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Effect of Ion Concentrations on Uranium Absorption From Sodium Carbonate Solutions

UNITED STATES DEPARTMENT OF THE INTERIOR

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By D. E. Traut, N. M. T. El Hazek, G. R. Palmer,
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UNITED STATES DEPARTMENT OF THE INTERIOR
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EFFECT OF ION CONCENTRATIONS ON URANIUM ABSORPTION FROM SODIUM CARBONATE SOLUTIONS

by

D. E. Traut,[1] N. M. T. El Hazek,[2] G. R. Palmer,[3] and I. L. Nichols[3]

ABSTRACT

The effect of various ion concentrations on uranium absorption from a sodium carbonate solution by a strong-base, anion resin was investigated by the Bureau of Mines in support of its objective to help assure an adequate uranium supply for future needs. The studies were conducted to improve the recovery of uranium from in situ leach solutions by ion exchange. The effects of carbonate, bicarbonate, chloride, and sulfate ions were examined. Relatively low (less than 5 g/l) concentrations of chloride, sulfate, and bicarbonate were found to be detrimental to the absorption of uranium. High (greater than 10 g/l) carbonate concentrations also adversely affected the uranium absorption. In addition, the effect of initial resin form was investigated in tests of the chloride, carbonate, and bicarbonate forms; resin form was shown to have no effect on the absorption of uranium.

INTRODUCTION

Because the demand for uranium is increasing and resources are limited, technology for treating low-grade and marginal ores must be developed. Techniques such as in situ leaching are being investigated in an effort to develop improved methods of recovering uranium from small, relatively deep deposits. Most in situ leaching operations use alkaline leach solutions and produce pregnant liquors containing 50 to 200 parts per million U_3O_8. Because of the low uranium content, the pregnant liquors are generally treated with an anion exchange resin to recover the uranium. The anion content of the pregnant solution can affect the efficiency of the uranium ion exchange. To determine this anion effect, the Bureau of Mines investigated the influence of carbonate, bicarbonate, sulfate, and chloride ions on the ion-exchange absorption of uranium. Also investigated was the effect of the initial resin form on the

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uranium absorption. The studies were performed to aid in achieving the Bureau's goal of assuring an adequate supply of uranium for future national economic and strategic needs.

RAW MATERIALS AND PROCEDURE

Solution Description

The synthetic feed solutions used for these studies were prepared from ammonium diuranate or sodium uranyl tricarbonate. The required carbonate, bicarbonate, chloride, or sulfate was added as a sodium salt using analytical-grade laboratory reagents. Table 1 summarizes the composition of the different solutions used in each of the experiments.

TABLE 1. - Composition of the different synthetic solutions used in equilibrium experiments

Experiment	Uranium product used	Composition, g/l					pH
		U_3O_8	Na_2CO_3	$NaHCO_3$	Cl	SO_4	
1............	Ammonium diuranate	0.540	4.22	1.43	0.0	0.0	10.28
2............	.....do..........	.570	9.81	4.36	.0	.0	10.05
3............	.....do..........	.580	20.00	8.09	.0	.0	10.05
4............	.....do..........	.531	3.15	.0	.0	.0	11.00
5............	.....do..........	.480	9.11	.0	.0	.0	11.01
6............	.....do..........	.490	18.10	.0	.0	.0	10.88
7............	Sodium uranyl tricarbonate.	.550	.73	.0	.0	.0	10.21
8............	.....do..........	.520	.65	.0	.6	.0	10.05
9............	.....do..........	.508	.63	.0	1.81	.0	9.95
10............	.....do..........	.508	.56	.0	2.92	.0	9.55
11............	.....do..........	.503	.67	.0	5.92	.0	9.45
12............	.....do..........	.501	.63	.0	.0	.66	10.15
13............	.....do..........	.512	.64	.0	.0	2.08	9.02
14............	.....do..........	.490	.58	.0	.0	3.37	9.15
15............	.....do..........	.506	.56	.0	.0	13.50	9.45
16............	Ammonium diuranate	.531	3.15	.0	.0	.0	11.00
17............	.....do..........	.531	3.15	.0	.0	.0	11.00

Resin Description

The ion-exchange resin used was a coarse-bead (minus 16 plus 20 U.S. Standard Sieve), strong-base type (Rohm and Haas Amberlite IRA-430[4]). Two resin batches, designated A and B (table 2), were used; each batch was conditioned before use by contacting first with Na_2CO_3 then with NaCl for three consecutive cycles. Most of the experiments were performed on the chloride form of resin; however, two experiments were carried out on resin converted to the carbonate and bicarbonate forms using 1 liter of 1-M Na_2CO_3 and 1 liter of 1-M $NaHCO_3$ solution, respectively, for each 10 milliliters of wet settled resin (WSR).

[4]Reference to trade names does not imply endorsement by the Bureau of Mines.

TABLE 2. - Initial condition of Amberlite IRA-430 resin

Resin batch	U_3O_8, g/l	Cl, g/l	Weight, g/10 ml WSR[1]	Experiment used
A..........	0.017	50.26	3.49	2, 4-5
B..........	.006	45.22	3.23	1, 3, 6-17

[1]Dried for 40 hours at 110° C.

Experimental Procedure

Equilibration between resin and solution was performed in 1-liter plastic bottles which were agitated for the specified time using a mechanical shaker. Unless otherwise stated, the aqueous-to-resin ratio was 60:1. The 10-milliliter portions of WSR were suction-dried on a Buchner funnel before being contacted with 600 milliliters of solution in the equilibrium bottles. Preliminary kinetic studies indicated that essentially complete equilibrium was achieved in 4 hours.

The equilibrium curves or distribution isotherms were determined by a crosscurrent, pyramidal batch-contact method. This method, shown in figure 1, uses a resin-solution-transfer technique similar to Treybal's[5] countercurrent contact technique for liquid-liquid batch shake-out experiments. In this study, only the right-hand side of the pyramid was used (stages 1, 3, 6, 10, 15, etc.). In these modified pyramid loading experiments, a single, 10-milliliter WSR portion was loaded by sequentially contacting with new,

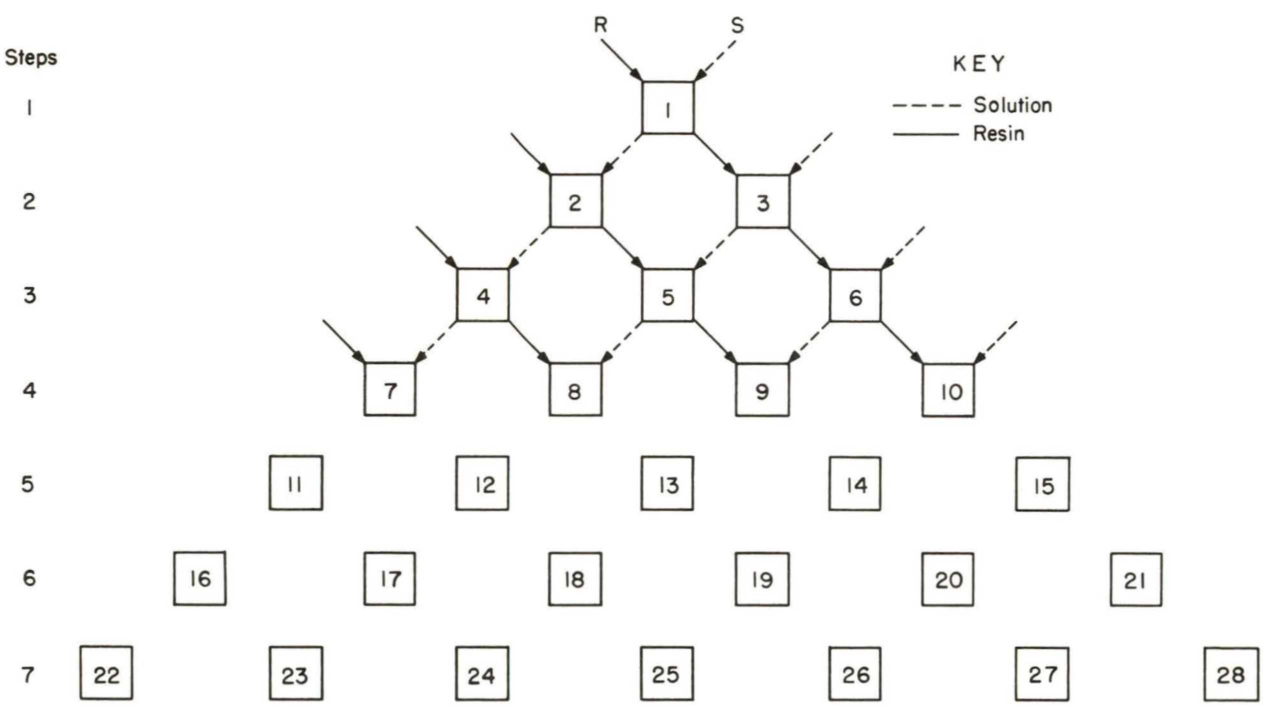

FIGURE 1. - Contact pyramid for resin and solution to obtain an equilibrium isotherm for the system.

[5]Treybal, R. E. Liquid Extraction. McGraw-Hill Book Co. Inc., New York, 2d ed., 1963, pp. 361-368.

600-milliter portions of the feed solution. After each equilibration, resin samples were suction-dried on a Buchner funnel without washing. At the final equilibration stage, the resin samples were suction-dried and then dried for about 40 hours at 100° C. The dried samples were then weighed and prepared for analysis by complete decomposition. In the modified pyramid absorption experiment, the U_3O_8 concentration of the intermediary portions of resin in each stage was calculated from the differences in solution concentrations.

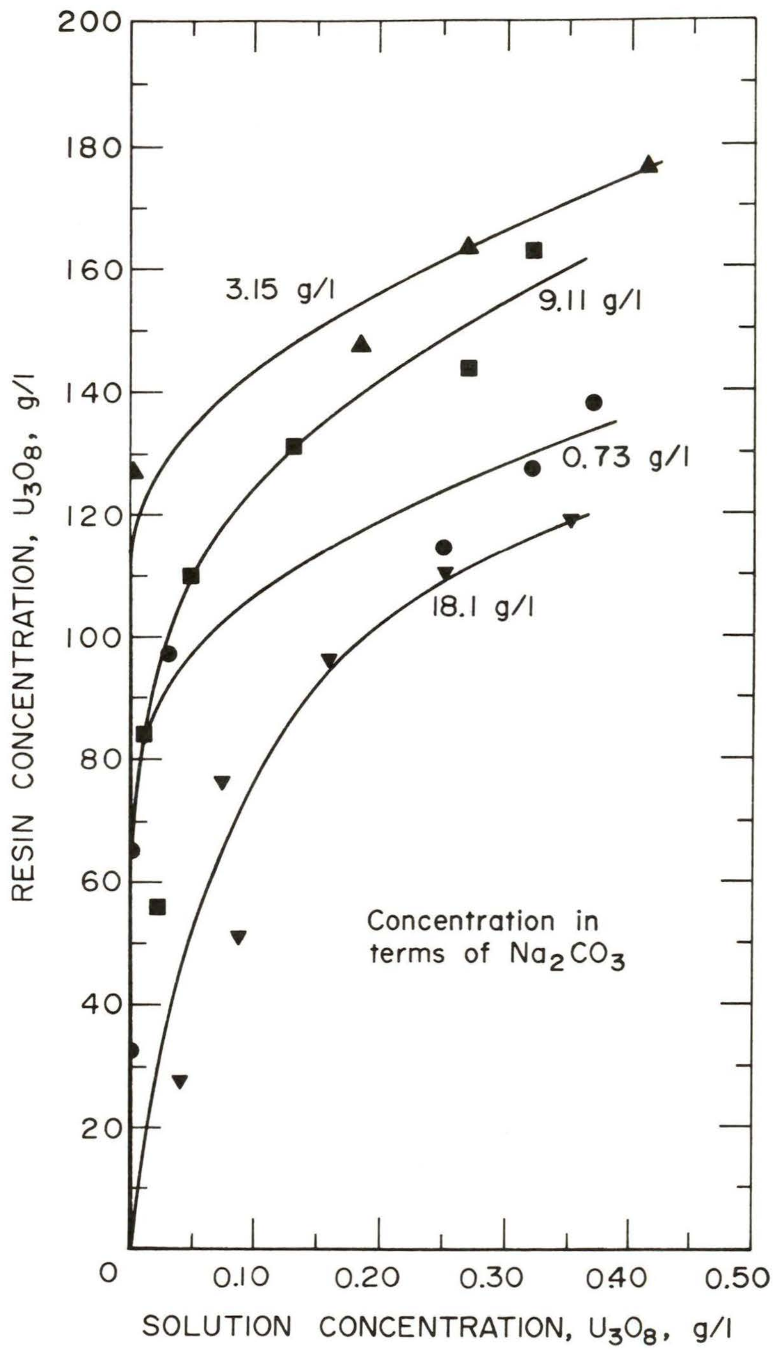

FIGURE 2. - Effect of carbonate on uranium absorption.

RESULTS AND DISCUSSION

Equilibrium experiments were run to investigate the effects of solution composition and resin form on the equilibrium profiles and on the maximum loading. The theoretical resin capacity for the uranium carbonate anion is approximately 185 grams per liter of WSR. The effects of variations in solution composition studied included the following:

1. Effect of carbonate concentration.

2. Effect of bicarbonate concentration.

3. Effect of chloride concentration.

4. Effect of sulfate concentration.

The following resin forms were studied:

1. Chloride form.

2. Carbonate form.

3. Bicarbonate form.

The equilibrium experiments were carried out by the modified pyramid absorption technique.

Effect of Carbonate Concentration

The effect of increasing carbonate concentration upon uranium absorption is relatively small in dilute solution, according to Kaufman and Lower.[6] A series of tests was run to determine the optimum carbonate concentration for maximum uranium absorption. Table 3 presents both the analyzed solution concentration and the corresponding calculated resin loading for each stage. These results were then plotted as equilibrium curves in figure 2.

TABLE 3. - Effect of carbonate concentration

(Equilibrium U_3O_8 concentration data for experiments 4-7)

	Experiment 7		Experiment 4		Experiment 5		Experiment 6	
INITIAL SOLUTION CONCENTRATION								
U_3O_8.....g/l..	0.55		0.531		0.48		0.490	
Na_2CO_3...g/l..	0.73		3.15		9.11		18.100	
$NaHCO_3$...g/l..	0.0		0.0		0.0		0.0	
pH............	10.21		11.00		11.01		10.88	
OUTPUT CONCENTRATION, g/l U_3O_8								
	Solution	Resin	Solution	Resin	Solution	Resin	Solution	Resin
Stage 1.......	0.001	32.94	0.001	31.80	0.005	28.50	0.039	27.06
Stage 3.......	.001	65.88	.001	63.60	.022	55.98	.085	51.36
Stage 6.......	.030	97.08	.002	95.36	.010	84.18	.071	76.50
Stage 10......	.250	115.08	.002	127.08	.048	110.10	.160	96.30
Stage 15......	.320	128.88	.183	147.96	.130	131.10	.250	110.70
Stage 21......	.370	139.68	.267	163.80	.270	143.70	.350	119.70
Stage 28......	.348	151.80	.412	177.60	.315	163.20	NA	NA

NA Not available.

The data of experiment 7, in which the feed solution contained 0.73 gram per liter Na_2CO_3, indicate that, although maximum theoretical uranium absorption is approached, it is at the expense of high residual uranium concentrations in the solution compared with those of experiment 4 with 3 grams per liter Na_2CO_3. The feed solution for experiment 7 contained only slightly more carbonate than required for the uranium tricarbonate complex; that is, in experiment 7, the free carbonate concentration in solution is too low to exchange with the chloride.

The highest resin loading with the lowest effluent value was obtained at about 3 grams per liter Na_2CO_3. Increasing the Na_2CO_3 concentration to about 9 grams per liter caused a decrease in the resin loading but produced reasonable effluent values. Further increases in the Na_2CO_3 concentration to 18 grams per liter caused a severe resin-loading decrease and further degradation of the effluent values.

[6] Kaufman, D., and G. W. Lower. A summary Report of the Ion Exchange Process for the Recovery of Uranium. U.S. Atomic Energy Commission Rept. No. ACCO-68, 1954, p. 29.

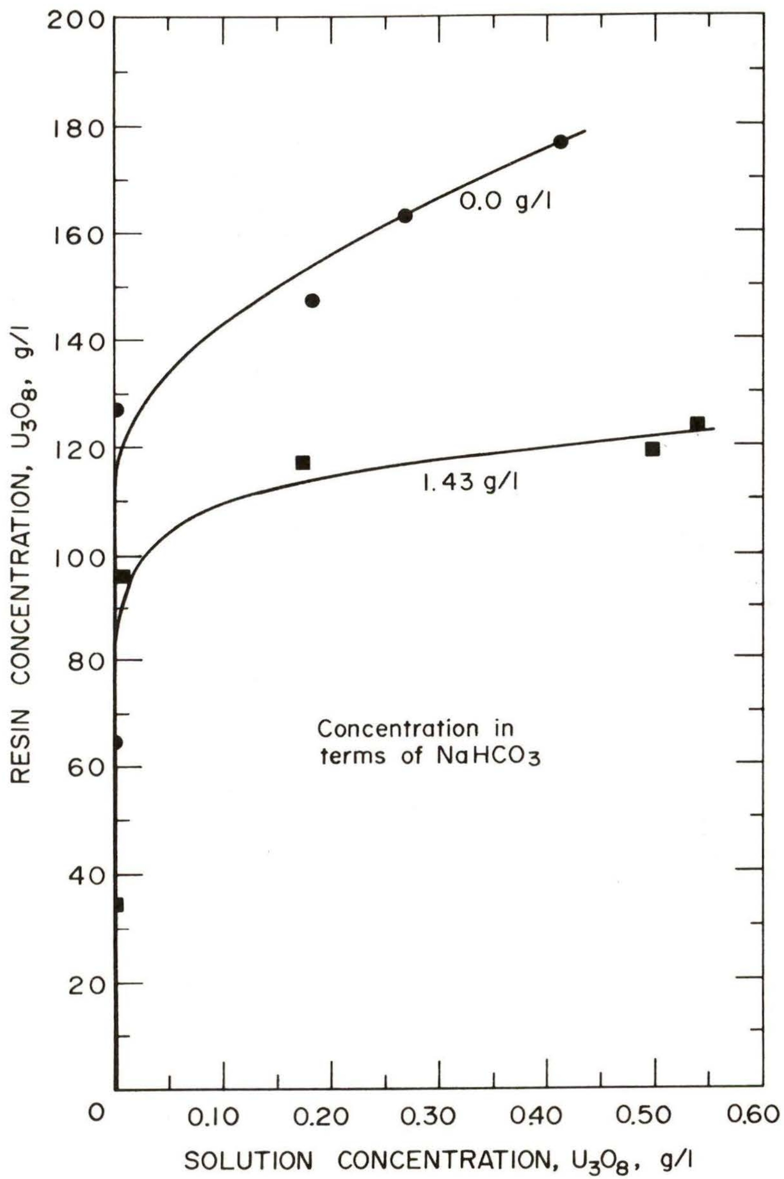

FIGURE 3. - Effect of bicarbonate on uranium absorption from 4-g/l Na_2CO_3 solution.

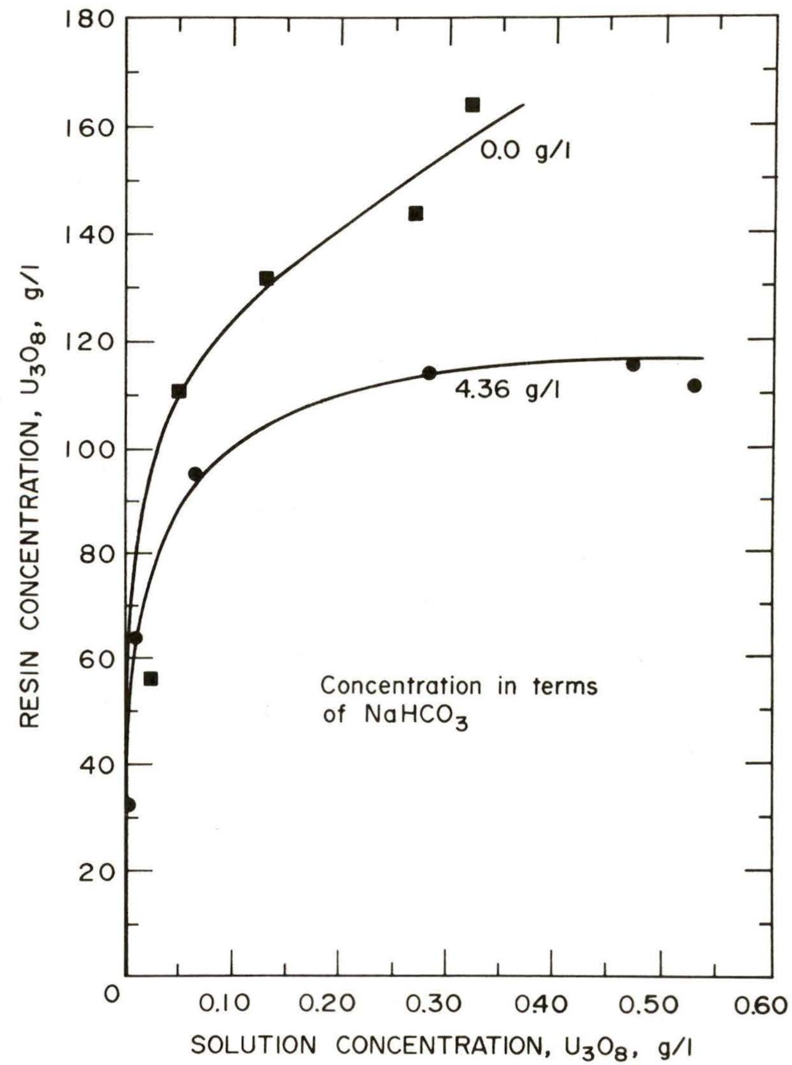

FIGURE 4. - Effect of bicarbonate on uranium absorption from 9-g/l Na_2CO_3 solution.

Effect of Bicarbonate Concentration

Merritt[7] reported that bicarbonate has an adverse effect upon uranium loading, similar to that of the bisulfate in the acid system. It was noted that uranium loading may decrease by as much as 50 to 80 percent when the pH is decreased from 10 to 9. At pH 9, uranium loadings of as low as 0.6 pound per cubic foot have been noted (about 10 grams of U_3O_8 per liter of resin). Decreasing the pH from 10 to 9 increases the bicarbonate concentration appreciably.

Three sets of experiments (1-6) were performed to determine the effect of bicarbonate-ion variations at carbonate concentrations ranging from about 3 to 20 grams per liter Na_2CO_3. In each set, one experiment was without bicarbonate in the solution. The uranium-, carbonate-, and bicarbonate-input solution values, along with the uranium-output solution values for each stage of contact, are shown in table 4. The sets of experiments illustrating the effect of bicarbonate are shown in figures 3-5.

Each set of experiments illustrates how bicarbonate can adversely affect the uranium absorption from the feed solution. The bicarbonate presence not only decreases the final resin loading, but increases the effluent U_3O_8 concentration in the early stages of contact.

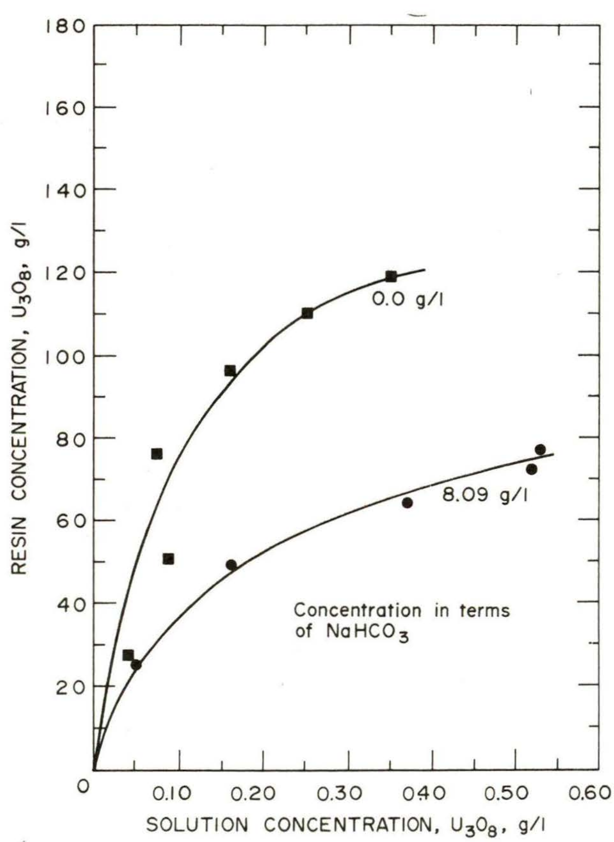

FIGURE 5. - Effect of bicarbonate on uranium absorption from 18-g/l Na_2CO_3 solution.

[7]Merritt, R. C. The Extractive Metallurgy of Uranium. Colorado School of Mines Research Institute, Golden, Colo. (under contract with the U.S. Atomic Energy Commission), 1971, pp. 151-152.

TABLE 4. - Effect of bicarbonate concentration

(Equilibrium U_3O_8 concentration data for experiments 1-6)

	Experiment 1		Experiment 4		Experiment 2		Experiment 5		Experiment 3		Experiment 6	
INITIAL SOLUTION CONCENTRATION												
U_3O_8.....g/l	0.54		0.531		0.57		0.480		0.58		0.49	
Na_2CO_3...g/l	4.22		3.15		9.81		9.11		20.00		18.10	
$NaHCO_3$...g/l	1.43		0.0		4.36		0.0		8.09		0.0	
pH..........	10.28		11.00		10.05		11.01		10.05		10.88	
OUTPUT CONCENTRATION, g/l U_3O_8												
	Solution	Resin	Solution	Resin	Solution	Resin	Solution	Resin	Solution	Resin	Solution	Resin
Stage 1.....	0.001	33.34	0.001	31.80	0.005	32.80	0.005	28.50	0.048	25.13	0.039	27.06
Stage 3.....	.002	64.78	.001	63.60	.011	63.57	.022	55.96	.160	49.42	.085	51.36
Stage 6.....	.006	95.04	.002	95.36	.067	94.18	.010	84.18	.370	64.24	.071	76.50
Stage 10....	.173	117.31	.002	127.08	.280	113.85	.048	110.10	.520	72.67	.160	96.30
Stage 15....	.499	119.97	.183	147.96	.470	115.88	.130	131.10	.530	77.00	.250	110.70
Stage 21....	.540	124.20	.267	163.80	.530	111.28	.270	143.70	-	-	.350	119.10
Stage 28....	-	-	.420	170.46	-	-	.320	153.30	-	-	-	-

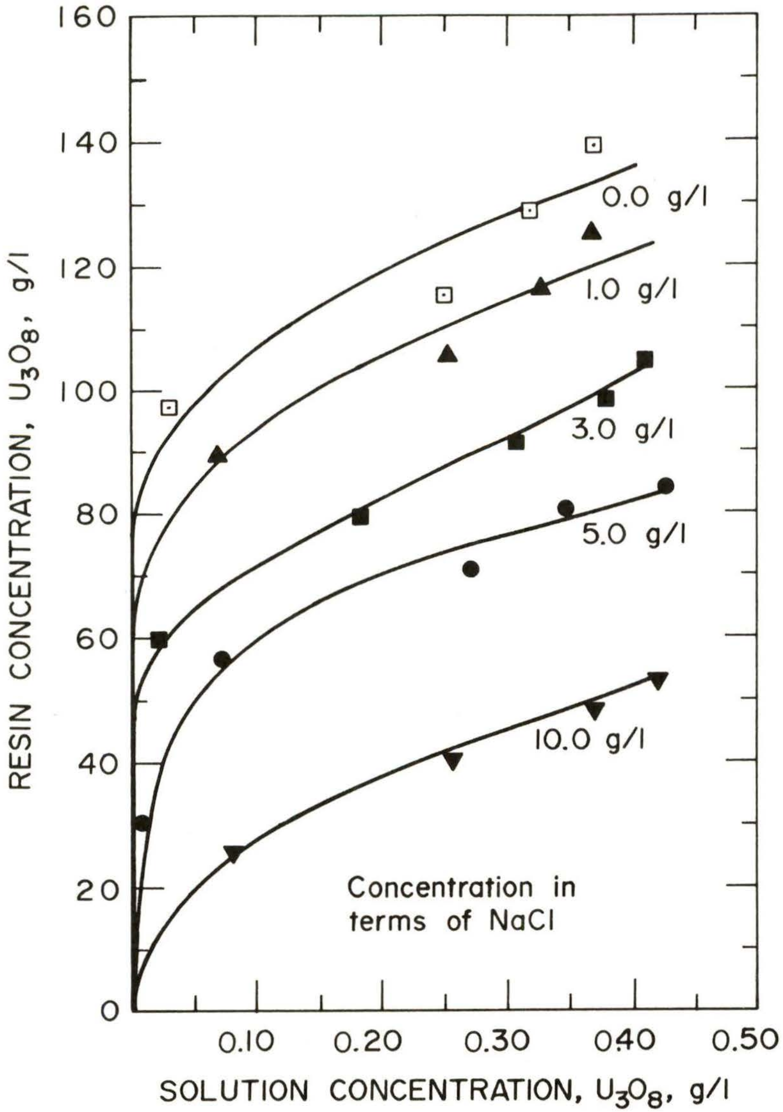

FIGURE 6. - Effect of chloride on uranium absorption.

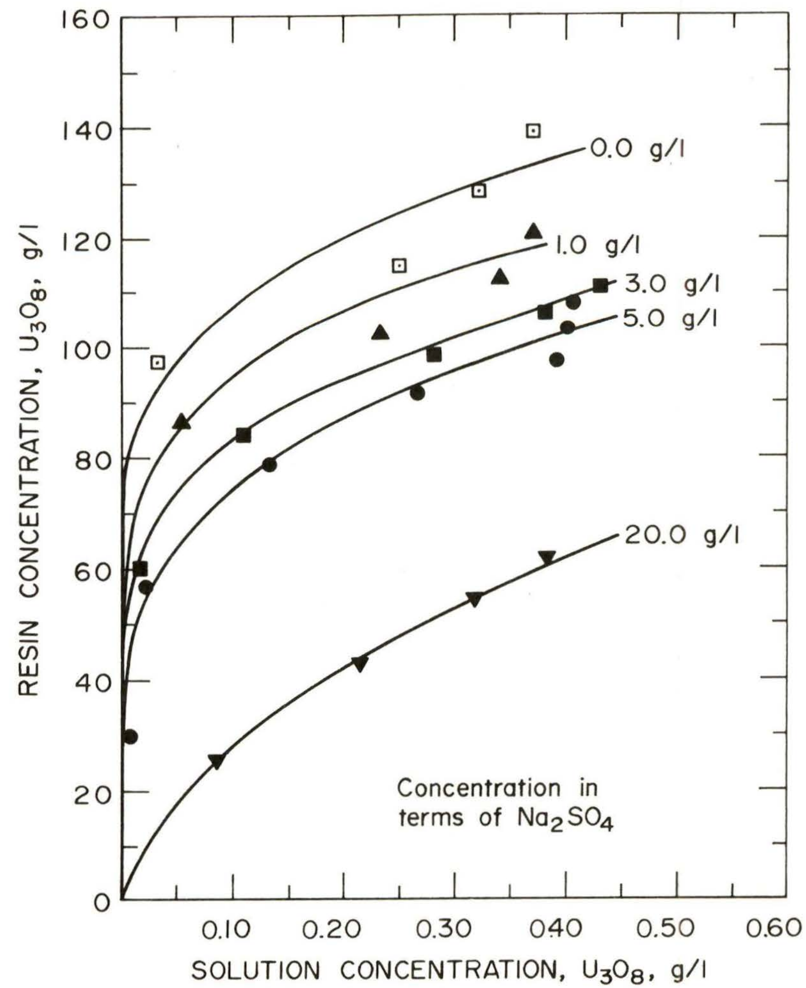

FIGURE 7. - Effect of sulfate on uranium absorption.

Effect of Chloride Concentration

When NaCl or NH_4Cl is used as an eluant, the resin sites are left in the chloride form. During subsequent absorption operations, this chloride is exchanged from the resin into the effluent. Because nearly all of the effluent is recirculated to the leaching step in the in situ operation, the chloride ions will build up in the recirculating solution. The effect of this increasing chloride concentration upon the uranium absorption was studied.

Four absorption equilibrium experiments were carried out using batch B resin and solutions of comparable uranium and carbonate concentrations. The chloride concentration varied from 0 to 10 grams per liter NaCl. The data presented in table 5 were used to plot the corresponding equilibrium curves (fig. 6). The results show that a chloride content as low as 1.0 gram per liter NaCl decreases resin loading by about 15 percent. Increasing the sodium chloride to 10 grams per liter decreased the maximum resin-loading capacity to about 60 grams per liter U_3O_8.

Effect of Sulfate Concentration

Most uranium ores contain sulfates and/or sulfides that are carbonate soluble and could, therefore, be present in the leach liquors. Four absorption equilibrium experiments were performed using batch B resin and solutions with sulfate concentrations varying between 0 and 20 grams per liter Na_2SO_4. The solution analysis was used to calculate the equilibrium resin loadings (table 6); the results then were used to plot the corresponding equilibrium curves shown in figure 7.

From the data, it is evident that sulfate in the pregnant carbonate solution is detrimental to the resin saturation capacity for uranium. Sulfate acts as a competitor for the ion-exchange resin sites.

Effect of Initial Resin Form

To overcome the buildup of chloride in the absorption effluent liquors, which are recycled to the in situ well field, it may be desirable to elute the loaded resin with a carbonate and/or bicarbonate solution; in this case, the resin sites during the subsequent absorption cycle would be occupied by carbonate and/or bicarbonate ions. In light of the previous discussions, it might be expected that the $CO_3^=$ ions would be beneficial to absorption, while the HCO_3 ions could be deleterious to the absorption. To determine if resins in the carbonate and/or bicarbonate form affect the absorption of uranium, two resin samples of batch B were converted to the $CO_3^=$ and HCO_3^- forms using 1-$\underline{M}$ Na_2CO_3 and 1-$\underline{M}$ $NaHCO_3$ solutions, respectively. The results from the absorption equilibrium experiments using these resin samples are reported in table 7, together with results from tests using the chloride resin form. These results have been used also to calculate the equilibrium resin loadings (table 8) which then were used to plot the corresponding equilibrium curves (fig. 8). The results show almost no perceptible differences in uranium loading characteristics or the final resin saturation capacity.

TABLE 5. - Effect of chloride concentration

(Equilibrium U_3O_8 concentration data for experiments 7-11)

	Experiment 7		Experiment 8		Experiment 9		Experiment 10		Experiment 11	
	INITIAL SOLUTION CONCENTRATION									
U_3O_8.....g/l..	0.550		0.520		0.508		0.508		0.503	
Na_2CO_3...g/l..	0.73		0.65		0.63		0.56		0.67	
NaCl.....g/l..	0.00		1.00		3.00		5.00		10.00	
pH...........	10.21		10.05		9.95		9.55		9.45	
	OUTPUT CONCENTRATION, g/l U_3O_8									
	Solution	Resin	Solution	Resin	Solution	Resin	Solution	Resin	Solution	Resin
Stage 1.......	0.001	32.94	0.001	31.14	0.002	30.36	0.007	30.06	0.081	25.32
Stage 3.......	.001	65.88	.002	62.22	.019	59.70	.073	56.16	.255	40.20
Stage 6.......	.030	97.08	.066	89.46	.181	79.32	.240	70.44	.370	48.18
Stage 10......	.250	115.08	.254	105.42	.309	91.26	.348	80.04	.422	53.04
Stage 15......	.320	128.88	.330	116.82	.380	98.94	.430	84.72	-	-
Stage 21......	.370	139.68	.370	125.82	.410	104.82	-	-	-	-

TABLE 6. - Effect of sulfate concentration

(Equilibrium U_3O_8 concentration data for experiments 7, 12-15)

	Experiment 7		Experiment 12		Experiment 13		Experiment 14		Experiment 15	
	INITIAL SOLUTION CONCENTRATION									
U_3O_8.....g/l..	0.550		0.501		0.512		0.490		0.506	
Na_2CO_3...g/l..	0.73		0.630		0.64		0.58		0.56	
Na_2SO_4...g/l..	0.00		1.00		3.00		5.00		20.00	
pH...........	10.21		10.15		9.02		9.15		9.45	
	OUTPUT CONCENTRATION, g/l U_3O_8									
	Solution	Resin	Solution	Resin	Solution	Resin	Solution	Resin	Solution	Resin
Stage 1.......	0.001	32.94	0.001	30.00	0.003	30.54	0.005	29.10	0.082	25.32
Stage 3.......	.001	65.88	.006	59.70	.015	60.36	.029	56.76	.213	42.78
Stage 6.......	.030	97.08	.051	86.70	.107	84.66	.132	78.24	.316	54.06
Stage 10......	.250	115.08	.231	102.90	.280	98.56	.267	91.62	.380	61.50
Stage 15......	.320	128.88	.340	112.56	.380	106.50	.390	97.62	-	-
Stage 21......	.370	139.68	.370	120.42	.430	111.42	.400	103.02	-	-
Stage 28......	-	-	-	-	-	-	.404	108.18	-	-

TABLE 7. - Effect of initial resin form on the output solution concentrations

(Analysis of uranium, sodium carbonate, and bicarbonate in output solution of continual loading stages in equilibrium experiments 4, 16-17)

	Experiment 4		Experiment 16		Experiment 17		
INITIAL SOLUTION CONCENTRATION							
Resin form..............	Cl		CO_3		HCO_3		
U_3O_8...............g/l..	0.531		0.531		0.531		
Na_2CO_3.............g/l..	3.15		3.15		3.15		
pH.....................	11.00		11.00		11.00		
OUTPUT CONCENTRATION, g/l							
	U_3O_8	Na_2CO_3	U_3O_8	Na_2CO_3	U_3O_8	Na_2CO_3	$NaHCO_3$
Stage 1..................	0.001	2.16	0.001	3.28	0.001	2.33	1.72
Stage 3..................	.001	2.74	.001	2.91	.001	3.05	.03
Stage 6..................	.002	2.85	.002	2.84	.002	2.92	.00
Stage 10.................	.002	2.90	.003	2.94	.004	2.98	.00
Stage 15.................	.183	3.07	.161	2.94	.203	3.12	.00
Stage 21.................	.267	3.02	.238	3.03	.280	3.05	.00
Stage 28.................	.420	3.08	.427	3.05	.430	3.05	.00

TABLE 8. - Effect of initial resin form on the solution-resin equilibria

(Equilibrium U_3O_8 concentration data for experiments 4, 16-17)

	Experiment 4		Experiment 16		Experiment 17	
INITIAL SOLUTION CONCENTRATION						
Resin form.............	Cl		CO_3		HCO_3	
U_3O_8..............g/l..	0.531		0.531		0.531	
Na_2CO_3............g/l..	3.15		3.15		3.15	
pH....................	11.00		11.00		11.00	
OUTPUT CONCENTRATION, g/l U_3O_8						
	Solution	Resin	Solution	Resin	Solution	Resin
Stage 1................	0.001	31.80	0.001	31.80	0.001	31.80
Stage 3................	.001	63.60	.001	63.60	.001	63.60
Stage 6................	.002	95.34	.002	95.34	.002	95.34
Stage 10...............	.002	127.08	.003	127.02	.004	126.96
Stage 15...............	.183	147.96	.161	149.22	.203	146.64
Stage 21...............	.267	163.80	.238	166.80	.280	161.70
Stage 28...............	.420	170.46	.427	173.04	.430	167.76

Practically all the HCO_3^- ions initially on the resin in test 17 (table 7) are exchanged into the solution of stage 1; this displacement corresponds to a resin capacity of 12.5 millimoles of HCO_3^- per 10 milliliters WSR, which, in turn, compares with the manufacturer's reported maximum theoretical resin capacity of 1.25 milliequivalents per milliliter WSR. This total displacement indicates that $CO_3^=$ is a very effective eluant for the HCO_3^- at these concentrations.

According to the data in tables 7 and 8, it can be concluded that the uranyl carbonate complex can be as readily absorbed by $CO_3^=$ and bicarbonate resin forms as by the normal chloride resin form.

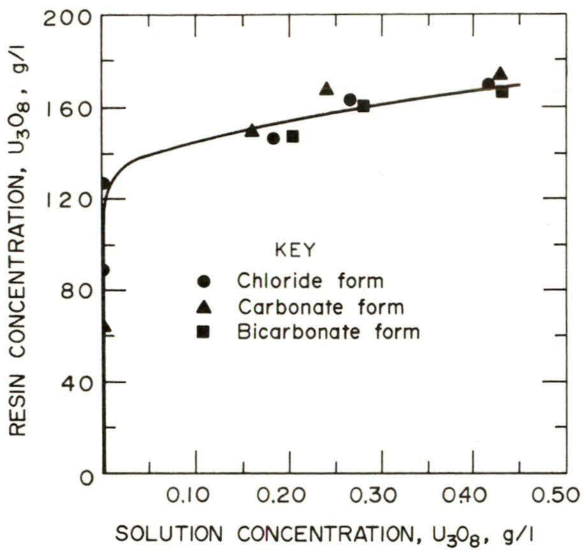

FIGURE 8. - Effect of initial resin form on uranium absorption.

CONCLUSIONS

Equilibrium profiles indicated that the optimum Na_2CO_3 concentration to obtain maximum absorption by a strong-base, anion resin was between 3 and 9 grams per liter Na_2CO_3. Equilibrium curves also indicated that bicarbonate, chloride, and sulfate were detrimental to uranium absorption from a sodium carbonate solution. The addition of 5 grams of sodium bicarbonate, chloride, or sulfate per liter of solution reduced the resin loading 50 percent.

The experiments also indicated that there was no difference in uranium absorption by chloride, carbonate, and bicarbonate initial resin forms.

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