~~CONFIDENTIAL~~

Report No. BMI-1115
Technology - Feed Materials
(M-3679, 18th Ed.)

UNCLASSIFIED

Contract No. W-7405-eng-92

INVESTIGATION OF AMMONIUM URANATES

by

Robert A. Ewing
Samuel J. Kiehl, Jr.
Arthur E. Bearse

Classification changed for change to UNCLASSIFIED
by H. H. Kiehl, Jr. from Declassification Bureau
Date August 20, 1956 - P. 56
H. H. Kiehl, Jr.

July 19, 1956

RESTRICTED DATA

This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmittal or disclosure of its contents in any manner to an unauthorized person is prohibited.

BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

CONFIDENTIAL

UNCLASSIFIED

~~CONFIDENTIAL~~

3 and 4

UNCLASSIFIED

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	5
INTRODUCTION	5
SURVEY OF THE LITERATURE	6
PRECIPITATION FROM DILUTE SOLUTIONS	9
PRECIPITATION FROM CONCENTRATED SOLUTIONS	12
MISCELLANEOUS PREPARATION METHODS	16
STABILITY AND STRUCTURE OF THE AMMONIA PRECIPITATE	18
CONCLUSIONS	23
ANALYTICAL METHODS	24
RECOMMENDATIONS FOR FUTURE WORK	26
REFERENCES	26

UNCLASSIFIED

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

5

INVESTIGATION OF AMMONIUM URANATES

Robert A. Ewing, Samuel J. Kiehl, Jr.,
and Arthur E. Bearse

Precipitation of aqueous uranyl salt solutions with excess ammonium hydroxide results in products with NH_4 : uranium mole ratios of approximately 0.5:1. This study has indicated that the theoretical ammonium diuranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7$, cannot be precipitated and isolated from an aqueous system under normal conditions, even in the presence of large excesses of concentrated NH_4OH .

The amorphous precipitate of a NH_4 : uranium ratio of approximately 0.5:1 loses essentially no ammonia at 105 C. Upon leaching in hot water, it hydrolyzes to a crystalline product with an NH_4 : uranium ratio of about 0.3:1. The X-ray diffraction pattern of this product suggests that it may be a definite compound, possibly analogous to the $\text{Na}_2\text{U}_2\text{O}_7$ sodium uranate.

Ammonium uranate precipitated from ammonium carbonate solution was significantly more crystalline and free filtering than that precipitated from uranyl salt solutions.

INTRODUCTION

In the present process for refining uranium, uranyl nitrate from the solvent-extraction step is thermally denitrated to UO_3 . This is subsequently reduced to UO_2 and then hydrofluorinated to UF_4 . It has long been known that a much more reactive form of UO_3 may be prepared by precipitation of the uranyl nitrate solution with ammonia, followed by calcination to convert the precipitate to the oxide. This desirable increased reactivity also carries on through the reduction and hydrofluorination steps. However, like many hydroxide and hydrous oxide precipitates, the ammonia precipitate is bulky and of low density. The UF_4 produced via this procedure is of considerably lower density than that resulting via the thermal-denitration procedure. This characteristic, which reduces the quantity of UF_4 which can be charged to the magnesium reduction bombs, has had much to do with the decision to use thermal denitration. However, recent advances in technology, which include methods of densifying UO_3 prepared via precipitation, have created renewed interest in this procedure, in order to take advantage of the increased reactivity.

UNCLASSIFIED

~~CONFIDENTIAL~~

UNCLASSIFIED

~~CONFIDENTIAL~~

The National Lead Company of Ohio, operators of FMPC, considering possible improvements and revisions in process technology, were interested in evaluating ammonia precipitation and calcination as an alternative to thermal denitration. In connection with this evaluation, it was desired to characterize ammonium uranate precipitates, and to obtain thermodynamic data on the true ammonium diuranate, $(\text{NH}_4)_2 \text{U}_2\text{O}_7$.

The work was done in cooperation with the chemical research and development groups at NLO, who were also attacking the problem of preparing ammonium diuranate, although their efforts were devoted primarily to studies on a pilot-plant scale.

SURVEY OF THE LITERATURE

The literature on the alkaline uranates presents a confused picture. These compounds have been investigated by a number of workers, especially in France, but the results have not always been concordant. Nearly all of the reported work has been conducted on either sodium or potassium uranates; the ammonium uranates have been virtually unexplored. There are numerous casual references to the precipitation of ammonium diuranate in AEC literature, but no systematic studies have been reported.

It was originally believed that the addition of alkali hydroxides to solutions of uranyl salts resulted in the precipitation of yellow uranyl hydroxide (or hydrated UO_3), which then reacted with alkali to form the orange diuranate. Britton^(1, 2), in his electrometric studies of the precipitation of hydroxides, considered the yellow precipitate to be $\text{UO}_2(\text{OH})_2$ hydrate.

Subsequently, Flatt and Hess⁽³⁾ established, by a phase-rule study, that the initial stage is not a hydroxide, but a uranate. They found only two uranates, most closely represented by the ratios $\text{K}_2\text{O} \cdot 7\text{UO}_3 \cdot x\text{H}_2\text{O} = \text{K}_2\text{U}_7\text{O}_{22} \cdot x\text{H}_2\text{O}$ (yellow) and $2\text{K}_2\text{O} \cdot 5\text{UO}_3 \cdot x\text{H}_2\text{O} = \text{K}_4\text{U}_5\text{O}_{17} \cdot x\text{H}_2\text{O}$ (orange), which were formed when uranyl nitrate was treated with potassium hydroxide. They considered precipitates of intermediate colors to be mixtures of these two precipitates. Flatt and Hess never observed the formation of the diuranate, $\text{K}_2\text{U}_2\text{O}_7$, even in solutions very strongly alkaline, and concluded that this compound was not obtainable by aqueous methods.

An analogous formula, $\text{Na}_4\text{U}_5\text{O}_{17}$, was also proposed earlier by Metzger and Heidelberg⁽⁴⁾, who investigated its composition in connection with its utilization in the analysis of uranium. However, they cautioned

(1) References at end.

UNCLASSIFIED

~~CONFIDENTIAL~~

~~UNCLASSIFIED~~
~~CONFIDENTIAL~~

7

that the formula was merely intended to express the analytical results and was not to be taken as indicating the exact composition of the compound.

Gulter(5, 6) attributed the formula $\text{Na}_2\text{U}_8\text{O}_{25}$ ($\text{Na}_2\text{O} \cdot 8\text{UO}_3$) to the uranate obtained with caustic and uranyl acetate, and $\text{Na}_4\text{U}_7\text{O}_{23}$ ($2\text{Na}_2\text{O} \cdot 7\text{UO}_3$) to the one obtained with uranyl nitrate.

Tridot(7), alone among the investigators, studied all three alkalies, NaOH , KOH , and NH_4OH . Largely on the basis of potentiometric and conductimetric titrations, he postulated that, upon the combination of sodium or potassium hydroxide and uranyl nitrate, the uranates $\text{Na}_2\text{U}_5\text{O}_{16}$, $\text{Na}_2\text{U}_2\text{O}_7$, and NaUO_4 are formed. He states that the diuranate is stable in the final mixture or in water, contrary to the views of others.

Tridot is one of the few workers who has studied the reaction of ammonium hydroxide with uranyl salts in any detail. He showed a sharp break in the conductivity curve at 2 moles of NH_4OH and concluded that this represented precipitation of uranyl hydrate, according to the reaction:

Upon the addition of 3 moles of NH_4OH , slight inflections in both the pH and conductivity curves were noted, at a pH of about 9.3. His conclusion was that this represented the diuranate, which he postulated is the final product obtained upon the addition of ammonia to a solution of uranyl nitrate. However, no analyses of ammonium diuranate are presented to substantiate this conclusion. His reported 1:1 ratios are based solely on back titration of filtrates, with the ammonia in the precipitate calculated by difference.

Wamser(8) and his collaborators, studying the uranates precipitated by the addition of sodium hydroxide to uranyl nitrate, concluded that two uranates $\text{Na}_2\text{U}_7\text{O}_{22}$ (yellow) and $\text{Na}_6\text{U}_7\text{O}_{24}$ (orange) (or mixtures thereof) are formed. When NaOH was added to the point of incipient precipitation (requiring 1 or more moles of NaOH per mole of uranium) basic uranyl ions of the type $\text{UO}_3\text{UO}_2^{++}$ and $(\text{UO}_3)_2\text{UO}_2^{++}$ were formed. In this conclusion they are in good agreement with Sutton(9), who has presented the results of an intensive study of the hydrolysis of the uranyl ion in perchlorate solutions. The further addition of NaOH (to NaOH :uranium = 2.29) effected the quantitative precipitation of uranium as $\text{Na}_2\text{U}_7\text{O}_{22}$, which reacted with further NaOH (to NaOH :uranium = 2.86) to produce $\text{Na}_6\text{U}_7\text{O}_{24}$, which they regarded as the species stable in the presence of excess alkali.

The precipitates were prepared by combining various mixtures of NaOH and uranyl nitrate solution, which were maintained at room temperature for five days to permit establishment of equilibrium. The precipitates were washed until the free alkalinity in the washings first reached the constant low value which it would maintain indefinitely thereafter.

~~CONFIDENTIAL~~

~~UNCLASSIFIED~~

CONFIDENTIAL

8

X-ray diffraction patterns obtained on these precipitates indicated that (1) the first permanent precipitate to appear and all of those obtained up to a pH of about 6 (yellow) had the same characteristic pattern, resembling, but not identical with, the uranyl hydroxide ($\text{UO}_3 \cdot \text{H}_2\text{O}$) pattern; (2) all the (orange) precipitates obtained in the presence of excess alkali ($\text{pH} > 10$) had a characteristic and different pattern; and (3) intermediate precipitates exhibited both patterns.

It was also noted in this report that treatment of uranyl nitrate with sodium hydroxide in no instance yielded a precipitate which could be identified as uranyl hydroxide, either on the basis of chemical or X-ray analysis. Even the first precipitate on treatment of uranyl nitrate with ammonia was stated to be a uranate containing ammonium. However, it was found that uranium could be precipitated as the hydroxide [$\text{UO}_2(\text{OH})_2$ or $\text{UO}_3 \cdot \text{H}_2\text{O}$] with certain weak bases such as pyridine or aniline.

Sutton⁽¹⁰⁾, who has done the most recent work on the alkaline uranates, disputes the formulas proposed by Flatt and Hess⁽³⁾ and Wamser⁽⁸⁾. His work led him to conclude that two uranates are formed, $\text{Na}_2\text{U}_{16}\text{O}_{49}$ (yellow) and the true diuranate, $\text{Na}_2\text{U}_2\text{O}_7$ (orange), on the addition of sodium hydroxide to uranyl chloride. Sutton allowed his samples to stand for weeks or months, to insure attainment of equilibrium. The precipitates were not washed, but centrifuged, and the phases analyzed for sodium, chlorine, and uranium, from which the composition of the precipitate proper could be calculated.

He also showed that equilibrium of the yellow uranate with a solution of pH below 7 led to the decomposition of the precipitate:

He states that the decomposition occurs very readily, and that the final product is best represented by the composition $\text{Na}_2\text{U}_7\text{O}_{22}$. For the orange precipitate at elevated pH, the reasoning was the same. Hydrolysis occurs upon washing with water, lowering the sodium:uranium ratio below the initial 1:1.

Sutton also prepared some sodium diuranate by fusion. The X-ray diffraction patterns of this material showed some of the same intense lines noted by Wamser⁽⁸⁾ in the pattern of the orange precipitate.

Sutton's postulations appear to explain many of the numerous disagreements among previous investigators. The assumptions that both the yellow and orange uranates are equilibrium compositions but slowly attained, and also that both are very susceptible to hydrolysis, are consistent

CONFIDENTIAL

CONFIDENTIAL

9

with most of the results presented. The amorphous nature of the products obtained by precipitation has resulted in much of the evidence being obtained by indirect methods. A potentially large source of error in this procedure (which may explain some of the disagreements) is the analytical difficulty encountered in accurately determining small quantities of sodium, potassium, and nitrate, especially the former two.

The assignment of the formula $M_2U_7O_{22}$ to the yellow uranate by numerous investigators suggests that this is a stable terminal state, quite readily attained, confirming Sutton's hypothesis. In the case of the diuranate, failure to attain equilibrium initially, plus a slower rate of hydrolysis, would appear to account for the many postulated compositions less alkaline than $M_2U_2O_7$. All evidence indicates that pure diuranate cannot be isolated from solution; any attempt to wash out occluded mother liquor also alters the composition, to something between $M_2U_2O_7$ and $M_2U_7O_{22}$.

No really conclusive evidence has been presented for the weak alkalis such as ammonium hydroxide; the evidence to date has been so tenuous and indirect as to be questionable. The work presented in this report, though also not entirely conclusive, tends to support the conclusion that ammonium diuranate, $(NH_4)_2U_2O_7$, cannot be obtained in aqueous media, at least under normal conditions.

PRECIPITATION FROM DILUTE SOLUTIONS

One of the primary objectives of the investigation was to prepare pure ammonium diuranate for subsequent thermodynamic studies. While purity of a presumably readily attainable compound was still the objective, most of the test work was conducted with dilute solutions. Later, when attempting only to prepare an ammonium diuranate, of any purity, more concentrated solutions, up to 0.7 M uranium and concentrated NH_4OH , were employed.

Uranyl sulfate solutions were used in most of the early tests. The uranyl sulfate solutions were prepared from Mallinckrodt UO_3 , which had been heated at 300 C for 25 to 60 hr to dehydrate it and to eliminate the slight quantity of residual nitrates. Based on the loss on ignition, this UO_3 contained 99.5 to 99.7 w/o UO_3 . After purity became of secondary importance, uranyl nitrate solutions were also utilized. Mallinckrodt $UO_2(NO_3)_2 \cdot 6H_2O$ was used, without treatment, for the uranyl nitrate solutions.

CONFIDENTIAL

CONFIDENTIAL

10

In the initial test, 1 N NH_4OH was added to an 0.035 M UO_2SO_4 solution, at the ratio of 3 moles to 1. Terminal pH was 8.6. The air-dried precipitate analyzed 1.90 w/o NH_4 and 73.0 w/o uranium, a ratio of NH_4 :uranium of 0.34:1.

At the suggestion of NLO personnel, reverse order of addition (addition of a uranyl sulfate solution to an ammonium hydroxide solution) was next tested. Eight liters of UO_2SO_4 (0.09 M) was added slowly, with vigorous agitation, to 8 liters of approximately 0.45 M NH_4OH . The molar ratio of NH_4OH :uranium was 5:1, an approximately twofold excess. Terminal pH was 9.7. The supernate was decanted and the precipitate repulped in approximately 15 liters of pH 9.5 NH_4OH (~0.005 M). Upon repulping a second time in pH 9.7 NH_4OH , appreciable peptization occurred, and settling became very poor; the supernate was still very turbid after several days of standing. Three samples from this test were analyzed. One comprised the extremely fine suspended material from the turbid supernate, which was decanted and coagulated by addition of a small quantity of $(\text{NH}_4)_2\text{SO}_4$. A sample of the coarse settled precipitate and a grab sample of the agitated slurry comprised the other two. The filtered, unwashed, precipitates were analyzed either as wet pulps, or after air drying at room temperature. Results were as follows:

	<u>Wet Precipitate</u>			<u>Air-Dried Precipitate</u>		
	<u>w/o</u>		<u>Mole Ratio,</u> <u>NH_4:U</u>	<u>w/o</u>		<u>Mole Ratio,</u> <u>NH_4:U</u>
	<u>NH_4</u>	<u>U</u>		<u>NH_4</u>	<u>U</u>	
Supernate (fines)				2.21	74.0	0.39
				2.48	73.7	0.44
				2.66	73.7	0.48
Sludge (coarse)	0.75	16.7	0.59	2.64	73.7	0.47
				2.88	73.7	0.51
Grab sample of slurry				2.66	73.7	0.48
				2.56	--	0.46

There appeared to be essentially no difference in composition between the fine and the coarse fractions. The NH_4 :uranium ratio of this test appeared to be of the order of 0.45-0.50:1, appreciably higher than that of the first test, but still only about half that of $(\text{NH}_4)_2\text{U}_2\text{O}_7$. Comparison of the analyses of the wet and dry sludge samples indicated that a slight amount of ammonia may have been lost on air drying, possibly constitutional ammonia, but more probably occluded NH_4OH .

Precipitation of a dilute (0.023 M) uranyl sulfate solution with excess 1 M NH_4OH (mole ratio 4:1) gave a slurry with a terminal pH>9. This

CONFIDENTIAL

CONFIDENTIAL

11

product had similar NH_4 :uranium ratios, as shown below:

	w/o		Mole Ratio, NH_4 :U
	NH_4	U	
Wet precipitate	1.22	34.0	0.47
Air-dried precipitate	2.48	73.4	0.45
	2.52	73.1	0.46

During some of the exploratory potentiometric titrations, it had been observed that very dilute uranyl solutions could be titrated to a pH over 9 with no visible precipitation occurring until the solution was warmed. Since this appeared to offer a means of skipping past the intermediate precipitate to a pH at which ammonium diuranate should precipitate, this approach was tested quantitatively. Eight liters of 0.004 M UO_2SO_4 was added slowly to 2 liters of 0.37 M NH_4OH (a mole ratio of NH_4 :uranium of about 20:1). No precipitation occurred upon adding all of the uranium; the solution was perfectly clear, showing no Tyndall effect. Terminal pH was 10.1, presumably well above the equilibrium pH for $(\text{NH}_4)_2\text{U}_2\text{O}_7$. Precipitation set in some time later; upon heating to 60 to 65 C precipitation appeared complete, although the precipitate remained suspended. When it showed no indications of settling upon standing, it was coagulated by the addition of 1 g per liter of $(\text{NH}_4)_2\text{SO}_4$. The unwashed precipitate analyzed as follows:

	w/o		Mole Ratio, NH_4 :U
	NH_4	U	
Wet precipitate	1.33	31.9	0.55
Air-dried precipitate	2.34	73.6	0.42
	2.68	73.6	0.48
	3.08	73.6	0.55
	2.58	73.7	0.46
	2.78	--	0.50

This technique, which somewhat resembles homogeneous precipitation, gave products with ratios differing little from those of the previous tests.

It will be noted that the agreement of replicate ammonia determinations was not good. This was a problem throughout the investigation. It was possible to spend only very little effort on study of the causes of the difficulty, and the source was not definitely ascertained.

The NH_4 :uranium ratio of the original wet precipitate in the above test was erroneously believed to be 0.99:1 for a considerable period.

CONFIDENTIAL

CONFIDENTIAL

12

Since some of the early data on the original wet precipitate in the above test led to the conclusion that true ammonium diuranate had been prepared by this procedure, but had degraded upon drying, several attempts were made to reproduce these results, without success. Results of the various attempts are summarized in Table 1.

In some of the reverse precipitations, there was no precipitation for some time after adding the uranyl sulfate, so that precipitate formation actually took place in an environment of pH 10.5. One would expect to obtain a significant yield of $(\text{NH}_4)_2\text{U}_2\text{O}_7$ under these conditions, even if not quantitative conversion, if the compound were attainable in an aqueous system. However, the NH_4 :uranium ratios of these precipitates likewise ranged around the usual 0.5:1 level.

Small quantities of $(\text{NH}_4)_2\text{SO}_4$ were added to the slurry in most of the tests, to coagulate the suspended precipitate into a filterable product. A few of the filtered precipitates were given a limited water wash, without apparent effect upon the composition. Both of these variables appeared to have a negligible effect upon the results.

PRECIPITATION FROM CONCENTRATED SOLUTIONS

When preliminary results from the investigation being conducted concurrently at NLO indicated that NH_4 :uranium ratios more nearly approaching 1:1 were attainable by reverse precipitation, using concentrated NH_4OH and about 0.4 M uranyl nitrate solutions, it was suggested that the use of more concentrated solutions be examined here.

A number of such tests were conducted, using both concentrated and 1:1 NH_4OH , and several uranium concentrations. With such strong ammonium hydroxide, elimination of occluded NH_4OH became somewhat of a problem. Various techniques were used. In the tests using 1:1 NH_4OH , the precipitates were either repulped or washed in place on the filter, using distilled water adjusted to a pH of 11.3 with NH_4OH . In the tests with concentrated NH_4OH , the precipitates were washed on the filter with distilled water, except in one case, in which concentrated NH_4OH was used. In this latter test, the odor of residual ammonia was strong until air drying was essentially completed; no ammonia analysis was therefore made of the wet precipitate.

None of the variables in ammonia concentration, uranium concentration, or in washing technique appeared to affect the composition of the precipitate significantly. The results, summarized in Table 2, indicate that NH_4 :uranium ratios were quite comparable to those from dilute

CONFIDENTIAL

CONFIDENTIAL

TABLE 1. AMMONIA PRECIPITATES FROM DILUTE SOLUTIONS

UO ₂ SO ₄		NH ₄ OH		Order of Addition	Terminal pH	Wet Precipitate			Air-Dried Precipitate		
Molar Concentration	Volume, liters	Molar Concentration	Volume, liters			w/o		Mole Ratio, NH ₄ :U	w/o		Mole Ratio, NH ₄ :U
						NH ₄	U		NH ₄	U	
0.0044	8	0.37	2	Reverse	9.9	1.21	26.9	0.59	2.32	73.2	0.42
0.0088	8	0.74	2	Reverse	10.2	1.28	25.1	0.67	2.32	73.2	0.42
0.0044	12	0.37	3	Reverse	9.6	1.20	29.5	0.54	2.44	73.3	0.44
0.0044	12	1.5	3	Reverse	10.5	1.48	31.8	0.61	2.76	72.8	0.50
									2.92	-	0.53
									2.97	-	0.54
0.0044	8	1.5	2	Reverse	10.6	1.26	32.3	0.52	2.48	73.5	0.44
0.0044	8	1.5	2	Forward	-	-	-	-	2.91	73.8	0.52

CONFIDENTIAL

TABLE 2. AMMONIA PRECIPITATES FROM CONCENTRATED SOLUTIONS

Salt Used	Uranium		NH ₄ OH Volume, ml	Terminal pH	Wet Precipitate			Air-Dried Precipitate		
	Concentration, g per liter	Volume, ml			w/o		Mole Ratio, NH ₄ :U	w/o		Mole Ratio, NH ₄ :U
					NH ₄	U		NH ₄	U	
1:1 NH ₄ OH										
UO ₂ (NO ₃) ₂	90	100	200	10.3	2.39	22.25	1.4	3.29	72.4	0.60
					1.39	31.0	0.59	3.15	72.7	0.58
					1.56	37.2	0.55	3.19	-	0.57
UO ₂ (NO ₃) ₂	90	100	300	10.8	1.29	25.1	0.68	3.29	72.4	0.60
					1.17	28.8	0.53	3.00	72.5	0.55
								3.09	-	0.56
UO ₂ (NO ₃) ₂	90	100	400	11.2				2.92	71.6	0.54
								2.93	-	0.54
								2.92	-	0.54
UO ₂ SO ₄	83	500	2000	11.2				2.58	73.6	0.46
								2.90	-	0.52
								2.64	73.7	0.47
								2.62	-	0.47
Concentrated NH ₄ OH										
UO ₂ (NO ₃) ₂	90	100	300	11.3				3.41	72.3	0.62
								3.08	72.3	0.56
UO ₂ SO ₄	42	100	400	11.45	1.46	30.4	0.63	2.65	66.8	0.52
UO ₂ SO ₄	84	100	400	11.40	1.45	28.8	0.67	2.74	72.9	0.50
					1.65	34.6	0.63	2.83	72.7	0.51
UO ₂ SO ₄	167	100	400	11.20	1.58	35.6	0.59	2.68	73.0	0.48

Note: Uranyl salt solution was added slowly to NH₄OH with vigorous agitation, at room temperature, and the precipitate filtered and washed.

CONFIDENTIAL

14

CONFIDENTIAL

CONFIDENTIAL

15

solutions. The apparently higher ratios in a few tests can presumably be attributed to the presence of occluded ammonia. The precipitate showing a ratio of 1.4:1, for example, had a strong odor of ammonia when analyzed while still wet. This precipitate was reanalyzed at intervals as it air dried. In 2 days the ratio had dropped to 0.59:1, at which level it appeared to remain thereafter.

Uranyl acetate, as a salt of a weak acid, sometimes behaves a little differently than the uranyl salts of strong acids. Tridot(7), for example, reports that the monouranate is the final product of the addition of an alkali to uranyl acetate. The behavior of uranyl acetate was examined in but one test. To 400 ml of concentrated NH_4OH was added 200 ml of 0.19 M uranyl acetate solution. In addition, gaseous NH_3 was passed through the slurry for 2 hr. Although the NH_4 content of the wet precipitate was higher (due probably to occluded NH_4OH) the air-dried product had essentially the same analysis as previous precipitates:

	w/o		Mole Ratio, $\text{NH}_4:\text{U}$
	NH_4	U	
Wet precipitate	1.71	33.4	0.75
Air-dried precipitate	2.81	72.9	0.51

The only known literature reference substantiating the existence of $(\text{NH}_4)_2\text{U}_2\text{O}_7$ with any analytical data is that of Tridot(7). Even in this instance, the ammonium diuranate precipitate was not itself isolated and analyzed. The NH_4 :uranium ratio was obtained only indirectly, by back titration of the excess NH_4OH in the filtrate, and by subtracting the NH_4OH required to form UO_3 hydrate and NH_4NO_3 (2 moles).

Attempts to confirm Tridot's results were unsuccessful. Duplicate samples of 100 ml of 0.098 N NH_4OH were added to 20 ml of 0.070 M UO_2SO_4 with vigorous agitation. After the precipitate had settled, samples of the supernate were added to excess standard sulfuric acid and then back titrated with standard NaOH . According to these analyses, the molar ratios of NH_4OH consumed to uranium added were 2.59 and 2.54:1, instead of the theoretical 3:1. If 2 moles of NH_4OH are required for the first step, the ratio of NH_4 :uranium in the precipitates would be 0.59 and 0.54, in good agreement with the numerous precipitate analyses. These data suggest that NH_4 :uranium ratios of 1:1 were not found in the precipitates because the reaction did not go to completion under the conditions used, or else that ammonium diuranate is a very transient and unstable form.

CONFIDENTIAL

CONFIDENTIAL

16

MISCELLANEOUS PREPARATION METHODS

During the course of the investigation several other methods potentially leading to $(\text{NH}_4)_2\text{U}_2\text{O}_7$ were briefly examined.

In one test, a quantity of low ratio (NH_4 :uranium = 0.59) wet precipitate from a precipitation test was placed in a covered fritted glass funnel and gaseous NH_3 passed up through it for approximately 10 hr. The final cake after air drying analyzed 2.70 w/o NH_4 and 73.4 w/o uranium, a NH_4 :uranium ratio of 0.48. The same ratio was obtained on air drying the original wet precipitate, indicating that treatment with NH_3 had no effect.

UO_3 prepared by way of peroxide precipitation is notably reactive. Some reactive UO_3 hydrate was prepared by peroxide precipitation of a uranyl nitrate solution. After ignition (275 C) the UO_3 was hydrated to the lemon-yellow UO_3 hydrate by stirring in water at room temperature for several hours. Gaseous NH_3 was then passed through the slurry for about 6 hr, the temperature being maintained at about 90 C. As the NH_4^+ concentration increased, the precipitate acquired an orange cast. The filtered precipitate was washed moderately and analyzed wet. It contained 1.74 w/o NH_4 and 42.0 w/o uranium, a NH_4 :uranium ratio of 0.55, indicating that UO_3 is also not readily converted to $(\text{NH}_4)_2\text{U}_2\text{O}_7$.

Possible interferences with this test were the temperatures of ignition and digestion. The test was repeated, including an ignition temperature of 200 C and with the NH_3 absorption conducted at room temperature. Terminal pH in this test was >11.5. Ratios, determined on the wet precipitates, were comparable to those of the first test:

	w/o		Mole Ratio, NH_4 :U
	NH_4	U	
275 C UO_3	1.25	33.7	0.49
200 C UO_3	1.30	34.8	0.49

Another approach examined was the displacement of the carbonate in the uranium tricarboxylate complex with NH_4OH . By starting with the uranium in an alkaline carbonate solution, the possibility of precipitation at a low pH is eliminated, since the solution is at all times on the alkaline side.

A quantity of ammonia precipitate (NH_4 :uranium = 0.46) was dissolved in an approximately stoichiometric quantity of $(\text{NH}_4)_2\text{CO}_3$ solution, giving a clear solution. This solution was maintained at the boiling point for 18 hr, with constant incremental additions of concentrated NH_4OH , to maintain an

CONFIDENTIAL

CONFIDENTIAL

17

excess of NH_4^+ ions at all times. After about 1 hr the precipitate had changed to a dense, rapid-settling form. Concurrently the color changed from the pale yellow of the starting precipitate to an orange. The precipitate was analyzed after air drying. The test was repeated so that a wet-precipitate analysis might be obtained. The results of both tests, summarized below, were in good agreement:

	w/o		Mole Ratio, $\text{NH}_4:\text{U}$
	NH_4	U	
First precipitate (air dried)	2.56	74.1	0.46
Second precipitate (wet)	0.99	24.9	0.52

Loss of ammonia upon drying was evidently not significant.

Perhaps the most interesting feature of these tests was the nature of the precipitates. They were not amorphous and bulky like the usual ammonia precipitate but were notably dense and rapid settling. As would be expected, filtration characteristics were extremely good.

These precipitates appear to have handling characteristics superior to any of those obtainable by straight reaction of a uranyl salt solution and ammonium hydroxide. It is anticipated that filtration rates greatly in excess of those of the usual amorphous ammonia precipitate could be realized in plant operations with this type of product.

Further study of this precipitation is needed. The composition of the precipitate is unknown. Also unknown is its reactivity. Although it is denser than the amorphous precipitates, UO_3 from it would still probably not be quite as dense as thermally denitrated UO_3 , and some densification might be necessary; the extent needed and its response to densification treatment would have to be established. Optimum conditions for precipitation would also require investigation. The precipitate showed some tendency to adhere to surfaces and this characteristic would also need studying.

The preparation of ammonia precipitates by this technique has apparently been studied very little. Stewart and Neace⁽¹¹⁾, aiming at the objective of a uniformly sized UO_2 or U_3O_8 of small micron size, studied a number of precipitation methods. They concluded that ammonium diuranate (sic) precipitated from an $(\text{NH}_4)_2\text{CO}_3$ solution produced UO_2 or U_3O_8 superior to that obtainable by other methods. Photomicrographs presented of the ammonium diuranate show it to be remarkably uniform in size and shape.

CONFIDENTIAL

CONFIDENTIAL

18

In order to avoid a completely aqueous system, precipitation of organic solutions of uranyl nitrate by NH_3 was examined briefly. Unfortunately, no solvent for anhydrous $\text{UO}_2(\text{NO}_3)_2$ is known; all known solvent complexes of uranium also contain water, and the systems are thus not completely anhydrous.

Approximately 0.067 M solutions of uranyl nitrate hexahydrate in ether, ethanol, and acetone were precipitated with gaseous NH_3 . From ether, a rapid-settling pale-yellow precipitate was obtained. The NH_4 :uranium ratio was low, presumably because of the low solubility of NH_3 in ether. From ethanol, a bulky, gummy, slightly orange precipitate resulted. From acetone, the precipitate was also bulky, and yellowish but with a distinct green cast, suggesting some reduction to +4 uranium. The solubility of NH_3 is greater in these latter two solvents, and NH_4 :uranium ratios were higher, as shown by the summarized analyses:

	Wet Precipitate			Air-Dried Precipitate		
	w/o		Mole Ratio, NH_4 :U	w/o		Mole Ratio, NH_4 :U
	NH_4	U		NH_4	U	
Ether	0.95	46.0	0.27	1.55	72.3	0.34
Ethanol	1.19	30.3	0.52	2.56	72.8	0.46
Acetone	1.39	31.9	0.57	2.62	72.3	0.48

The ratios of the precipitates from ethanol and acetone are in good general agreement with those from aqueous systems.

STABILITY AND STRUCTURE OF THE
AMMONIA PRECIPITATE

Toward the end of the investigation, the objectives were modified to include attempts to characterize the ammonia precipitate and to determine its stability. This is in itself a fairly complex problem, and it was not possible to exhaustively study it in the limited time remaining. Although some data were obtained, this phase of the work is incomplete.

Comparison of NH_4 :uranium ratios on air-dried precipitates which had aged several months with the originally determined ratios showed no changes, within the limits of precision of the ammonia analysis. Confirmation of this was offered by the analysis of a sample further dried for 68 hr at 105 C. The analyses, summarized below, indicated no significant change:

CONFIDENTIAL

CONFIDENTIAL

19

	w/o		Mole Ratio, NH ₄ :U
	NH ₄	U	
Air-dried precipitate	2.76 - 2.97	72.8	0.50 - 0.54
Dried 68 hr at 105 C	2.77	78.9	0.46

The difference in ratios is within the limits of error of the ammonia analysis, and ammonia loss is regarded as negligible.

All of the evidence to date indicates that precipitates with the maximum NH₄:uranium ratio attainable (~0.5) are stable in air up to 100 C.

Stability in an aqueous system was also checked in one test. An ammonia precipitate (precipitated from concentrated solution) with an original NH₄:uranium ratio (air-dried precipitate) of 0.48 was digested at 90 to 95 C for a prolonged period and analyzed at intervals. The analyses are summarized below:

	Wet Precipitate			Air-Dried Precipitate		
	w/o		Mole Ratio, NH ₄ :U	w/o		Mole Ratio, NH ₄ :U
	NH ₄	U		NH ₄	U	
Original precipitate	1.58	35.6	0.59	2.68	73.0	0.48
After a 4-hr digestion	0.98	37.9	0.34	1.85	73.1	0.33
After a 20-hr digestion	1.08	43.1	0.30	1.84	73.3	0.33
After a 45-hr digestion				1.76	73.3	0.31

The crystallinity of the precipitate increased noticeably during the digestion; concurrently, the orange cast of the precipitate disappeared, the color turning to yellow. When the analysis after a 20-hr digestion showed no further change in ratio, the slurry was ball milled moderately in an attempt to decrease particle size and thus promote ammonia removal. The slurry showed considerably more turbidity and poorer settling after ball milling, evidence that some size reduction had been accomplished. Upon additional digestion, the turbidity soon vanished, indicating that the condensed crystal structure had been reattained. After 25 hr of additional digestion, the NH₄:uranium ratio was still essentially the same.

The data available are insufficient to show conclusively that this is a definite compound. However, there may be an analogy between this and the similar sodium uranate. According to Sutton's data⁽¹⁰⁾, the final precipitate in equilibrium with a solution of pH 7 has the composition Na₂U₇O₂₂. The corresponding ammonium uranate would have the formula

CONFIDENTIAL

CONFIDENTIAL

20

(NH_4)₂U₇O₂₂, a NH_4 :uranium ratio of 0.286:1, in fair agreement with the 0.31-0.33 ratios found. Wamser⁽⁸⁾ presented X-ray diffraction data on a yellow sodium uranate, for which the formula $\text{Na}_2\text{U}_7\text{O}_{22}$ was given. The X-ray diffraction pattern obtained (Fe K_α radiation) on the above ammonia precipitate after 45 hr of digestion showed good crystallinity (Figure 1) and it is believed probable that this is indeed a definite compound. The X-ray diffraction data, shown in Table 3, most closely resembled, but were not identical with, Wamser's $\text{Na}_2\text{U}_7\text{O}_{22}$. No exactly identical pattern has been found.

The pattern for a typical air-dried ammonia precipitate (NH_4 :uranium ratio ~0.52) was sufficiently amorphous to preclude definite identification, but appeared to be the same. That it is not $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ is suggested by the pattern of this material after heating to 300 C; instead of altering to Type III UO_3 as the dihydrate would have done, the pattern was unchanged, except to become still more amorphous. Heating the hydrated precipitate (NH_4 :uranium = 0.31) to 450 C apparently converted it to amorphous UO_3 , except for vestiges of the original pattern.*

Thermal heating curves were obtained on a number of samples, using the method of differential thermal analysis, in an attempt to help characterize the nature of the precipitates. The curves on these precipitates were quite reproducible and invariably exhibited the characteristic inflections shown. The first reactions were low-temperature endothermic reactions, with a shoulder at about 125 C, and the main peak at 212 to 216 C, probably representing the loss of water and ammonia. Samples withdrawn after heating to 265 C had the characteristic orange-yellow of UO_3 . The peak of the subsequent exothermic reaction, evidently a major one, was reached at 441 to 447 C. The abruptness of this peak, particularly on the back side, suggests that it is primarily a phase transition, rather than a chemical reaction. Samples taken after heating to 485 C, just beyond this peak, were rather olive green in color. The nature of this exothermic reaction is not quite clear. Unfortunately, time did not permit securing analyses of material at this stage of decomposition. At about 550 C, decomposition to U_3O_8 began, reaching a peak at approximately 600 to 605 C. This, incidentally, was about 120 C lower than the corresponding temperature for a sample of MCW thermally denitrated UO_3 . The product, after heating to 700 C, was a green U_3O_8 . No further reactions beyond this temperature were noted.

*J. R. Bridge of Battelle is responsible for the X-ray diffraction data and its interpretation.

CONFIDENTIAL

CONFIDENTIAL

21

FIGURE 1. X-RAY DIFFRACTION PATTERN OF A HYDRATED
AMMONIA PRECIPITATE

CONFIDENTIAL

CONFIDENTIAL

22

TABLE 3. X-RAY DIFFRACTION DATA

Interplanar Spacings and Visually Estimated Intensities					
UO ₃ · 2H ₂ O		NH ₄ : U = 0.3		Na ₂ O · 7UO ₃ (a)	
d, Å	I/I ₀	d, Å	I/I ₀	d, Å	(b)
-	-	-	-	7.50	VS
-	-	7.17	100	-	-
7.37	100	-	-	-	-
-	-	3.73	60	-	-
-	-	-	-	3.70	W
3.66	40	-	-	-	-
3.57	90	-	-	-	-
-	-	-	-	3.53	M
-	-	3.51	80	-	-
3.47	80	-	-	-	-
-	-	-	-	3.25	S
-	-	3.21	100	-	-
3.20	90	-	-	-	-
-	-	-	-	3.18	M
3.13	80	-	-	-	-
-	-	2.81	20	-	-
2.57	50	2.57	50	-	-
2.51	20	2.50	20	2.54	M
-	-	2.31	20	-	-
-	-	-	-	2.10	W
-	-	2.04	80	2.06	M
2.03	15	-	-	2.03	W
2.00	40	-	-	-	-
-	-	1.97	50	1.98	M
1.95	60	-	-	-	-
-	-	1.88	20	-	-
-	-	1.80	20	-	-
-	-	1.78	20	1.79	W
1.77	40	-	-	-	-
-	-	-	-	1.75	W
1.74	30	-	-	-	-
-	-	1.71	20	-	-
1.70	20	-	-	-	-
-	-	1.69	40	-	-
-	-	1.66	50	-	-
-	-	1.54	20	-	-
1.44	20	-	-	-	-
-	-	1.41	20	-	-
-	-	1.38	50	-	-
1.35	30	-	-	-	-
-	-	1.31	20	-	-
-	-	1.29	20	-	-
-	-	1.26	40	-	-
-	-	1.23	40	-	-
-	-	1.21	20	-	-
1.19	25	1.19	20	-	-
-	-	1.18	20	-	-
-	-	1.15	20	-	-
-	-	1.14	20	-	-
-	-	1.12	20	-	-
1.11	15	1.11	20	-	-
-	-	1.10	50	-	-

(a) Data from Wamser, Reference (8).

(b) VS = very strong; S = strong; M = moderately strong; W = weak.

CONFIDENTIAL

CONFIDENTIAL

23

CONCLUSIONS

Reaction of aqueous uranyl salt solutions with excess ammonium hydroxide produces precipitates with maximum NH_4 :uranium mole ratios of approximately 0.5:1. The theoretical ratio for ammonium diuranate is 1:1; this latter ratio was not attained even in the presence of large excesses of concentrated NH_4OH . Concentrations employed in this work ranged from 0.0044 M uranium solutions and dilute NH_4OH , to 0.7 M uranium and concentrated (14.8 N) NH_4OH . Both forward precipitation (addition of the NH_4OH to the uranyl solution) and reverse precipitation were used; order of addition appeared to have no effect upon the NH_4 :uranium ratio. Uranyl solutions tested included sulfate, nitrate, and acetate. No differences were noted between the various anions.

Among other reactions studied were treatment of 0.5 ratio precipitates with gaseous NH_3 , treatment of a slurry of reactive UO_3 with NH_3 , and displacement of the carbonate from a solution containing uranium as the uranyl tricarbonat complex with NH_4OH . Products from these tests had NH_4 :uranium ratios of 0.46 to 0.52, in good agreement with those from aqueous precipitations. Precipitation of solutions of uranyl nitrate in several organic solvents by treatment with gaseous NH_3 gave products with similar or lower ratios.

Ammonia precipitates with an apparent NH_4 :uranium ratio around 0.5 appeared to be stable in air, at temperatures up to at least 105 C. Upon leaching in hot water, ammonia is lost, and the precipitate becomes crystalline. The residual product has an NH_4 :uranium ratio of about 0.3:1. X-ray diffraction studies of this material indicated that it may be a definite compound, possibly an ammonium uranate analogous to the postulated $\text{Na}_2\text{U}_7\text{O}_{22}$ (yellow) sodium uranate (Na :uranium ratio = 0.29).

Air-dried precipitates (NH_4 :uranium $\approx$ 0.5) have a pattern which, though too amorphous to identify with certainty, appears to be the same. X-ray diffraction furnished no evidence to indicate that the precipitates with a ratio of $\approx$ 0.5 contained any compound other than that found in the hydrated crystalline precipitate. The current exploratory studies do not explain how the approximately 0.2 moles of additional NH_4 is bound in these precipitates. The considerable variations found in NH_4 :uranium ratios among these precipitates suggest that the additional ammonia may be bound physically, by adsorption, rather than chemically. The precipitates are amorphous and may have a considerable capacity to adsorb ammonia or ammonium salts.

One notable exception to the generally amorphous nature of the precipitates was the dense crystalline product precipitated from ammonium carbonate solution. Precipitation from solutions containing carbonate ion

CONFIDENTIAL

CONFIDENTIAL

24

appears to merit further study, in connection with the problem of obtaining ammonium uranate precipitates with satisfactory handling properties.

The chemistry of the formation of the alkaline uranates from aqueous systems has been the subject of considerable disagreement in the literature, which is still not satisfactorily resolved. Most progress appears to have been made on the uranates of the strong bases; the chemistry of the uranates of the weak base ammonia appears to be still virtually unknown. The exploratory work here, while not conclusive, suggests that references in the literature to the precipitation of ammonium diuranate from aqueous uranyl salt solutions are erroneous. In view of the fact that the analysis and structure has nowhere been conclusively demonstrated, there exists a strong suspicion that true ammonium diuranate has never been prepared and isolated from an aqueous system. The experimental data obtained in this investigation suggest also that this may be impossible of attainment.

ANALYTICAL METHODS

Ammonia was determined in the various precipitates by the distillation of the ammonia from a sodium carbonate solution into a measured quantity of standard sulfuric acid. The excess sulfuric acid was then titrated to the methyl red end point with standard caustic. The difference between the titer of standard caustic required for the aliquot of sulfuric acid taken and the actual titer for the sample is the titer for the distilled ammonia.

Samples of precipitates were taken from both wet and air-dried filter cakes. Two to three-gram samples of wet cakes and 1-g samples of dried cakes were weighed. These samples were dissolved in 50 ml of water containing 1 ml of 25 volume per cent sulfuric acid in a 100-ml beaker, transferred with several rinsings of deionized water, to a 300-ml round-bottom flask, and connected to the distilling apparatus. This apparatus consisted of the 300-ml flask containing the sample, connected by a Claisen distilling head to an 8-in. Vigreux column; a second Claisen head which connected to a vertical water condenser; and a 4-in. -long tube 12 mm in ID dipping below the surface of the standard sulfuric acid solution contained in a 250-ml Erlenmeyer flask. A 250-ml separatory funnel was used for the addition of the sodium carbonate solution to the sample. Standard taper joints were used throughout.

After the flask with the sample was connected to the system, 50 ml of 5 per cent Na_2CO_3 and 100 ml of deionized water were added successively through the separatory funnel. No precipitation occurred during the

CONFIDENTIAL

CONFIDENTIAL

25

carbonate addition or the subsequent distillation. After boiling to remove CO_2 , the distillate was cooled and titrated with standard sodium hydroxide.

The above-described procedure was the final modified method used in the majority of the analyses. In the initial tests, sodium carbonate solution was added directly to the solid sample. However, it was observed that the solid phase remained throughout the distillation. The possibly incomplete liberation of ammonia from the solid particles led to the later sulfuric acid dissolution. Originally 1 N ammonia was used for the standardization of the method, but later, when it appeared that volatilization during the pipetting step was giving anomalous results, this concentration was changed to 0.1 N ammonia.

The method was checked in the following manner. To a 300-ml distilling flask 5 ml of 167 g per liter uranium (as UO_2SO_4), 3 ml of 25 volume per cent H_2SO_4 , 50 ml of deionized water, and 20 ml of 0.1 N NH_4OH were added. To this mixture 100 ml of 5 per cent Na_2CO_3 was added and the resulting solution distilled into 20 ml of 0.2 N NH_2SO_4 plus 80 ml of deionized water. The test was run in triplicate and 2.236, 2.244, and 2.245 millimoles of ammonia were found. Direct titration of 20 ml of 0.1 N NH_4OH in 20 ml of 0.2 N H_2SO_4 resulted in the finding of 2.236, 2.244, and 2.238 millimoles of ammonia. The results are in good agreement, indicating that spray entrainment was not affecting the determinations. Earlier results had also indicated good recoveries of ammonia from a different system, 30 ml of 40 g per liter uranium, 10 ml of 1.01 N NH_4OH , 200 ml of deionized water, and 20 ml of 5 per cent Na_2CO_3 . The distillate was caught in 100 ml of water containing 10 ml of 2 N H_2SO_4 . The results were: (1) direct titration of a mixture of 10 ml of 1 N NH_4OH and 10 ml of 2 N H_2SO_4 , 10.09, and 10.12 millimoles of ammonia; (2) distillation of 10 ml of 1 N NH_4OH from 20 ml of 5 per cent Na_2CO_3 solution and 200 ml of water, 10.08 and 10.12 millimoles; and (3) distillation from an ammonia-uranium-sodium carbonate mixture described above, 10.11, 10.12, and 10.09 millimoles.

The reason for the divergence in the ammonia analyses of the unknown precipitates was not disclosed by the standardization tests, which, conducted under almost identical conditions, showed satisfactory precision and reproducibility. Difficulties in weighing the separate samples used for determination of ammonia and uranium would explain some, but not all, of the divergence among the wet precipitates.

Excellent agreement was obtained on uranium analyses of dry precipitates, but not on ammonia analyses, indicating that weighing errors were not at fault. An inherent interference, of unknown cause, may be the explanation. Since, during most of the program, it was sufficient to know that the NH_4 :uranium ratios were $\sim 0.5:1$ and not $1:1$, little effort was

CONFIDENTIAL

UNCLASSIFIED

~~CONFIDENTIAL~~

26

diverted toward the problem of ammonia analysis. The limited studies made did not uncover the cause of the disagreements.

Early standardization tests indicated low results (1-3 per cent) when sodium hydroxide was used to displace the ammonia from ammonia precipitates, and its use was not studied further.

Uranium was the only nonvolatile constituent of the precipitates, and uranium analyses were readily accomplished by simple ignition. As indicated by the results, agreement of these analyses was satisfactory. The slight differences can be attributed largely to difficulties in weighing the hygroscopic air-dried precipitates or in handling the wet precipitates.

RECOMMENDATIONS FOR FUTURE WORK

In view of the potential application of ammonia precipitation of uranyl nitrate solutions, and the current limited knowledge of the chemistry of ammonium uranates, research in this field should be continued and extended. Very little is known about the composition or characteristics of the compounds formed upon the addition of ammonium hydroxide to a uranyl salt solution. Out of such a study should come not only the desired basic information, but information of direct use in a plant utilizing this process.

The very promising characteristics of the product precipitated by ammonia from a uranyl solution containing carbonate ion also appear to merit further investigation, as a possible answer to the poor filtration characteristics of the normal ammonia precipitate.

REFERENCES

- (1) Britton, H. T., "Electrometric Studies of the Precipitation of Hydroxides", J. Chem. Soc., 127, 2148-59 (1925).
- (2) Britton, H. T., and Young, A. E., "Electrometric Studies of the Precipitation of Hydroxides: Part VI. Sexivalent Uranium Chloride Solutions", J. Chem. Soc., 134, 2467-9 (1932).
- (3) Flatt, R., and Hess, W., "On the Uranates of Potassium", Helv. Chim. Acta, 21, 1506-12 (1938).

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

~~27 and 28~~

- (4) Metzger, F., and Heidelberger, M., "On the Nature of Certain Sodium-Uranium Compounds", JACS, 31, 1040-45 (1909).
- (5) Guiter, H., "Studies of the Curves of the Potentiometric Analysis of Uranyl Nitrate With Caustic Soda", Bull. Soc. Chimie, 403-4 (1946).
- (6) Guiter, H., "Studies of the Curves of the Potentiometric Analysis of Uranyl Acetate With Caustic Soda", Bull. Soc. Chimie, 275-6 (1947).
- (7) Tridot, G., "Studies of the Conditions of Precipitation and the Stability in Aqueous Media of the Uranates of Ammonium, Sodium, and Potassium", Ann. Chem., 5, 358-97 (1950).
- (8) Wamser, C. A., Belle, J., Bernsohn, E., and Williamson, B., "The Constitution of the Uranates of Sodium", AECD-2933 (May 1, 1951).
- (9) Sutton, J., "The Hydrolysis of the Uranyl Ion: Part I", J. Chem. Soc. Supplement, 275-286 (1949).
- (10) Sutton, J., "Hydrolysis of the Uranyl Ion and Formation of Sodium Uranates", J. Inorg. and Nucl. Chem., 1, 68-74 (1955).
- (11) Stewart, R. L., and Neace, J. C., "Investigation of the Production of Uniform Particles of U_3O_8 by Chemical Precipitation", APEX-168 (August 3, 1954).

RAE:SJK:AEB/ims:mk

END