicarbonate Concentrations

Table 26

Carbonate to Uranium Ratio for Residual Uranium

Chloride Capacity	Column 1	Column 2	Column 3
Before Uranium Loading	8.2	8.0	7.8
After* Uranium Loading	7.4	7.2	7.0
UO ₂ ⁺⁺ present, millimoles	0.500	0.450	0.364
CO ₃ ⁼ present, millimoles	0.514	0.525	0.507
Mole Ratio CO ₃ ⁼ /UO ₂ ⁺⁺	1.03	1.17	1.39

* After loading with uranium but with residual uranium still on resin