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PREPARATION AND USE OF AMMONIUM DIURANATE IN THE ETHER EXTRACTION PROCESS

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Written By: Dr. E. O. Brimm
Mr. P. Mohr

Work Done By: Dr. E. O. Brimm
Mr. P. Mohr

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PREPARATION AND USE OF AMMONIUM DIURANATE IN THE ETHER EXTRACTION PROCESS

I. INTRODUCTION

In the ether extraction process, as originally developed, purified uranium dioxide was obtained by evaporation and calcination of the uranyl nitrate solution, followed by calcination of the resultant UO_3. It was suggested that an alternate procedure might be developed, involving the precipitation of uranium from the nitrate solution as ammonium diuranate. This material could then be calcined to uranosic acid, or reduced directly to the dioxide.

II. DISCUSSION

It had already been established that ammonium diuranate could be precipitated completely from uranyl nitrate solutions. Experiments were carried out to determine whether a basic nitrate, analogous to a known sulfate salt, would be formed in the process. Both direct reduction of the diuranate to UO_2 and calcination to uranosic acid were investigated to determine the physical characteristics and residual nitrogen of the resultant brown oxide.

III. EXPERIMENTAL

Preparation: Since a basic nitrate, analogous to the basic sulfate, might be formed when ammonia is added to a uranyl nitrate solution, the precipitation of ammonium diuranate from solutions with various concentrations of uranyl nitrate was studied. Concentrated ammonium hydroxide was added dropwise to uranyl nitrate solutions to pH 7.0-7.5. The precipitates were filtered, washed thoroughly, and dried at 105°C. The analytical results in the following table show that no basic nitrate is formed:

Concentration Nitrate·$6H_2O$ in gms./100 ml.	Temperature, °C.	Composition		
		NH_3	NO_3	U_3O_8
1	95	1.68	0.10	76.9
10	95	1.77	0.07	78.0
10*	95	1.44	0.30	78.9
10	25	1.65	nil	77.5
30	95	2.20	0.20	74.4
50	95	1.92	0.10	77.5

* Digested for two hours after precipitation was complete.

In every case the precipitate was easily filtered. When the preparation was carried out at room temperature, a denser product was obtained.

Calcination: In order to determine the conversion to U_3O_8 and the nitrogen retention, the ammonium salt was calcined at various temperatures.

The conditions and results are tabulated below:

Temperature, °C.	Time, Hrs.	N	UO_2	UO_3
400	1	-	1.12%	95.10%
"	3	.003%	14.81	83.84
500	1	-	15.28	84.26
"	3	nil	28.43	70.84
600	1	-	27.59	72.34
"	3	nil	30.57	69.04
700	1	-	30.37	69.60
"	3	.001%*	31.52	68.25
800	1	-	31.60	68.47
"	3	nil	32.34	67.68

* Probably in error

The results obtained corroborated the results of the calcination of "acid leach" cake; i.e., ammonia is volatilized at 400°C., and the resulting uranic oxides first decompose completely to uranosic oxide at 600 to 700°C.

Reduction: It would be advantageous if ammonium diuranate could be reduced directly to the dioxide. A direct reduction of ammonium diuranate was carried out in order to determine whether calcination to uranosic oxide could be eliminated and whether excessive amounts of nitrogen are retained by the uranium dioxide so produced. The following table shows the nitrogen content of samples obtained by reducing ammonium diuranate and uranosic oxide with hydrogen and ammonia:

Material	Reducing Agent	Nitrogen Content
Ammonium Diuranate	Hydrogen	nil
" "	"	10 p.p.m.
" "	Ammonia	60 p.p.m.
Uranosic Oxide	"	nil

The reductions in the above table were all made at 1000°C. The dioxide prepared from the ammonium diuranate was found to be pyrophoric in every test; however, if the product was treated with water before exposure to oxygen, it lost it pyrophoric nature. Another run was made to test above reductions of the diuranate with hydrogen. The material was found to be pyrophoric and of nil nitrogen content. Ammonium diuranate, when calcined at 800°C. before reduction with hydrogen, resulted in a product that was non-pyrophoric.

A study of the elimination of nitrogen from dioxide by treatment with hydrogen fluoride was contemplated, but the nitrogen content of oxide produced by direct reduction with hydrogen at 1000°C. is negligible since the nitrogen contents of three oxides produced in this way have been nil, nil, and 10 p.p.m. However, it will not be possible to utilize direct reduction of the ammonium salt unless operations are carried out in such a way that no oxygen comes in contact with the oxide before conversion to fluoride, or

unless the pyrophoric property of the oxide is minimized, as by treatment with water.

Reactivity of product with HF: Samples of uranium dioxide, which had been prepared from ammonium diuranate and U_3O_8 with various times and temperatures of calcination and reduction (calcined at 500, 600, 700 and 800°C. and reduced at 800°C.), were digested with 10% hydrofluoric acid. No correlation could be found between reactivity and conditions of preparation. There were only minor differences in reactivity, which can be ascribed to differences in particle size.

Large Scale Estimates: Runs were made on precipitation of ammonium diuranate. On the basis of data obtained, it was calculated that, by this procedure, 1000 gal. of liquors containing 4200 lb. of dioxide would be processed per day. The ammonia requirement (0.1 lb./lb. hexahydrate) would be 600 lb. per day. The material filters and washes at a rate of 2.7 gal. per min. per ft.^{2} at 10 psi. to give a cake containing 41% water and weighing 90 lb. per ft.^{3} in the filter. On the basis of these figures, 250 ft.^{2} of filter area to handle 95 ft.^{3} of cake per 24 hours were recommended for a filter press.

IV. SUMMARY

Ammonium diuranate can be precipitated from uranyl nitrate solutions to produce a product containing 1.7 to 2.2% ammonia, and 76.9 to 78.9% U_3O_8. This product can be calcined to uranosic acid of nil nitrogen content in one hour at 400°C. It can also be reduced directly with either hydrogen or ammonia at 1000°C. to produce UO_2. The product of the latter reaction is extremely pyrophoric, although this property can be eliminated by treatment with water.