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STUDIES IN THE CARBONATE-URANIUM SYSTEM

Part I. Investigations in the Four Component System
 $\text{UO}_3 - \text{Na}_2\text{O} - \text{CO}_2 - \text{H}_2\text{O}$

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Abstract

Numerous solubility studies in the UO_3 , Na_2O , CO_2 , H_2O system have been made. This system is characterized by a narrow region of solubility and a deep solubility well. Solutions containing greater than 320 grams of uranium per liter have been obtained. A cross cut of the important solubility regions is given by the Na_2CO_3 , UO_2CO_3 , H_2O , plane.

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INVESTIGATIONS IN THE FOUR COMPONENT SYSTEM

INTRODUCTION

The carbonate-uranium system is an important one in the field of uranium chemistry. Plant applications of this system have been made at several places including some of the Western carnotite mills. In addition, some use has been made of the uranyl carbonate complex in analytical procedures. In spite of this wide usage, only a limited amount of fundamental information is available. Consequently a program for the rather complete characterization of this system has been undertaken by this laboratory.

The present report describes investigations of the important regions of solubility in the uranium trioxide, sodium oxide, carbon dioxide, water system. A subsequent report¹, Part II of this series, deals with the effect of certain sodium salts on the solubility of sodium uranyl tricarboxylate. Other work on the identification of the ionic species in solution will be reported later.

Related studies have been presented by several workers, notably those made on sodium uranyl tricarboxylate $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ at Princeton² and at Y-12³; brief investigations with uranyl carbonate made at Battelle Memorial Institute⁴ and at Y-12⁵; and those made at Monsanto⁶ on uranium trioxide. Some of these measurements have been included below in the more extensive treatment of the system.

The experimental data can best be represented by considering a four component system defined by uranium trioxide, sodium oxide, carbon dioxide and water. Schematically, they can be presented in the form of a pyramid with one component at each vertex. Such a pyramid is shown in Figure 1. Also indicated are the positions corresponding to the important chemical combinations of the components.

The description of the phase relationships is made easier if several cross-sections are made of the pyramid and if each of the planes so formed is considered individually. The problem thus reduces to the study of several related three component systems and a summary of the results obtained in some of these systems follows.

The region of solubility in the UO_2CO_3 , Na_2CO_3 , H_2O plane is small and is characterized by a sharp eutectic between solution in contact with tricarbonates solid and that in contact with uranyl carbonate.

Measurements with excess sodium oxide also have been made. Under such conditions no appreciable solubility exists other than in the region of the above mentioned eutectic, and the solubility here is somewhat greater than in the UO_2CO_3 , Na_2CO_3 , H_2O system. Therefore, in the pyramid and on the Na_2O side of the latter system is a wall rising sharply to the water vertex. The quaternary eutectic for the complete system apparently lies between this wall and the eutectic of the UO_2CO_3 , Na_2CO_3 , H_2O system.

The solubility of UO_3 in NaHCO_3 indicates that the back wall of the depression leading to the eutectic is steep. An attempt has been made to determine the boundary which lies on the carbon dioxide side of this depression. It was thought that addition of CO_2 to carbonate-uranium

Figure 1.

The UO_3 , Na_2O , CO_2 , H_2O Pyramid.

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solutions might cause a precipitate. This has not been accomplished as yet, but high pressure work involving the solubility of UO_2CO_3 in NaHCO_3 is being considered.

The solubility of sodium uranyl tricarboxylate in NaHCO_3 has been measured at Princeton.² Further results show solubilities very similar to those in the tricarboxylate, Na_2CO_3 system and indicate a region in which the solubility is decreasing only slightly with an increase in percentage of CO_2 . How far this trend continues has yet to be determined. The UO_2CO_3 , NaHCO_3 experiments will aid in defining the boundaries in this region.

EXPERIMENTAL METHODS

Preparation of Uranyl Carbonate and Uranium Trioxide

Uranyl carbonate has been prepared by reacting a water slurry of UO_3 with CO_2 at increased temperatures and pressures. The details of the method have been described previously.⁵ The special precautions necessary for the preparation of reactive UO_3 should be noted.

Analyses of the products have given mole ratios, U/CO_3 , ranging from 1.01 to 1.03. Since this material is sufficient for experimental purposes, extended efforts to obtain greater purities have not been made.

Preparation of Sodium Uranyl Tricarboxylate

The preparation of the tricarboxylate follows the general method first proposed by Ebelman⁷ and later used by workers at Princeton, New Jersey.² A more detailed account of the procedure used at Y-12 has been described

previously.⁵

Analyses of the products give values very close to the calculated stoichiometric quantities.

Measurement of Solubility

In each of the experiments appropriate weights of the solid or solids to be studied were placed in a small plastic (polyfluorethylene) bottle or pyrex flask to which water had been added. The vessel then was stoppered tightly and placed in a mechanical agitator. All tests were run in a constant temperature room held at $26^{\circ} \pm 2^{\circ}\text{C}$.

After sufficient time had elapsed, the agitation was stopped and the solution and residue were separated by centrifuging. Samples of the solution and wet residue were submitted for analysis. No sample was agitated for less than 10 days and as a general rule the length of a run was three weeks or more. Preliminary investigation showed that this is sufficient time for equilibrium to be established in all but the most concentrated of the tr carbonate solutions. This was also verified by the ease of duplication of several results.

Analysis of Experimental Samples

Most of the analyses were performed by the ORNL Analytical Division, Y-12. High level uranium samples were analyzed by potentiometric titration with ferric sulfate. Sodium was obtained by the flame photometer method and carbonate was determined by the absorption and weighing of carbon dioxide.

The composition of the solid phase was determined by a method similar

to that of Schreinmakers.⁸ In the method used the difference between the weight of the wet residue and the sum of the analyzed quantities (after conversion of uranium to UO_2^{++}) is the weight of water on the residue. Since the density and composition of the solution in contact are known, the amounts of the solid constituents contributed by the adhering solution can be calculated and the composition of the dry residue thus obtained.

The weight percentages of the components in solution are calculated from the solution analyses and solution density. These are the values which are used in the determination of the configuration of the phase diagram.

DISCUSSION OF RESULTS

The UO_2CO_3 , Na_2CO_3 , H_2O System

Of the three component systems investigated, the one for UO_2CO_3 , Na_2CO_3 , H_2O is the most completely defined. A summary of the results is presented in Tables 1 and 2 while they appear graphically on Figure 2. Table 1 includes experiments in which the solution is in contact with UO_2CO_3 , while the solutions in Table 2 are in contact with $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$. In experiment 1030, both solids are in contact. For each test the starting solids and/or solutions are indicated. The percentages listed under the four component system are to be used in plotting in the pyramid of Figure 1. Those in the last columns for the three component system are the values which are plotted in Figure 2. The data for succeeding

Table 1
The UO_2CO_3 , Na_2CO_3 , H_2O System

UO_2CO_3 Solid Phase

Test No.	How Prepared	Solution Analysis (gram/liter)				Weight Percent Based On						
		U	Na	CO_3	d _{25°}	Four Component System				Three Component		
						UO_3	Na_2O	CO_2	H_2O	UO_2CO_3	Na_2CO_3	H_2O
1003	UO_2CO_3 + 1% Na_2CO_3	20.7	4.5	10.5	1.020	2.4	0.5	0.8	96.2	2.8	0.0	96.3
1005	" + 2% "	41.4	9.2	21.2	1.061	4.7	1.0	1.4	92.9	5.5	1.8	92.0
1034	" + 4% "	80.5	18.4	40.4	1.121	8.6	2.0	2.7	86.7	10.0	3.4	86.0
1000	" + Tricarb.	88.0	18.9	42.2	1.132	9.4	2.1	2.7	85.8	10.8	3.3	85.0
1004	" + 6% Na_2CO_3	124.0	26.2	61.4	1.180	12.6	3.0	3.8	80.6	14.5	4.0	80.0
1008	" + 8% "	176.6	35.6	81.2	1.257	17.1	4.0	4.7	74.2	19.4	6.5	74.1
1041	" + 10% "	211.0	39.9	98.3	1.314	19.3	4.1	5.5	71.1	22.2	7.0	70.8
1010	" + 12% "	259.0	45.4	113.4	1.373	22.6	4.5	6.1	66.8	26.2	7.6	66.2
1043	" + 15% "	278.0	59.8	141.0	1.421	23.5	5.7	7.3	63.5	27.1	8.8	64.1
1030	" + Tricarb.*	309.0	62.8	144.0	1.470	25.2	5.8	7.2	61.8	29.2	9.9	60.0
1031	" + 18% Na_2CO_3	321.0	61.0	144.0	1.474	26.2	5.6	7.2	61.1	30.2	9.6	60.3
1048	" + 18% "	335.0	71.8	172.0	1.490	27.0	6.5	8.5	58.0	31.2	10.8	58.0
403	" + NaHCO_3	12.9	2.9	6.9	1.010	1.5	0.4	0.5	97.6	1.8	0.6	97.0
404	" + "	53.0	10.1	27.2	1.070	5.0	1.3	1.9	90.9	6.8	2.2	91.0
405	" + "	106.0	19.8	53.6	1.100	11.0	2.3	3.4	83.3	12.7	3.9	83.4

* Solid residue shows presence of $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$.

Table 2
The UO_2CO_3 , Na_2CO_3 , H_2O System

$\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ Solid Phase

Test No.	How Prepared	Solution Analysis (gram/liter)			d_{250}	Weight Percent Based On						
		U	Na	CO_3		Four Component System				Three Component		
						UO_3	Na_2O	CO_2	H_2O	UO_2CO_3	Na_2CO_3	H_2O
*	Tricarb. + Na_2CO_3	1.45	149.6	195.9	1.278	0.1	15.8	11.2	72.9	0.2	27.0	72.8
*	Tricarb. + Na_2CO_3	5.4	99.1	130.6	1.202	0.5	11.1	8.0	80.4	0.6	19.0	80.4
*	Tricarb. + Na_2CO_3	16.3	53.7	74.2	1.128	1.7	6.4	4.8	87.1	2.0	11.0	87.0
*	Tricarb. + Na_2CO_3	32.4	35.9	55.1	1.106	3.5	4.4	3.7	88.4	4.1	7.5	88.4
*	Tricarb. + H_2O	63.2	24.5	47.7	1.118	6.8	3.0	3.1	87.1	7.9	5.0	87.1
145	Tricarb. + H_2O	65.6	26.1	51.6	1.128	7.0	3.1	3.4	86.5	8.1	5.3	86.6
146	Tricarb. + H_2O	68.6	27.7	54.8	1.128	7.3	3.3	3.6	85.8	8.5	5.7	85.8
1018	Tricarb. + Dicarb.**	95.8	29.1	61.7	1.164	9.9	3.4	3.9	82.8	11.4	5.8	82.8
1017	UO_2CO_3 + Tricarb.	226.0	46.9	115.0	1.349	20.2	4.7	6.3	68.8	23.2	8.0	68.8
1052	Tricarb. + Dicarb.**	306.0	59.0	151.0	1.451	25.3	5.5	7.6	61.6	29.2	9.3	61.5

*Princeton data.²

**Solution.

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Figure 2
The Na_2CO_3 , $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$, H_2O System

three component systems are to be treated in a similar fashion.

The region of solubility for this system is small and is characterized by the sharp eutectic between solution in contact with tr carbonate solid and that in contact with uranyl carbonate. It is interesting that the line leading directly from the H_2O vertex to the eutectic represents solutions which have mole ratios of $CO_3/U = 2$ as well as $Na/U = 2$. The compositions of such solutions can be expressed by the formula $Na_2UO_2(CO_3)_2$ and suggest the possibility of the existence of a dicarbonate ion, $UO_2(CO_3)_2^{2-}$. These solutions are prepared by dissolving UO_2CO_3 in Na_2CO_3 solutions. Similar ones made by contacting UO_2CO_3 with $NaHCO_3$ solutions will be discussed below.

The position of the eutectic is somewhat uncertain due to difficulties in obtaining precise analyses of these concentrated solutions (300 gm U/l) and the fact that solutions in this region tend to lose CO_2 readily. The subsequent dissolution of even greater quantities of uranium upon loss of CO_2 from these solutions suggests that the eutectic for the four component system does not lie in the plane of UO_2CO_3 , Na_2CO_3 and H_2O .

The Quaternary Eutectic

It has been noted that loss of CO_2 from solutions originally on the UO_2CO_3 , Na_2CO_3 , H_2O plane allows the dissolution of more uranium. Data showing this are presented on Table 3 along with results for other tests deficient in CO_2 . There is a tendency toward supersaturation in solutions

Table 3

Solutions Close to UO_2CO_3 , Na_2CO_3 , H_2O Plane but Deficient in CO_2

Test No.	How Prepared	Solution Analysis (gram/liter)			d_{250}	Weight Percent Based On Four Component System				Three Component		
		U	Na	CO_3		UO_3	Na_2O	CO_2	H_2O	UO_2CO_3	Na_2CO_3^a	H_2O
1047 ^b	UO_3 + Dicarb. Sol'n	129.0	26.5	101.5	1.148	13.5	3.1	6.5	76.9	15.6	7.9	76.5
1045 ^b	UO_3 + Dicarb. Sol'n	131.0	23.1	52.1	1.20	13.1	2.6	3.2	81.1	15.1	3.6	81.3
1044 ^c	Tricarb. + Dicarb. ^e	202.0	42.4	97.3	1.293	18.7	4.4	5.5	71.4	21.6	6.9	71.5
1046 ^c	Tricarb. + Dicarb. ^e	274.0	51.3	130.0	1.400	23.5	4.9	6.8	64.8	27.1	8.1	64.8
1051 ^c	Tricarb. + Dicarb. ^e	277.0	56.0	130.0	1.405	23.7	5.4	6.8	64.1	27.4	8.4	64.2
1049 ^d	UO_2CO_3 + 20% Na_2CO_3	373.0	79.5	194.0	1.544	29.0	7.0	9.2	54.8	33.5	11.7	54.8
1050 ^d	UO_2CO_3 + 23% Na_2CO_3	428.0	89.0	209.0	1.618	31.8	7.4	9.5	51.3	36.8	11.8	51.4

- a. Na_2CO_3 percentage adjusted to coincide with UO_2CO_3 , Na_2CO_3 system.
b. Solid phase UO_3 .
c. Solid phase $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$.
d. Solid phase UO_2CO_3 .
e. Dicarbonate solution.

having concentrations as high as shown by experiments 1049 and 1050.

Such a possibility will be discussed in the second report of this series.

Further investigations of these solutions are in progress.

Measurements in this laboratory and by Bersohn and Brady⁶ indicate that no appreciable solubility exists in excess sodium oxide other than in the region of the eutectic. Thus, the eutectic may be considered as being at the bottom of a relatively narrow and deep depression or sink. Several attempts to define the positions of the walls of this depression have been made.

The dissolution of UO_3 in NaHCO_3 yields data which may be represented by a nearly straight line from the water vertex downward and parallel to the dicarbonate line of Figure 2. The back wall of the sink thus appears steep and may be characterized by these lines. These data appear in Table 4 and Figure 3.

The results presented in Table 5 give additional information about the wall toward the Na_2O vertex and show it to be very steep there also. The analyses of the solutions show that, on a dry basis, the percentages of each of the components Na_2O , UO_3 , and CO_2 are almost identical. This means that the points representing these experiments all lie on a line which is nearly vertical and which may be drawn to the water vertex from the point on the base of the pyramid corresponding to the composition of the dried solute. The analyses of the corresponding residues indicate that these solutions are in contact with UO_2CO_3 as well as some slightly soluble uranate or polyuranate or, perhaps, a solid solution of uranates. These solutions thus represent the line of intersection between

Table 4

The UO_3 , NaHCO_3 , H_2O System UO_3 Solid Phase

Test No.	How Prepared	Solution Analysis (gram/liter)			d ₂₀	Weight Percent Based On							
		U	Na	CO ₃		Four Component System				Three Component			
						UO ₃	Na ₂ O	CO ₂	H ₂ O	UO ₃	NaHCO ₃	H ₂ O	
*	UO ₃ + NaHCO ₃	0.03	3.23	0.00	1.005	0.00	0.03	0.04	99.95	0.00	0.00	99.94	
*		4.50	0.00	1.00	1.010	0.54	0.00	0.13	99.24	0.54	0.25	99.21	
*		5.10	0.02	2.40	1.020	0.61	0.12	0.17	99.10	0.61	0.33	99.08	
*		5.34	1.15	3.00	1.030	0.62	0.15	0.21	99.02	0.62	0.41	98.97	
*		6.05	1.50	3.00	1.040	0.77	0.10	0.25	98.80	0.77	0.40	98.74	
*		7.20	1.04	4.80	1.050	0.63	0.24	0.34	98.59	0.63	0.64	98.53	
*		7.05	2.07	5.40	1.060	0.67	0.20	0.37	98.50	0.67	0.71	98.42	
*		10.50	2.50	6.00	1.070	1.15	0.20	0.41	98.15	1.15	0.70	98.00	
*		17.25	3.45	6.00	1.080	1.92	0.43	0.61	97.04	1.92	1.17	96.91	
*		20.25	4.00	12.00	1.090	2.23	0.57	0.61	96.59	2.23	1.54	96.23	
310		30.1	4.1	12.8	1.05	3.5	0.5	0.9	95.1	3.5	1.5	95.0	
*		45.25	6.00	16.0	1.100	4.95	0.85	1.20	93.00	4.95	2.20	92.70	
309		50.0	7.4	16.8	1.08	5.6	0.9	1.1	92.4	5.6	2.4	92.0	
308		51.1	7.0	16.9	1.06	5.7	0.9	1.3	92.1	5.7	2.4	91.9	
5-84		64.8	14.5	22.2	1.082	7.2	1.8	2.2	88.8	7.2	4.9	87.9	

Bershen and Brady.⁶

Figure 3
The UO₃, NaHCO₃, H₂O System

Table 5
Solutions* in Equilibrium With a
UO₂CO₃ - Diuranate Solid Phase

Test No.	Solution Analysis (gram/liter)			d ₂₅ ^o	Weight Percent Based on Four Component System			
	<u>U</u>	<u>Na</u>	<u>CO₃</u>		<u>UO₃</u>	<u>Na₂O</u>	<u>CO₂</u>	<u>H₂O</u>
406	47.8	9.3	22.7	1.070	5.36	1.17	1.55	91.8
407	50.6	9.8	23.7	1.075	5.65	1.23	1.62	91.4
408	54.6	10.9	25.2	1.080	6.07	1.36	1.71	91.0
434	87.7	17.5	37.4	1.111	9.5	2.1	2.5	85.9
437	216.0	39.0	102.4	1.300	20.0	4.4	5.8	69.8
438	220.0	39.4	103.0	1.318	20.0	4.0	5.7	70.3
439	234.0	44.6	104.0	1.333	21.1	4.4	5.7	68.8

* Prepared by contacting UO₂CO₃ and Na₂CO₃ with NaOH solution.

the field which is in equilibrium with UO_2CO_3 and the one which is in equilibrium with the mixed uranate phase.

The addition of CO_2 to various carbonate-uranium solutions was made to provide information concerning the boundary which lies on the CO_2 side of the depression. The CO_2 concentration reached was not great enough for precipitates to form so the data do not define a solution boundary and can only indicate regions of solubility. These data appear on Table 6. The need for high pressure solubility measurements is here demonstrated.

Measurements were made on a mixture of UO_2CO_3 and NaHCO_3 solution in order to obtain additional information about the CO_2 side of this depression. Evolution of CO_2 gas commenced at contact and the final analysis showed almost complete conversion of the bicarbonate into carbonate while the solutions correspond to ones obtained from the dissolution of UO_2CO_3 in Na_2CO_3 . The results have been shown on Table 2. The applicability of high pressure solubility determinations in this system is being considered also.

To determine the exact composition at the eutectic, solubility tests are being made with a mixture of UO_2CO_3 , $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ and $\text{Na}_2\text{U}_2\text{O}_7$. The diuranate is used in this series because of the obvious difficulty in the preparation of the correct polyuranate solid phase. In addition, solutions having compositions near the eutectic of Figure 2 and still in contact with the solid phase are having CO_2 removed by scrubbing with nitrogen. It is hoped that such treatment will drive the concentration of the original solution to a new value corresponding to that at the eutectic.

Table 6Solutions with High CO₂ Content not inContact with Solid Phase

Test No.	Solution Analysis (gram/liter)			d_{25}^0	Weight Percent Based on Four Component System			
	U	Na	CO ₃		UO ₃	Na ₂ O	CO ₂	H ₂ O
321	8.48	2.06	6.46	1.012	1.00	0.23	0.46	98.3
316	44.2	18.5	42.2	1.118	4.75	2.23	3.57	89.5
317	53.2	17.2	40.9	1.120	5.95	2.07	2.68	89.3
318	79.6	18.2	44.9	1.153	8.23	2.13	2.85	86.7
319	123.6	26.8	66.2	1.233	12.0	2.93	3.93	81.2
320	162.8	32.2	85.0	1.301	14.98	3.37	4.78	76.8

The Na₂O, CO₂, H₂O System

The discussion thus far has concerned the UO₂CO₃, Na₂CO₃, H₂O plane which dissects the pyramid into what has been termed a Na₂O side and a CO₂ side. The region on either side of this plane and in the vicinity of its eutectic also has been considered. For a further investigation of the regions high in CO₂ or Na₂O it becomes necessary to describe the plane which corresponds to the Na₂O, CO₂, H₂O face of the pyramid.

For this plane data from the indicated sources are presented in Table 7 and Figure 4, and these data show that its region of solubility exists almost completely on the Na₂O side of the plane of Figure 2.

The UO₃, Na₂CO₃, H₂O System

Results obtained by Bersohn and Brady⁶ indicate no appreciable solubility on the UO₃, Na₂CO₃, H₂O plane. The data appear on Table 8 and Figure 5. In this figure the scale has been magnified greatly to represent the data. Since the volume in the pyramid bounded by this plane and the plane of Figure 2 is small, and since there is appreciable solubility on the latter plane and practically none on the former, there must be a rather steep wall between them which represents this sharp decrease in solubility.

It is an experimental fact that extreme dilution of dicarbonate or tricarbonates solutions will result in the formation of a precipitate which analyzes to be a uranate. The presence of this sharply rising wall, for convenience called the mixed uranate wall, makes two explanations possible. All planes of the pyramid of Figure 1 are necessarily

Table 7
The Na₂O, CO₂, H₂O System

Reference	Solid Phase	Weight Percent		
		Na ₂ O	CO ₂	H ₂ O
9	NaOH·H ₂ O	42.1	0	57.9
9	Na ₂ CO ₃	41.7	2.5	55.8
9	"	36.0	1.0	63.0
9	Na ₂ CO ₃ + Na ₂ CO ₃ ·H ₂ O	35.9	6.3	57.8
9	Na ₂ CO ₃ ·H ₂ O	27.6	0.4	72.0
9	"	18.7	5.7	75.6
9	"	16.7	7.8	73.5
9	Na ₂ CO ₃ ·H ₂ O + Na ₂ CO ₃ ·7H ₂ O	18.9	9.1	72.0
9	Na ₂ CO ₃ ·7H ₂ O	18.5	10.1	71.4
9	"	18.1	10.7	71.2
9	Na ₂ CO ₃ ·7H ₂ O + Na ₂ CO ₃ ·10H ₂ O	18.3	11.1	70.6
9	Na ₂ CO ₃ ·10H ₂ O	17.9	11.0	71.1
10	"	16.6	11.8	71.6
10	Na ₂ CO ₃ ·10H ₂ O + Trona*	16.7	11.5	71.8
10	Trona*	16.4	11.8	71.8
10	"	14.7	10.9	74.4
10	"	14.4	10.6	75.0
10	"	13.3	10.1	76.6
10	"	12.3	9.6	78.1
10	NaHCO ₃ + Trona*	11.9	9.5	78.6
10	NaHCO ₃	9.0	7.9	83.1
10	"	6.2	6.4	87.4
10	"	3.6	5.1	91.3
10	CO ₂ gas 1 atm.	0	12.5	87.5
	CO ₂ gas 0.03 mm.	0	0.05	99.95

* Trona = NaHCO₃·Na₂CO₃·2H₂O.

Figure 4
The Na_2O , CO_2 , H_2O System

Table 8
The UO_3 , Na_2CO_3 , H_2O System

UO_3 Solid Phase

Test No.	How Prepared	Solution Analysis (gram/liter)				Weight Percent Based On						
		U	Na	CO_3	d_{250}	Four Component System				Three Component		
						UO_3	Na_2O	CO_2	H_2O	UO_3	Na_2CO_3	H_2O
*	$\text{UO}_3 + \text{H}_2\text{O}$	0.064	0	0	1.00	0.008	0	0	99.99	0.008	0	99.99
*	$\text{UO}_3 + \text{Na}_2\text{CO}_3$	2.25	2.30	3.00	1.00	0.27	0.31	0.22	99.2	0.27	0.53	99.2
*	"	2.27	2.76	3.60	1.00	0.27	0.37	0.26	99.10	0.27	0.63	99.10
*	"	2.48	3.68	4.80	1.01	0.30	0.49	0.35	99.86	0.30	0.84	98.86
*	"	2.52	4.04	5.28	1.01	0.30	0.54	0.38	98.78	0.30	0.92	98.78
*	"	2.82	4.60	6.00	1.02	0.33	0.61	0.43	98.63	0.33	1.04	98.63
*	"	2.87	6.90	9.0	1.03	0.34	0.90	0.64	98.12	0.34	1.54	98.12
*	"	3.07	9.20	12.0	1.04	0.35	1.19	0.85	97.61	0.35	2.04	97.61
*	"	3.18	13.8	18.0	1.05	0.36	1.77	1.26	96.61	0.36	3.03	96.61
*	"	3.72	18.4	24.0	1.06	0.42	2.34	1.66	95.58	0.42	4.00	95.58
427	$\text{UO}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 + \text{NaOH}$	14.0	79.0	110.0	1.1	1.6	9.7	7.4	81.3	1.6	17.0	81.4
427-L	"	18.2	93.3	125.2	1.2	1.8	10.5	7.7	80.0	1.8	18.2	80.0

*Bersohn and Brady.⁶

Figure 5
The UO₃, Na₂CO₃, H₂O System

very close together at the water apex. It would upon dilution, require only a very small loss of CO_2 from these solutions for the composition to shift toward this mixed uranate wall, and upon reaching it, for precipitation to take place. Such loss of CO_2 from dicarbonate solutions of pH 7 is quite possible. It is more difficult to explain this loss in tricarbonate solutions of pH 9, but it must be remembered that only a very little CO_2 must be lost for precipitation to take place.

If the supposition is made that at very high water percentages the mixed uranate wall overhangs or projects through the plane of Figure 2 it is apparent that continued dilution of dicarbonate or tricarbonate solutions will finally bring about precipitation when the composition reaches that value defined by the face of the overhanging wall. Data have been obtained by an independent method in which UO_2CO_3 and Na_2CO_3 were contacted with sodium hydroxide solution. Each of these tests indicates the presence of this diuranate wall at very high water content, but the experimental accuracy is not such as to prove or disprove either of the above propositions. These data appear on Table 9 as tests 435 and 436.

The manner in which the base of the mixed uranate wall joins the field in equilibrium with tricarbonate is under investigation. On the basis of tests reported in Table 9 it appears that the line of intersection is below the level of the tricarbonate curve of Figure 2 and only slightly displaced from the plane of Figure 2. This line thus defines a pass between the mixed uranate wall and the field in contact with tricarbonate and which leads from the front face of the pyramid to

Table 9
The Mixed Uranate Wall

Test No.	How Prepared	Solution Analysis (gram/liter)			d_{250}	Weight Percent Based On Four Component System			
		U	Na	CO ₃		UO ₃	Na ₂ O	CO ₂	H ₂ O
440	Tricarb + Na ₂ CO ₃ + Na ₂ U ₂ O ₇ *	38.9	34.8	87.7	1.101	4.2	4.3	3.8	87.7
441	" "	28.5	41.9	86.5	1.107	3.1	5.1	4.4	87.4
442	" "	23.4	49.9	73.9	1.116	2.5	6.0	4.9	86.6
443	" "	18.4	72.6	96.4	1.147	1.6	8.5	6.2	83.7
444	" "	10.7	84.0	119.0	1.177	1.1	9.6	7.4	81.9
445	" "	4.5	126.6	173.0	1.245	0.4	13.7	10.2	75.7
435	UO ₂ CO ₃ + Na ₂ CO ₃ + NaOH**	48.6	22.5	43.0	1.085	5.3	2.8	2.9	89.0
436	" "	11.6	29.2	40.4	1.055	1.3	3.7	2.8	94.0

*Solids in contact - Na₂U₂O₇ and Tricarbonate.

**Solids in contact - Mixed uranates.

the eutectic of the system. Solutions existing along this line are in equilibrium with tricarbonates solid and the mixed uranates.

The UO_3 , NaOH System

It has been shown⁶ that the solubility of UO_3 in NaOH does not exceed a few hundredths of a percent over the whole range of concentrations investigated. Further determinations with added Na_2CO_3 exhibit similar properties. This agrees with the data of the UO_3 , Na_2CO_3 , H_2O system which predicts a steep wall rising to the water vertex.

Due to the very low uranium solubility these data can be presented on a plane which is placed just slightly behind the Na_2O , CO_2 , H_2O plane. This has been done in Figure 6, the data being presented in Tables 10 and 11. The solution line of this diagram exhibits the same characteristics shown by that portion of the Na_2O , CO_2 system which appears on Figure 6 as the dotted line. The complexity of the residue makes it difficult to determine the exact composition of the solids, but it is felt that there are both Na_2CO_3 and sodium uranates present in a majority of the tests with $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ being present in tests 426 and 429. The latter tests may well be the start of the pass between the mixed uranate wall and the $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ mound and which leads from the front of the pyramid to the quaternary eutectic. This pass has been discussed in the previous section using the data of Table 9.

The $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$, NaHCO_3 , H_2O System

Work has been carried out at Princeton² on the solubility of $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ in NaHCO_3 . Two additional experiments at this laboratory

Figure 6

Experiments in which the solution compositions correspond
nearly to those of the Na_2O , CO_2 , H_2O system
(Uranium < 0.006%)

Table 10

The UO_3 , Na_2O , H_2O System* UO_3 Solid Phase

Solution Analysis (gram/liter)			Weight Percent Based on Four Component System		
<u>U</u>	<u>Na</u>	<u>d_{25}^{20}</u>	<u>UO_3</u>	<u>Na_2O</u>	<u>H_2O</u>
0.0036	1.18	1.0	0.0004	0.16	99.84
0.009	2.37	1.0	0.0011	0.32	99.68
0.014	4.72	1.01	0.0017	0.63	99.37
0.016	7.08	1.01	0.0019	0.95	99.05
0.025	11.8	1.02	0.0029	1.56	98.44
0.034	23.7	1.03	0.0040	3.1	96.9
0.035	58.9	1.07	0.0039	7.4	92.6
0.034	118.0	1.17	0.0035	13.6	86.4
0.053	258.0	1.36	0.0047	25.6	74.4

* Data of Bersohn and Brady⁶.

Table 11

Solutions Close to Na_2O , CO_2 , H_2O Plane

Test No.	How Prepared	Solution Analysis (gram/liter)			d_{250}	Weight Percent Based on Four Component System				Solid Phase
		U	Na	CO_3		UO_3	Na_2O	CO_2	H_2O	
426	$\text{UO}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 + \text{NaOH}$	0.04	130.0	133.0	1.25	0.004	14.0	7.9	78.1	Na_2CO_3 , (Tricarb)
431	"	0.02	165.0	111.2	1.27	0.002	17.5	6.4	76.1	Na_2CO_3 , $\text{Na}_2\text{U}_2\text{O}_7$
429	Tricarb + $\text{Na}_2\text{CO}_3 + \text{NaOH}$	0.01	170.0	163.0	1.30	0.0008	17.6	9.2	73.2	" "
425	$\text{UO}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 + \text{NaOH}$	0.06	177.0	53.5	1.25	0.006	19.1	3.1	77.8	" "
432	"	0.04	179.0	94.4	1.28	0.004	18.9	5.3	75.8	" "
424	"	0.01	181.0	13.2	1.23	0.001	19.8	0.8	79.4	" "
430	Tricarb + $\text{Na}_2\text{CO}_3 + \text{NaOH}$	0.01	183.0	51.0	1.25	0.001	19.7	3.0	78.3	Na_2CO_3 , Tricarb
433	$\text{UO}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 + \text{NaOH}$	0.04	202.0	20.4	1.26	0.004	21.6	1.2	77.2	Na_2CO_3 , $\text{Na}_2\text{U}_2\text{O}_7$
424-L	"	0.03	214.0	13.4	1.27	0.002	22.7	0.8	76.5	" "

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are included with this data in Table 12, and on Figure 7. The shape of the solution curve which is in equilibrium with $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ resembles the corresponding curve in Figure 2, and indicates the presence of a region in the center of the pyramid the cross section of which is characterized by these curves. In this region the solubility of $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ decreases only slightly with increasing concentration of CO_2 . How far this trend continues has yet to be determined. The UO_2CO_3 , NaHCO_3 experiments will aid in defining this portion of the system.

Solubility of UO_2CO_3 in H_2O and NaOH

Table 13 shows that the solubility of UO_2CO_3 in H_2O and NaOH is negligible.

Table 12

The $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$, NaHCO_3 , H_2O System

Test No.	How Prepared	Solution Analysis (gram/liter)			d ₂₅₀	Weight Percent Based On Four Component System				Three Component		
		U	Na	CO ₃		UO ₃	Na ₂ O	CO ₂	H ₂ O	Tri ^a	NaHCO ₃	H ₂ O
b	Tricarb + NaHCO ₃ ^a	18.15	31.2	76.7	1.100	2.00	3.82	5.12	89.06	3.76	8.0	88.3
b	" " c	22.3	27.7	66.7	1.092	2.46	3.42	4.48	89.64	4.65	6.38	89.0
b	" " c	38.8	24.4	54.0	1.098	4.25	3.00	3.61	89.14	8.06	3.14	88.8
315	" " d	11.3	31.0	77.5	1.112	1.22	3.75	5.11	89.8	2.3	9.6	88.8
314	" " d	22.8	37.5	84.2	1.140	2.41	4.43	5.42	87.8			

a $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$.b Princeton data.²

c Solid phase tricarb only.

d Solid phase NaHCO₃ only.

Figure 7

The Na₄UO₂(CO₃)₃, NaHCO₃, H₂O System

Table 13

Solubility of UO_2CO_3 in H_2O and NaOH

Test No.	How Prepared	Solution Analysis (gram/liter)			d _{25°}	Weight Percent			
		U	Na	CO ₃		UO ₃	Na ₂ O	CO ₂	H ₂ O
412	$\text{UO}_2\text{CO}_3 + \text{H}_2\text{O}$	0.003	-	0.0008	1.00	0.0003	-	0.00008	99.99
410	$\text{UO}_2\text{CO}_3 + \text{NaOH}$	0.35	0.14	-	1.00	0.03	0.02	0.60	99.89
409	"	0.56	0.094	-	1.00	0.07	0.01	0.10	99.68
411	"	0.86	0.23	3.0	1.00	0.10	0.03	0.22	99.65
1033	"	0.077	3.19	4.03	1.003	0.093	0.43	0.29	99.19

SUMMARY

1. The UO_2CO_3 , Na_2CO_3 , H_2O system provides a representative cross section of the region of solubility which exists in the four component system of UO_3 , Na_2O , CO_2 , and H_2O .

2. The UO_2CO_3 , Na_2CO_3 , H_2O system is characterized by a sharp eutectic between two solubility fields. One of these fields represents solution in contact with tricarbonat solid $[\text{Na}_4\text{UO}_2(\text{CO}_3)_3]$ while the other is in contact with uranyl carbonate. Solutions existing along the curve defining the latter field appear to have a composition corresponding to the empirical formula $\text{Na}_2\text{UO}_2(\text{CO}_3)_2$. The eutectic occurs at about 29% UO_2CO_3 , 10% Na_2CO_3 and 61% H_2O . The solubility of uranium at this point is approximately 300 grams per liter. The exact location of the eutectic is somewhat uncertain due to analytical difficulties and the possibility of supersaturation.

3. Addition of sodium oxide to the above solutions results in a marked decrease in solubility of the uranium except in the immediate vicinity of the plane of the Na_2CO_3 , UO_2CO_3 system. The decrease in solubility is represented on the four component solubility diagram by a wall which rises so sharply that the region of solubility is negligible on the UO_3 , Na_2CO_3 , H_2O plane even though it is only slightly removed from that of the UO_2CO_3 , Na_2CO_3 , H_2O system. This wall defines a region in which are present solution and a solid phase consisting of a slightly soluble mixed or polyuranate.

4. The loss of CO_2 from solutions near the eutectic mixture of the

UO_2CO_3 , Na_2CO_3 , H_2O plane allows greater dissolution of uranium to take place. This would indicate that the quaternary eutectic for the system lies near the first eutectic but slightly displaced toward the Na_2O side of the system. Due to difficulty in the reproduction of the correct uranate which would exist at the eutectic, its position is not known accurately, but it appears to be located at the bottom of a rather deep and narrow solubility well. Experiments with UO_3 in NaHCO_3 and a mixture of UO_2CO_3 and Na_2CO_3 in NaOH show that the walls of this depression are very steep.

5. The $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$, NaHCO_3 , H_2O system shows solubilities very similar to those in the $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$, Na_2CO_3 , H_2O system. The results indicate a region between these two planes in which the solubility of uranium is decreasing only slightly with increasing CO_2 content. How far this trend continues has yet to be determined.

6. The solubility of UO_2CO_3 in water and sodium hydroxide is negligible.

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