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CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS
MINES BRANCH

STUDIES ON THE
PRECIPITATION OF SODIUM POLYURANATES
FROM SOLUTIONS OF SODIUM URANYL TRICARBONATE

by

H. J. HERBST

RADIOACTIVITY DIVISION

Price 25 cents

Technical Paper No. 15

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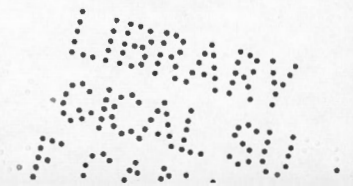
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CONTENTS

	<u>Page</u>
Summary.....	1
Discussion.....	2
Effect of Sodium Carbonate on Precipitation.....	3
Experimental.....	6
Effect of U_3O_8 Concentration on Rate of Precipitation.....	7
Effect of Seeding Low-Grade Pregnant Solutions.....	11
Effect of Sodium Sulphate on Precipitation.....	12
Effect of Temperature on Precipitation.....	15
Rate of Precipitation.....	16
Effect of NaOH on the Apparent Composition of the Precipitate.....	17
Appendix.....	24-29
Factors for Addition of NaOH.....	24
Activity Coefficients.....	24-25
Analytical methods.....	26-29
Table 1 Effect of Na_2CO_3 Concentration on Precipitation.....	4-5
Table 2 Effect of U_3O_8 Concentration on the Rate of Precipitation.....	9
Table 3 The Effect of Seeding Low-Grade Solutions.....	12
Table 4 The Effect of Na_2SO_4 Concentration on Precipitation.....	13
Table 5 The Effect of Temperature on Precipitation.....	15-16
Table 6 The Effect of NaOH Excess on the Composition of the Precipitate.....	17
Table 7 Effect of Time on the Amount of NaOH in the Barren.....	19
Figure 1 Effect of Na_2CO_3 and NaOH Concentration on Precipitation of $Na_2U_2O_7$ at various temperatures.....	8
Figure 2 Effect of initial U_3O_8 Concentration on Rate of Precipitation.....	10
Figure 3 Effect of Na_2SO_4 Concentration on Rate of Precipitation ..	14
Figure 4 Apparent Effect of NaOH Excess on the Na_2O/UO_3 ratio in the Precipitate.....	22
Figure 5 Titration of Sodium Bicarbonate with 2.6N Sodium Hydroxide.....	28
Figure 6 Titration of NaOH with 0.1N HCl using $BaCl_2$ to remove Na_2CO_3	29

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STUDIES ON THE PRECIPITATION OF SODIUM POLYURANATES
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Radioactivity Division

Summary

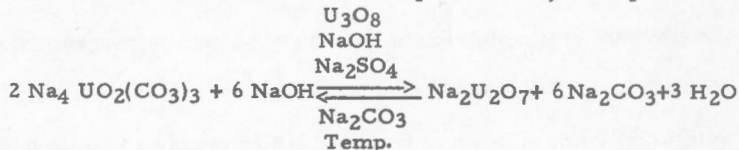
By addition of sodium hydroxide, sodium polyuranates are precipitated from solutions or leach liquors containing sodium carbonate and sodium uranyl tricarbonate.

Excess hydroxide is required in amounts directly proportional to the concentration of sodium carbonate in the barren.

The rate of precipitation, and consequently the efficiency, appear to vary directly with the amount of uranium present, and also to a limited extent with the concentration of sodium sulphate present.

Precipitation is more efficient at 25°C than at higher temperatures.

The effects of varying the carbonate, uranium, sulphate and sodium hydroxide concentrations, and the temperature are discussed in this paper. The reaction is considered to be represented by the equation:



The equilibrium constant has been approximately determined as:

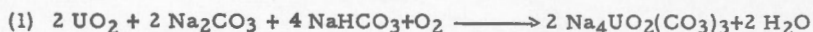
$$\sqrt{K} = \frac{(\text{Na}_4\text{UO}_2(\text{CO}_3)_3) \gamma \times (\text{NaOH})^3 \gamma^3}{(\text{Na}_2\text{CO}_3)^3 \gamma^3} = 1.35 \times 10^{-5}$$

where γ = activity coefficient as in Table 1,
and () denotes molar concentrations.

A working curve has been drawn to show the relationship between U_3O_8 gm/litre and the ratio $(\text{NaOH gm/l}) / (\text{Na}_2\text{CO}_3 \text{ gm/l})$ at various temperatures.

Discussion

This investigation was begun in 1950 in connection with work which has been underway at the Mines Branch on leaching of uranium ores with alkaline carbonate solutions. In leaching with solutions of sodium carbonate and bicarbonate, the essential chemical reaction is considered to be as shown by equation (1) Other oxidizing agents may replace the O_2 shown.



When the ores treated contain sulphides, bicarbonate and sulphate can form as in equation (2).

Specialized analytical procedures for the determination of bicarbonate, carbonate and hydroxide are included in the appendix. These procedures were all developed at the Radioactivity Division laboratories in 1950-1951 as a preliminary step required for the investigation. As carbonate, bicarbonate and sulphate are present in the leach liquors, it was necessary to study their effects on the precipitation reaction, which is considered to be similar to equation (3).



This assumes that sodium diuranate is formed, but formulae of varying composition from $\text{Na}_4\text{U}_5\text{O}_{17}$ to $\text{Na}_9\text{U}_{10}\text{O}_{35}$ have been suggested. Analysis of the product commonly indicates the diuranate, but there are indications that the precipitate has a tendency to lose sodium hydroxide when washed with water. There is evidence that the precipitate may vary in composition depending on the concentration of uranium present, and on the amount of hydroxide excess used.

The Effect of Sodium Carbonate on Precipitation

The results included here were obtained by two independent investigators working with different solutions, and at different times. The carbonate concentrations were varied from 6-170 gm/litre and the sodium hydroxide from 0.1 gm/litre-10 gm/litre. Some error is introduced in determining small amounts of sodium hydroxide. This is evident in the wide discrepancy in the equilibrium constants in these tests.

An approximate average equilibrium constant has been calculated, omitting the results of the tests where NaOH concentrations were small. The required activity coefficients were taken from the literature. The constants \sqrt{K} are listed in Table 1, calculated from the equation

$$\sqrt{K} = \frac{(\text{Na}_4\text{UO}_2(\text{CO}_3)_3 \gamma \times (\text{NaOH})^3 \gamma^3}{(\text{Na}_2\text{CO}_3)^3 \gamma^3} = 1.35 \times 10^{-5}$$

where () denotes molar concentrations

$$\text{Na}_4\text{UO}_2(\text{CO}_3)_3 = (\text{U}_3\text{O}_8 \text{ gm/l}) \times 3 / 842.21$$

and γ = respective activity coefficients. The activity coefficient for $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ is assumed to be approximately equal to that of $\text{K}_4\text{Fe}(\text{CN})_6$ in the low ranges.

Table 1 Effect of Na₂CO₃ Concentration

Test No	Pregnant Sol'n gm/l			Barren Assays gm/l		
	U ₃ O ₈	Na ₂ CO ₃	NaHCO ₃	U ₃ O ₈	Na ₂ CO ₃	NaOH
1	7.73	12.4	13.3	0.055	37.9	2.43
2				0.048	"	2.74
3				0.039	"	3.28
4				0.032	"	3.60
5	"	81.7	"	0.61	107.2	2.45
6				0.43	"	2.74
7				0.24	"	3.18
8				0.19	"	3.37
9	"	79.5	"	0.074	105.0	4.8
10	"	133.5	"	0.41	159.0	3.06
11	"	139.5	"	0.34	165.0	3.55
12	"	"	"	1.13	165.0	2.30
13	3.0	-	-	0.001	6.98	2.20
14	"	-	-	0.02	6.73	0.57
15	"	-	-	0.26	5.3	0.10
16	"	-	-	0.018	19.1	1.86
17	"	-	-	0.20	19.1	0.52
18	"	-	-	1.10	16.9	0.10
19	"	-	-	0.028	33.5	3.19
20	"	-	-	0.086	33.5	1.91
21	"	-	-	0.17	171.0	5.32
22	2.0	33.7	12.4	0.19	46.6	1.85
23	"	"	"	0.034	47.2	3.40
24	"	"	"	0.015	46.8	4.95

on Precipitation

γ Coefficients			* $\sqrt{K} \times 10^5$	NaOHx10 ² **	Remarks
K ₄ Fe(CN) ₆	Na ₂ CO ₃	NaOH			
1	0.341	0.805	1.28	6.4	<u>Group 1</u>
1	"	0.798	1.54	7.24	
1	"	0.785	1.98	8.65	
1	"	0.775	2.14	9.50	
0.925	0.262	0.805	1.28	2.28	
0.950	"	0.795	1.26	2.55	
0.980	"	0.785	1.06	2.96	
1.0	"	0.783	1.05	3.14	
1.0	0.265	0.758	1.10	4.57	
0.970	0.230	0.788	0.76	1.93	
0.975	0.225	0.778	0.92	2.15	
0.900	0.225	0.815	0.88	1.39	
1.0	0.55	0.82	0.69	31.5	<u>Group 2</u>
1.0	0.56	0.95	(0.39)	8.45	not included in average
0.98	0.605	1.0	(0.04)	1.89	"
1	0.385	0.835	1.10	9.75	
0.98	0.385	1.0	(0.45)	2.73	"
0.90	0.4	1.0	(0.32)	0.59	"
1.0	0.33	0.785	2.14	9.53	
1.0	0.33	0.83	1.66	5.70	
1.0	0.209	0.75	1.57	3.11	
1.0	0.310	0.832	1.50	3.94	<u>Group 3</u>
1.0	"	0.775	1.38	7.22	<u>Simard</u>
1.0	"	0.75	1.64	10.6	and Light

* Average $\sqrt{K} = 1.35 \times 10^{-5}$

** gm/l ratio in barren x 10²

The activity coefficient curves are nearly parallel for NaOH and Na₂CO₃ and advantage was taken of this to plot the results using the following relationship: (Fig. 1)

$$U_3O_8 \text{ gm/litre} = C \cdot \frac{NaOH}{Na_2CO_3}$$

where the concentrations of NaOH and Na₂CO₃ are as gm/litre in the barren solution, and C is an overall constant correcting for conversion of molality to gm/litre, equilibrium constant, and the relative differences in the activity coefficients.

Experimental. The solution used for Group 1 was a pilot plant leach liquor with the following analysis:

<u>U₃O₈</u> <u>gm/l</u>	<u>Na₂CO₃</u> <u>gm/l</u>	<u>NaHCO₃</u> <u>gm/l</u>
7.73	12.4	13.3

Calculation of the NaOH requirements for precipitation was based on equation



$$\begin{array}{rcl} \text{ie. NaOH for NaHCO}_3 & = & 13.3 \times 0.476 = 6.34 \text{ gm/l} \\ \text{" " Na}_2\text{U}_2\text{O}_7 & = & 7.73 \times 0.428 = 3.31 \\ \text{+ excess NaOH} & = & 3.0 \\ \text{Total NaOH} & & \underline{12.65 \text{ gm/l}} \end{array}$$

The sodium hydroxide was added in drops as 10N NaOH until the desired excess was obtained.

Precipitation was continued for 24 hours at 25°C. The barrens were filtered and analysed for Na₂CO₃, U₃O₈ and NaOH.

Group 2 results were obtained from a synthetic stock solution of $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ diluted to various U_3O_8 concentrations and doctored with different amounts of Na_2CO_3 . The stock solution was prepared by mixing an excess of freshly precipitated diuranate in a saturated solution of sodium bicarbonate for 24 hours at room temperature and filtering the solution free of undissolved diuranate.



The stock solution analysed:

U_3O_8 <u>gm/l</u>	Na_2CO_3 <u>gm/l</u>	NaHCO_3 <u>gm/l</u>	Na_2SO_4 <u>gm/l</u>
78.9	4.23	21.2	15.0

For the tests shown in Table 1 the stock solution was diluted to contain 3.0 gm/l U_3O_8 .

Group 3 results were obtained by R. Simard and D. Light from a leach liquor produced under different leaching conditions. Analysis of Group 2 liquors showed:

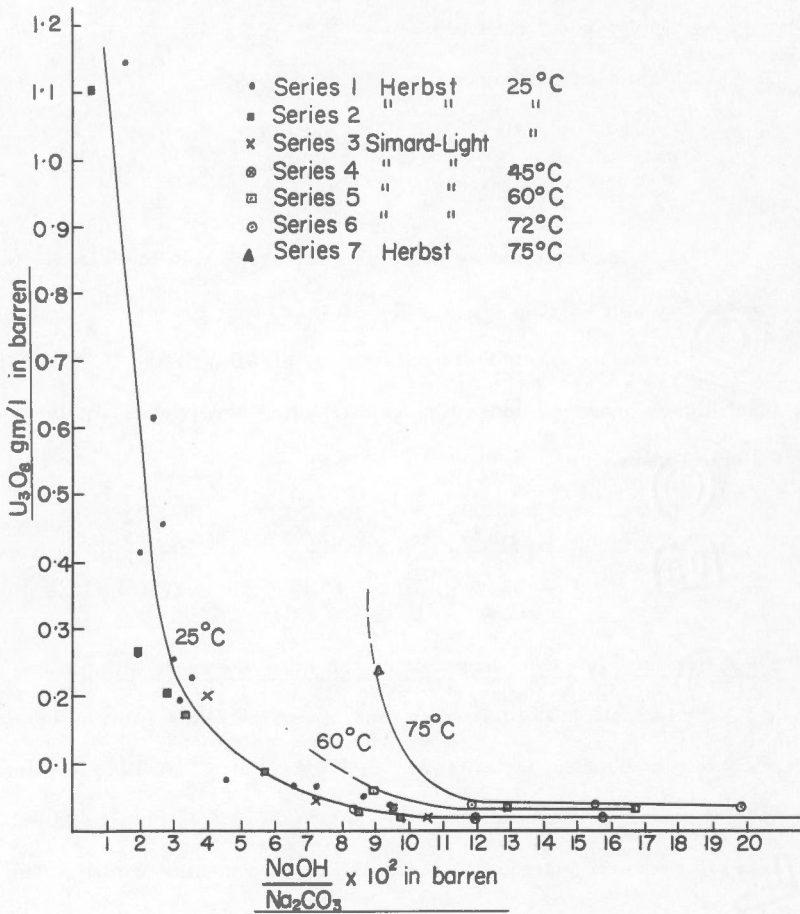
U_3O_8 <u>gm/l</u>	Na_2CO_3 <u>gm/l</u>	NaHCO_3 <u>gm/l</u>	S/ SO_4 <u>gm/l</u>
2.0	33.7	12.4	2.90 (12.9 gm/l Na_2SO_4)

The Effect of U_3O_8 Concentration on the Rate of Precipitation

Synthetic solutions were made from the stock solution by dilution to contain amounts of U_3O_8 from 0.5-7.0 gm/litre. A fixed amount of sodium carbonate was added and the solution precipitated by adding a fixed excess of sodium hydroxide as closely as could be determined. The results of these tests contained in Table 2, show that if the U_3O_8 concentration drops

FIGURE 1

EFFECT OF Na_2CO_3 AND NaOH CONC. ON
PPTN. OF $\text{Na}_2\text{U}_2\text{O}_7$ AT VARIOUS TEMPERATURES



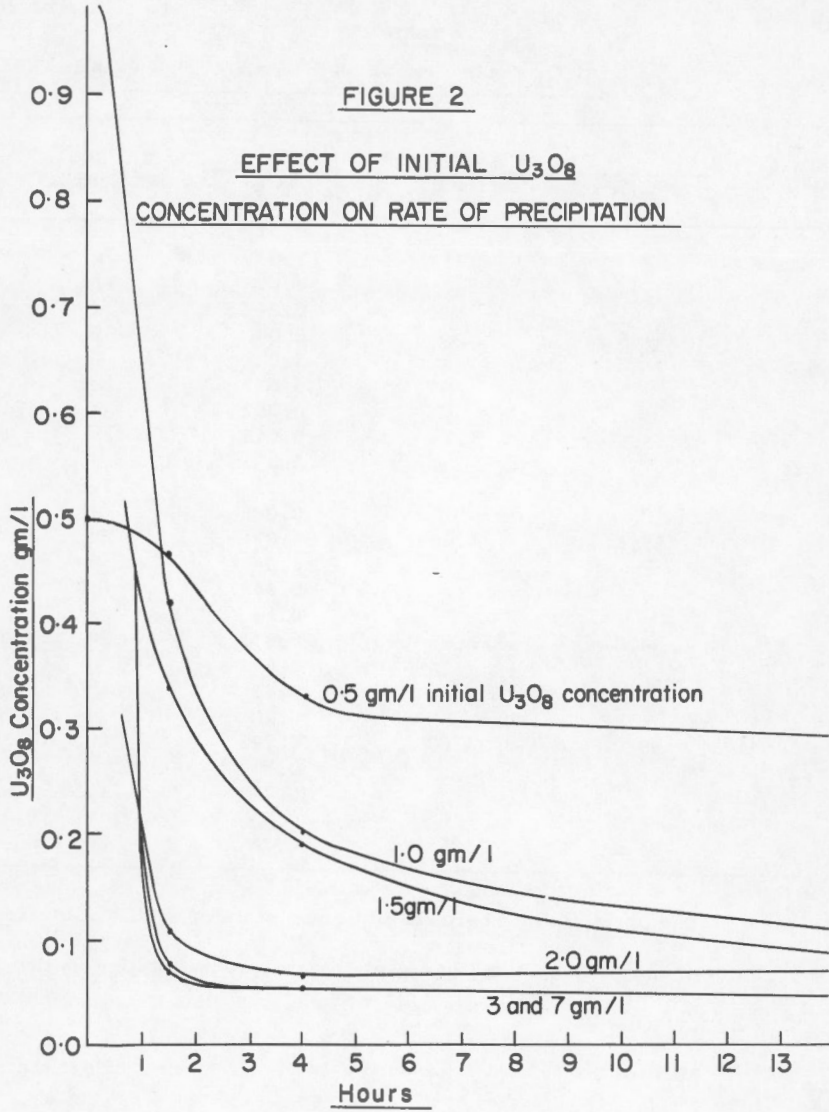
below 2-3 gm/litre, the rate of precipitation decreases. The results of Table 2 are plotted in Figure 2.

Table 2
Effect of U_3O_8 Concentration on the Rate of Precipitation

Test No.	Barren Assays gm/l			Time Hours
	Na_2CO_3	NaOH	U_3O_8	
522			7.0	0
			0.07	1.5
			0.054	4
523	59.5	3.68	0.041	20
			3.0	0
			0.077	1.5
524	55.5	3.76	0.052	4
			0.045	20
			2.0	0
525	55.1	4.00	0.11	1.5
			0.065	4
			0.071	20
526	54.0	3.68	1.5	0
			0.34	1.5
			0.19	4
527	53.0	3.60	0.072	20
			1.0	0
			0.42	1.5
528	54.0	3.56	0.20	4
			0.093	20
			0.5	0
529	54.0	3.56	0.47	1.5
			0.33	4
			0.28	20

The precipitate is believed to be in a state of equilibrium with uranium in solution, continually dissolving and reprecipitating on the particles already formed.

Most of the precipitation occurs in the first hour and yet the results are better when the initial U_3O_8 concentration is high. It appears from



this that the rate of precipitation depends upon the amount of precipitate already formed.

Because of this, several experiments were run to upgrade the pregnant solution by seeding with precipitate so that low grade liquors could be efficiently precipitated.

The Effect of Seeding Low Grade Pregnant Solutions

The results of these tests (Table 3), show that low grade liquors that are seeded with freshly precipitated diuranate behave as if the uranium were originally in solution, even though the precipitate is not completely dissolved. It is essential that the slurry be adequately stirred as sufficient precipitate must remain in suspension to be equivalent to 2-3 gm/litre U_3O_8 . The results are divided into two groups: Group (a) were obtained on beaker scale tests while Group (b) were produced from a pilot plant operation.

The added precipitate should be conditioned for a few minutes in the pregnant solution, before adding caustic, to improve its surface characteristics, although there is no evidence to show that this is absolutely necessary. In the tests conducted in the pilot plant, the assay on the pregnant was taken after the addition of precipitate and includes the precipitate that was still in slurry form.

Table 3

The Effect of Seeding Low Grade Solutions

Test No.	Hours	Pregnant U ₃ O ₈ gm/l	Total U ₃ O ₈ gm/l after seeding	Barren Assays gm/l		
				Na ₂ CO ₃	NaOH	U ₃ O ₈
(a) 527	1/2	0.5	0.5			0.47
	4			54	3.56	0.33
551	1/2	0.5	1.9			0.28
	6			56.9	4.32	0.14
552	1/2	0.5	3.3			0.28
	6			58.2	4.50	0.099
553	1/2	0.5	4.7			0.25
	6			57.3	4.47	0.072
Above tests seeded with dry concentrate.						
593	2	0.5	2.25			0.067
	4					0.060
	6			54.0	3.35	0.061
594	2	0.5	6.8			0.028
	4					0.026
	6			53.8	3.88	0.024
593-594 seeded with fresh wet precipitate.						
(b) 70-79	6	1.14	no seeding	45.3	7.6	0.134
Average						
80-89		1.14	1.73	51.2	6.6	0.055
Average						
70-89 conducted during pilot plant run using freshly precipitated wet diuranate.						

The Effects of Sodium Sulphate on Precipitation

Sodium sulphate builds up in the recycled carbonate barrens, as a result of the reaction of sulphides and sodium carbonate with oxygen (eq. 2 p. 2).

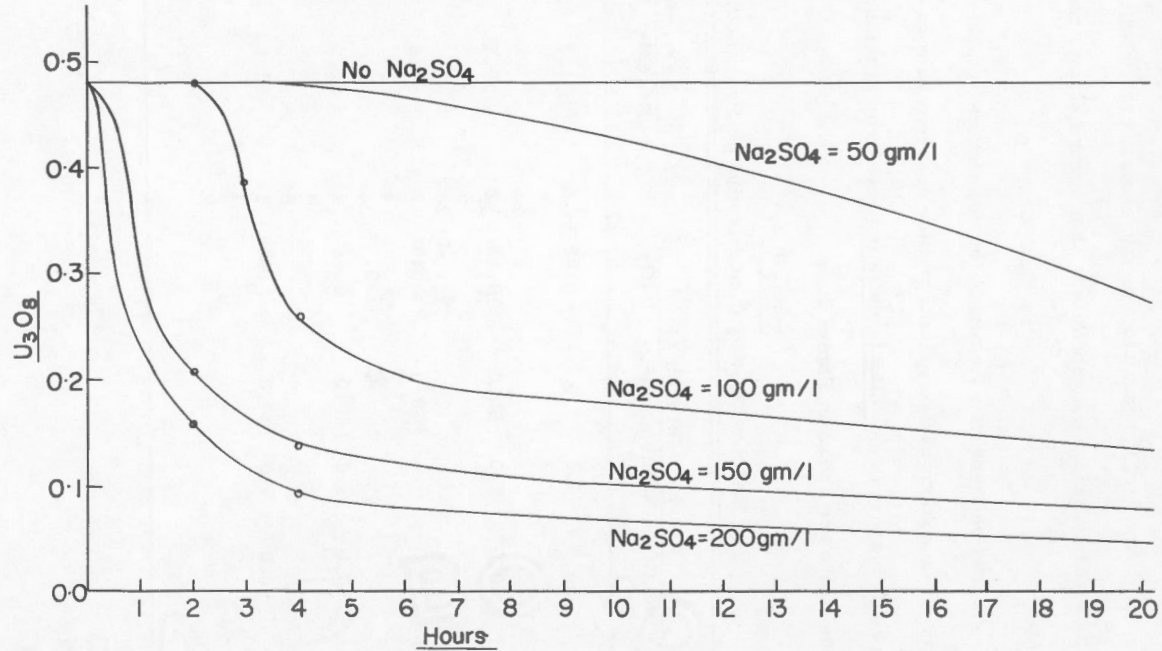
A synthetic pregnant liquor was made from the stock solution and various amounts of sodium sulphate were added. The following results (see Table 4) confirm that sodium sulphate assists precipitation. The sodium carbonate and hydroxide concentrations shown were kept as constant as possible.

It is believed that the highly ionised sodium sulphate inhibits the activity of the sodium carbonate to a greater degree than it affects the activity of the sodium hydroxide, which tends to improve precipitation. The results of these tests are shown in Figure 3.

Table 4
The Effect of Na₂SO₄ Concentration on Precipitation

Test No.	Pregnant Sol'n gm/l				Hours	Barren Assays gm/l		
	Na ₂ CO ₃	NaOH	Na ₂ SO ₄	U ₃ O ₈		Na ₂ CO ₃	NaOH	U ₃ O ₈
5111	50.0	5.0	0	0.48	2	51.3	3.6	0.48
					4			0.48
					24			3.45
5112	50.0	5.0	50.0	0.48	2	50.5	4.20	0.48
					4			0.48
					24			3.70
5113	50.0	5.0	100.0	0.48	2	50.3	4.22	0.48
					4			0.26
					24			3.48
5114	50.0	5.0	150.0	0.48	2	51.5	3.85	0.21
					4			0.14
					6			3.60
5115	50.0	5.0	200.0	0.48	2	52.1	3.90	0.16
					4			0.097
					6			3.56

FIGURE 3
EFFECT OF Na_2SO_4 CONCENTRATION ON THE
RATE OF PRECIPITATION



The Effect of Temperature on Precipitation

Data from tests to study the effects of temperature on precipitation appear in Table 5. If the temperature of precipitation is raised a larger excess of caustic is required. This is readily apparent in Figure 1 which shows plots for various temperatures of U_3O_8 concentration versus the ratio of NaOH to Na_2CO_3 in the barren.

Table 5
The Effect of Temperature on Precipitation

Test No.	Temp °C	Time Hour	Barren Assays gm/l		
			NaOH	U_3O_8	Na_2CO_3
7-233 a	25	2	1.75	0.38	
		4	1.80	0.22	
		6	1.80	0.19	
		8	1.85	0.19	46.6
7-233 b	25	2	3.30	0.067	
		4	3.32	0.041	
		6	3.32	0.033	
		8	3.40	0.034	47.2
7-233 c	25	2	4.90	0.023	
		4	4.90	0.018	
		6	4.90	0.017	
		8	4.95	0.015	46.8
7-234 a	45	2	3.91	0.020	
		4	3.91	0.025	
		6	3.91	-	
		8	3.91	0.024	47.0
7-234 b	45	2	5.63	0.021	
		4	5.63	0.018	
		6	5.63	0.015	
		8	5.63	0.015	47.0
7-234 c	45	2	7.44	0.048	
		4	7.44	0.015	
		6	7.44	0.010	
		8	7.44	0.012	47.4
7-235 a	60	2	4.2	0.045	
		4	4.2	0.040	
		6	4.2	0.049	
		8	4.2	0.048	47.3

Table 5 (continued)

Test No.	Temp °C	Time Hour	Barren Assays gm/l		
			NaOH	U ₃ O ₈	Na ₂ CO ₃
7-235 b	60	2	6.12	0.072	
		4	6.12	0.042	
		6	6.12	0.027	
		8	6.12	0.030	47.5
7-235 c	60	2	7.93	0.050	
		4	7.93	0.026	
		6	7.93	0.018	
		8	7.93	-	47.5
7-236 a	72	2	5.94	0.083	
		4		0.031	
		6		0.031	
		8		0.034	50.0
7-236 b	72	2	7.89	0.045	
		4		0.031	
		6		0.030	
		8		0.032	50.4
7-236 c	72	2	10.0	0.032	
		4	10.0	0.025	
		6	10.0	0.025	
		8	10.0	0.024	50.5
531	75-80	0		3.0	
		0.5		0.47	
		1		0.42	
		4		0.20	
		6		0.23	
		20	4.96	0.22	55.0
532	25	0		3.0	
		0.5		0.23	
		1		0.17	
		4		0.07	
		6		-	
		20	4.30	0.05	60.0

The Rate of Precipitation

In Table 2 and Figure 2, the results show that approximately 4-6 hours are required for complete precipitation, depending on the concentrations above 2.0 gm U₃O₈ per litre.

The Effect of NaOH Excess on the Apparent Composition of the Precipitate

The results of these tests were inconclusive. Many of the tests previously listed show that the precipitate changes composition with the amount of precipitate added, while others do not. The assayed caustic excess was always less than the calculated excess, indicating a uranate of higher sodium/uranium ratio than the diuranate. The results in Table 6 were obtained by precipitating solutions made by diluting a stock solution of the following composition:

<u>U₃O₈</u> gm/l	<u>Na₂CO₃</u> gm/l	<u>NaHCO₃</u> gm/l
48.0	18.4	51.7

In calculating caustic excess, the formation of sodium diuranate, Na₂U₂O₇, is assumed.

Table 6

The Effect of NaOH Excess on the Composition of the Precipitate

Test No.	Pregnant Sol'n gm/l			Barren Sol'n gm/l		Δe 5 Hr	24 hr
	U ₃ O ₈	Na ₂ CO ₃	Calc. NaOH excess	assayed NaOH excess 5 Hr	24 hr		
5131	4.9	50	4.0	3.26		-0.74	
5132	4.9	50	6.0	4.96		-1.04	
5133	4.9	50	8.0	6.70		-1.30	
5134	4.9	18.4	2.0	1.47		-0.53	
5141	4.9	18.4	0.97	0.58		-0.39	
5142	4.9	18.4	3.97	3.31		-0.66	
5143	4.9	18.4	5.95	5.22		-0.73	
5144	4.9	18.4	7.99	6.52		-1.47	
5145	4.9	100.0	9.99	8.93		-1.06	
5146	4.9	100.0	5.95	4.95		-1.02	
5147	4.9	100.0	7.99	7.05		-0.94	
5148	4.9	100.0	9.99	8.90		-1.09	
5149	9.8	50.0	3.86	3.18		-0.68	
5150	9.8	50	5.90	5.20		-0.70	
5151	9.8	50	7.70	6.40	24 hr	-1.30	
5152	2.4	50	3.95	3.24	<u>2.94</u>	-0.71	-1.02
5153	2.4	50	5.97	5.55	4.91	-0.42	-1.05
5154	2.4	50	7.97	7.50	6.92	-0.47	-1.05
5155	2.4	50	12.0	11.25	10.43	-0.75	-1.57

Solutions of different carbonate samples were used, and the amount of hydroxide used was varied. Δe is the difference obtained by subtracting the barren NaOH assays from the calculated excess added. In all cases it is negative, indicating that a uranate of higher Na/U ratio than the diuranate is found. Figure 4 shows the results of these tests, and indicates how the factor used for calculating the NaOH excess might change with the excess required.

In tests 5149-5151, the amount of U_3O_8 is doubled. This should increase the discrepancy in caustic excess by the same factor, which it does not. It is possible that when the U_3O_8 is increased, a precipitate is formed containing more uranium than would be found in the precipitates from a lower grade solution. However, in tests 5152-5155 the U_3O_8 is half the concentration existing in 5131. This should produce only half the error, assuming the precipitate does not change composition. There is no significant difference in Δe between the low and high caustic excesses, although the difference does increase with time.

Table 7 contains the results of tests devised to see what change in NaOH excess took place with time.

These results show that there was no conversion of NaOH to Na_2CO_3 by CO_2 absorption. The observed differences do change with time, but the titration error obscures the results to some extent. Analyses of precipitates produced under similar conditions show the composition of the dry product to be essentially $Na_2U_2O_7$. The following assays were made on precipitates from a solution * containing 8.5 gm/litre U_3O_8 , approximately 53 gm/litre Na_2CO_3

* Reported by V. Harrison. Dept. of Mines SR-220/54.

Table 7

Effect of Time on the Amount of NaOH in the Barren

Test No.	Pregnant Sol. gm/l		NaOH Excess	Hours	Barren Assays gm/l			Δe
	U ₃ O ₈	Na ₂ CO ₃			NaOH	Na ₂ CO ₃	U ₃ O ₈	
571	2.5	48.0	5.2	1	4.70	47.0	0.087	0.50
				24	4.78	49.0	0.024	0.42
				48	4.48	51.0	0.021	0.72
				120	4.48	47.0	0.014	0.72

and 3.2 gm/litre NaOH (Calculated excess 4.0 gm/litre).

<u>Precipitate</u>	<u>% U₃O₈</u>	<u>% Na</u>
A	83.2	6.6
B	82.8	7.0
C	80.4	6.5
Average	82.2	6.7

The ratio of U₃O₈ to Na for the average product above is almost the same as the theoretical U₃O₈ to Na ratio for sodium diuranate.

<u>Theoretical Compositions</u>	<u>% U₃O₈</u>	<u>% Na</u>
Sodium uranate Na ₂ O . UO ₃	81.0	13.2
Sodium diuranate Na ₂ O . 2 UO ₃	88.0	7.25

The sodium diuranate U₃O₈/Na ratio is the same as for the averaged precipitates.

$$\frac{88.0}{7.25} = \frac{82.2}{6.76} \text{ compared with } \frac{82.2}{6.7} \text{ above.}$$

For this reason the precipitate is believed to be sodium diuranate when it is washed and dried. For calculating the approximate excess of sodium hydroxide, assuming an accurate assay for the sodium bicarbonate, the factor 0.428 has been used to compute the sodium hydroxide requirements for converting Na₄UO₂ (CO₃)₃ to Na₂U₂O₇, (equation 3, p.2). It is proposed to increase the factor to a value which might give a closer

prediction of the actual excess that would be present after precipitation. A curve for performing this calculation (based on experimental results) is given in Figure 4.

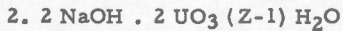
The experimental data, although inconsistent, indicate that part of the sodium hydroxide may be loosely attached to the precipitate, and is removed during filtration and washing. The results also indicate that the amount of caustic removed varies directly with the excess added, over a limited range.

Changes in the sodium carbonate concentration do not seem to change the amount of bound hydroxide.

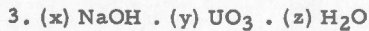
According to the results obtained, less sodium hydroxide is bound when the uranium is high than when it is low. A suggested mechanism for the formation of the diuranate, containing bound hydroxide follows:



Rearranging the hydrated diuranate in (1) we get



Writing this generally we have



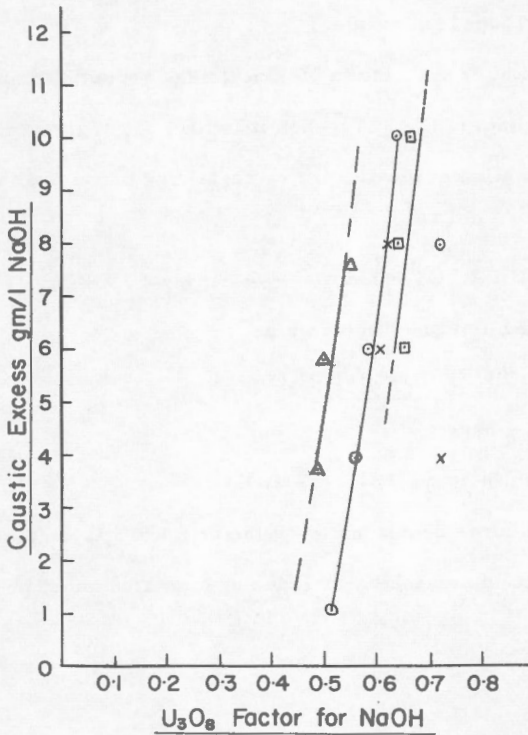
If (x) is large compared to (y) the compound is unstable, and some sodium hydroxide is washed out reducing it to a composition similar to the diuranate.

FIGURE 4

APPARENT EFFECT OF NaOH EXCESS ON THE

$\frac{\text{Na}_2\text{O}}{\text{UO}_3}$ RATIO IN THE PRECIPITATE

○ Tests 5141-5145	50 gm/l Na_2CO_3	4.8 gm./l U_3O_8
△ Tests 5149-5151	50 gm/l Na_2CO_3	9.6 gm./l U_3O_8
□ Tests 5146-5148	100 gm/l Na_2CO_3	4.9 gm./l U_3O_8
x Tests 5152-5154	50 gm/l Na_2CO_3	2.4 gm./l U_3O_8



Acknowledgment

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The writer has drawn freely upon the results and work of other people in the Radioactivity Division in preparing this paper, notably the results of R. Simard, D. Light and V. Harrison.

References

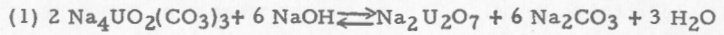
Trans, Far Society 45, 618, 1949

Chem. Review 28, 443, 1941

J. Phys. Chem. 59, 653, 1955

APPENDIX

The following factors are used for determining the amount of caustic soda required as excess.



$$\text{NaOH required for U}_3\text{O}_8 = \text{U}_3\text{O}_8 \times 0.428$$

$$\text{" " " NaHCO}_3 = \text{NaHCO}_3 \times 0.476$$

The excess required depends on Na₂CO₃ and U₃O₈ value required in barren. (See Figure 1.)

The activity coefficients shown are taken from the literature, Na₂CO₃ activity coeff. γ J. Phys Chem. 59, 653, 1955.

M	15°C	25°C	375°C	50°C	65°C
0.1	0.448	0.465	0.504	0.524	0.529
0.2	0.371	0.393	0.441	0.466	0.471
0.4	0.306	0.331	0.382	0.405	0.405
0.6	0.273	0.300	0.349	0.367	0.365
0.847	0.249	0.276	0.321	0.334	0.325
1.0	0.237	0.263	0.303	0.316	0.303
1.536	0.210	0.230	0.268	0.274	0.263

Trans Far, Society 45;618, 1949
Chem. Review 28, 443, 1941

Activity Coefficients

M	NaOH	$K_4Fe(CN)_6$	Na_2SO_4
0.05	0.818	0.189	0.529
0.1	0.766	0.139	0.445
0.2	0.727	0.100	0.365
0.3	0.708	0.081	0.321
0.4	0.697		
0.5	0.690		0.268
0.6	0.685		
0.7	0.681		0.234
0.8	0.679		
0.9	0.678		
1.0	0.678		0.203
1.2	0.681		0.188
1.4	0.686		
1.6	0.692		
1.8	0.700		
2.0	0.709		0.153

Determination of Na₂CO₃

A 2, 5 or 10 ml aliquot, depending on concentration, is diluted to approximately 150 ml and titrated with 0.1 N HCl using a pH meter (preferably of the automatic recording type) to increase the end points at pH 8.3 and 4.1.

In the presence of NaHCO₃, such as occurs in leach liquors, the carbonate is calculated using end point pH 8.3.

$$\text{gm/1 Na}_2\text{CO}_3 = \frac{\text{ml} \times \text{N HCl} \times 106}{\text{aliquot}}$$

If NaOH is present (barren solution), titrate to pH 8.3 and pH 4.1. The Na₂CO₃ is calculated as

$$\text{gm/1 Na}_2\text{CO}_3 = \frac{(\text{ml pH } 4.1 - \text{ml pH } 8.3) \times \text{N HCl} \times 106}{\text{aliquot}}$$

Determination of NaHCO₃

A 100 ml aliquot is titrated with 2-2.5 N NaOH *(carbonate-free) using a pH meter to measure the end point at pH 11.5. (Figure 5)

$$\text{gm/1 NaHCO}_3 = \frac{\text{ml} \times \text{N NaOH} \times 84}{\text{aliquot}}$$

* NaOH will precipitate U₃O₈ in concentrated solution unless extra Na₂CO₃ is added to keep it in solution.

Determination of NaOH

A 20 ml aliquot is diluted to 150 ml and 12-15 gms of BaCl₂ is added to precipitate the carbonate. The solution is then titrated with 0.1 N HCl to pH 9.0 using a pH meter to determine the end point. (See Fig. 6)

$$\text{gm/1 NaOH} = \frac{\text{ml} \times \text{N HCl} \times 40}{\text{aliquot}}$$

Standard Solutions

HCl is standardized against Na_2CO_3 .

Weigh approx. 2 gm Na_2CO_3 and titrate to pH 8.3.

$$N = \frac{\text{Sample wt} \times 1000}{106 \times \text{ml}}$$

NaOH is standardized against 2 gm NaHCO_3 at pH 11.5

$$N = \frac{\text{Sample wt} \times 1000}{84 \times \text{ml}}$$

Calculation of Approximate U_3O_8 Content

Continue the titration of Na_2CO_3 to pH 4.1 using the pH meter and calculate the apparent NaHCO_3 content as follows:

$$\frac{(\text{Titration pH 4.1} - 2 \times \text{titration pH 8.3}) \times N \text{ HCl} \times 84}{\text{aliquot}} = \text{apparent NaHCO}_3 \text{ gm/l}$$

Using values obtained for true NaHCO_3 calculate the approximate U_3O_8 content as follows:

$$(\text{NaHCO}_3 \text{ apparent} - \text{NaHCO}_3 \text{ true}) \times 0.555 = \text{U}_3\text{O}_8 \text{ gm/l}$$

Note

It was reported by the writer in 1951 at the Department of Mines, that the complex $\text{UO}_2(\text{CO}_3)_3^{-4}$ did not titrate at pH 8.3, but did react at pH 4.1, producing an error in the bicarbonate determination which depended upon the U_3O_8 concentration. If the solution is analyzed for HCO_3^{-1} by using NaOH, the true bicarbonate is determined.

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FIGURE 5

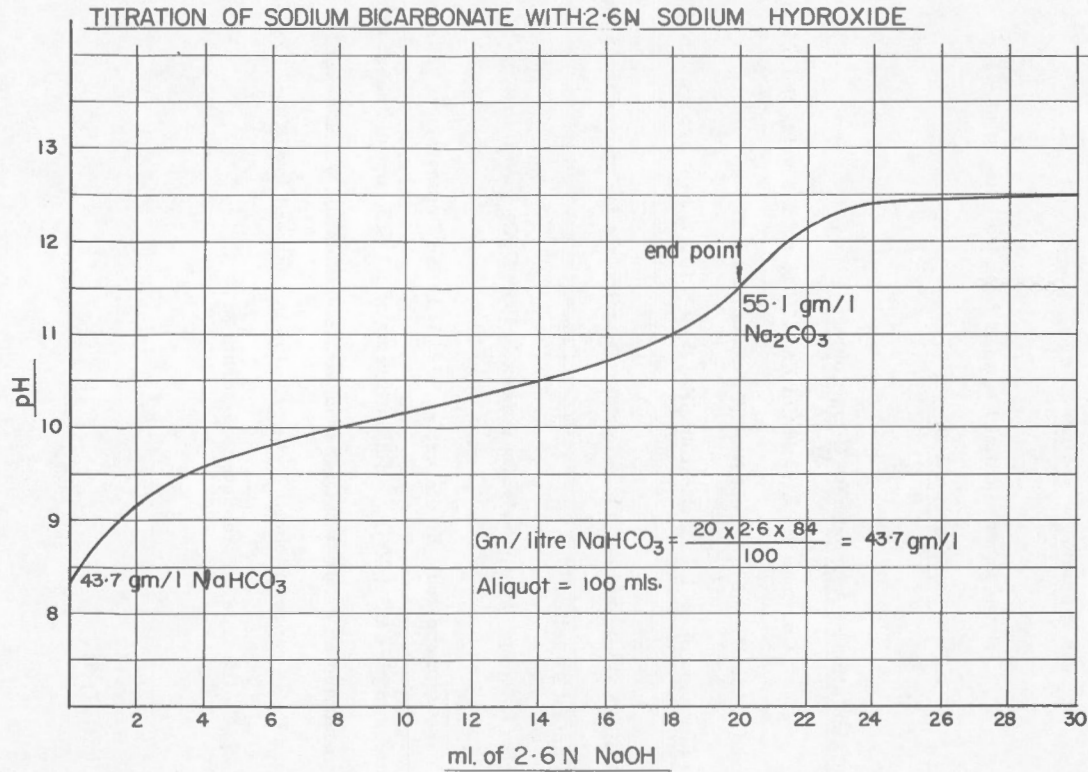
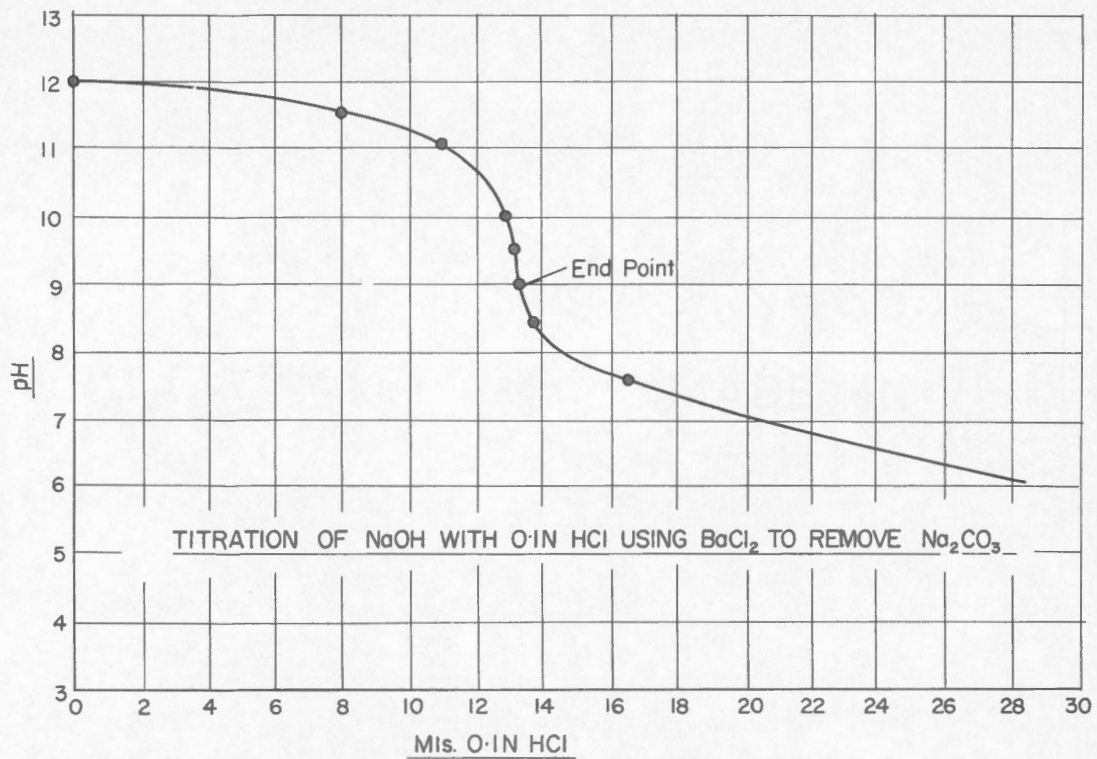
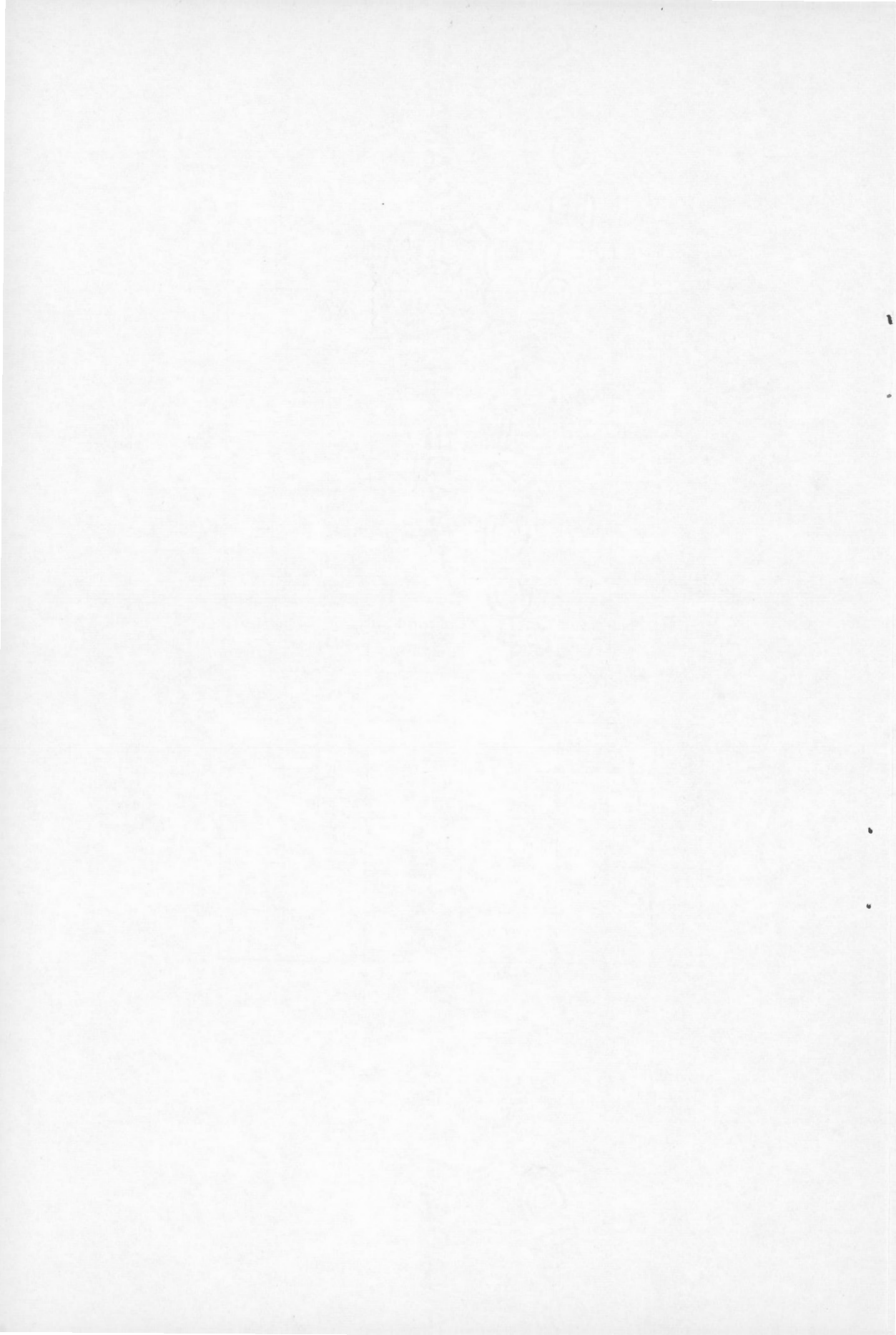


FIGURE 6





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