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THE PREPARATION OF URANOUS AND URANYL
SULFATE

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A N D U R A N Y L S U L F A T E S

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I. INTRODUCTION

Requests for several hundred pounds each of relatively pure uranous sulfate and uranyl sulfate made it necessary to devise procedures suitable for the production of these salts on a pilot plant scale.

Many methods for the preparation of uranous sulfate, most of them involving the reduction of uranyl sulfate solutions, are described in the literature (1). A number of these methods were considered before the reaction between uranium dioxide and concentrated sulfuric acid (2) was selected for attention.

The preparation of uranyl sulfate presented no special difficulties, the reaction between uranium trioxide and sulfuric acid (3) being readily adapted to a large scale.

II. DISCUSSION

After preliminary experiments on the various methods of preparing uranous sulfate described in the literature, the reaction

was selected as the most practical approach to the problem.

Initial trials using micro-pulverized uranium dioxide showed promise, fifty per cent of the uranium dioxide being converted to uranous sulfate after heating with sulfuric acid at 70°C for two

days. Further experiments to determine the optimum conditions for the reaction indicated that stirring the micro-pulverized uranium dioxide into a hot (95°C) solution consisting of a ten per cent excess by weight of sulfuric acid together with sufficient water to yield the tetrahydrate salt, followed by baking the pasty reaction mixture for sixteen to twenty hours at 150°C was capable of converting 76-78 per cent of the uranium dioxide to uranous sulfate.

On the basis of the laboratory data, 20 to 22.5-pound charges of micro-pulverized uranium dioxide were reacted in porcelain dishes according to the conditions outlined above. Conversions to uranous sulfate ranged from seventy-five to eighty per cent in the first charges to eighty to ninety-three per cent in later charges, apparently depending on the fact that the uranium dioxide was added at a much faster rate in the later charges and the heat of reaction was correspondingly greater. A sample of material prepared in this way was found to be soluble in water at 28°C to the extent of 12.5 per cent. A typical analysis, made on a composite sample, gave total uranium 52.0%, water insoluble 8.6%, water soluble uranium 44.45%, water soluble sulfate 43.7% and water soluble iron 0.0012%. Analysis of individual preparations showed that the water-insoluble limit should be not more than ten per cent and preferably not more than five per cent, while iron should not exceed 0.001%.

By following the amount of water-insoluble residue present in samples withdrawn at intervals from the reaction mixture, it was established that seven to ten hours' heating at 160°C should be sufficient for at least an eighty per cent conversion of the micro-pulverized uranium dioxide to uranous sulfate. When an attempt was made to substitute ordinary, granular uranium dioxide for the micro-pulverized material, it was necessary to heat the reaction mixture at 150°C for at least two days in order to obtain approximately 86% conversion to uranous sulfate. The use of micro-pulverized brown oxide was therefore considered more satisfactory, as its reaction time was shorter.

The initial attempts to recrystallize uranous sulfate by dissolving it in water, filtering, evaporating the solution to about one third its original volume, collecting the crystals in a centrifuge and drying them at 50°C were not successful. The resultant crystals had only a limited water solubility, in marked contrast to the ready solubility of the crude material. Analyses showed that the crude crystals contained from 8 to 24% excess sulfate, while the recrystallized salt had a 22 to 31% deficiency of sulfate. It was possible to dissolve the recrystallized material only in the presence of a high concentration of sulfuric acid. Further portions of the crude uranous sulfate were recrystallized from a six per cent sulfuric acid solution and the resultant crystals were soluble in water to the extent of nine per cent.

After several preliminary trials, a satisfactory procedure for preparing uranyl sulfate was devised. The stoichiometric quantity of uranium trioxide was added to a 21.5% sulfuric acid solution to give a clear yellow solution of uranyl sulfate. Crystals of uranyl sulfate were obtained by evaporating the filtered solution, cooling it, centrifuging, and drying the crystals at about 70°C. Three crops of crystals were obtained in which the mol ratio of uranium to sulfate varied from 1.006 to 0.985. The water content of the crystals was calculated by difference to correspond to a mixture of the dihydrate and trihydrate.

III. EXPERIMENTAL

1. The Preparation of Uranous Sulfate on a Small Scale

The first trials in the preparation of uranous sulfate consisted of grinding together the stoichiometric quantities of micro-pulverized uranium dioxide and concentrated sulfuric acid in a mortar. After heating at 70°C for forty-eight hours, the mixture was set to a solid cake. The conversion to uranous sulfate was determined to be fifty per cent by analyzing the water-soluble fraction of the cake for quadrivalent uranium. Further qualitative experiments indicated that the reaction was more satisfactory when sufficient water was present initially to yield uranous sulfate tetrahydrate, which is presumably stable at temperatures up to 300°C.

Some larger scale experiments were next performed, of which the following is typical:

In a porcelain dish, 1075 gm of micro-pulverized uranium dioxide was treated with a mixture of 144 cc of distilled water and 784 gm (426 cc) of concentrated sulfuric acid. Considerable heat was evolved during mixing, the temperature rising to 180°C . The mixture was maintained at $150\text{--}190^{\circ}\text{C}$ for two hours by heating in a sand bath, and was stirred at intervals. It was then placed in an oven overnight at 150°C . When removed from the oven, the material was light green in color and, while hot, gave off a large quantity of white fumes resembling sulfur trioxide. Although solid, it was easily dug out of the dish.

From experiments of this type, it was found to be more satisfactory to add the uranium dioxide to the hot (95°C) sulfuric acid-water mixture, rather than the reverse. The conversion to uranous sulfate was 76-78% even when a twenty per cent excess of sulfuric acid was used, so it was felt that a ten per cent excess of acid would be ample for future experiments. The reactivity of the unreacted uranium dioxide was tested by extracting all of the water-soluble uranous sulfate, drying the residue of uranium dioxide and fluorinating it in the uranium

tetrafluoride plant. The uranium tetrafluoride obtained assayed 98.34% pure, indicating that the reactivity of the uranium dioxide not converted to uranous sulfate was normal.

2. The Preparation of Uranous Sulfate on a Large Scale

Based on the laboratory experiments, large-scale preparations were made according to the following procedure:

Sixteen pounds (10% excess) of A.R. sulfuric acid (sp.gr. = 1.84) was added slowly, with stirring, to 2.7 pounds (1215 cc) of distilled water in an eighteen-inch diameter porcelain dish set in a large stainless steel tray, in case of breakage. Twenty pounds of micro-pulverized uranium dioxide was added to the hot (95°C) solution over a period of about ten minutes while stirring with a porcelain spatula. At the end of this time, the temperature rose rapidly to about 150°C, the mass became greenish and thickened appreciably. It finally boiled vigorously and set to a pasty mass on further stirring. The stiff paste was put in the oven overnight at 160°C. The product was light green in color, fumed considerably while hot and was readily broken up.

A total of about twenty-five dishes was prepared in this manner. It was found that the hotter the acid, and the more vigorous the initial reaction, the higher was the conversion to uranous sulfate. Thus, the conversion in the first prepara-

tions was 75-80%, while later preparations in which the uranium dioxide was added more rapidly and the reaction was more vigorous attained conversions of 80-93%. The solubility of this material in water was found to be about 12.5% at 28°C. Some typical analyses are shown in Table 1.

TABLE 1
Typical Analyses of Uranous Sulfate

No.	Water Insoluble, %	Total Uranium, %	SO ₄ , %	Fe ppm	Excess SO ₄ , Based on calculated U ⁺⁴ Content, %
1	8.6	52.0	43.7	12	+ 19.3
2	4.6	54.7	43.5	9	+ 6.4
3	6.3	53.4	43.0	6	+ 10.2
4	11.6	52.1	43.0	5	+ 21.4
5	3.8	53.8	44.8	11	+ 9.2
6	5.6	52.9	44.3	9	+ 12.9

In Table 1, column 6, the U⁺⁴ content of the preparation is considered to be the difference between the per cent total uranium and the per cent water-insoluble uranium as calculated by assuming the per cent water insoluble to consist entirely of uranium dioxide.

At intervals, samples were withdrawn from one batch in order to follow the rate of the reaction. This was done by determining the water-insoluble residue present in the sample and from this value calculating the quantity of unreacted dioxide present. The results are given in Table 2, and indicate

that seven to ten hours' heating at 160°C should be sufficient for at least an eighty per cent conversion to uranous sulfate tetrahydrate.

TABLE 2

The Rate of Reaction of Micro-Pulverized Uranium Dioxide with Concentrated Sulfuric Acid at 160°C

<u>Hours Heating at 160°C</u>	<u>Conversion to $U(SO_4)_2 \cdot 4H_2O$, %</u>
0	64.5
1.3	67.5
3.3	72.6
4.0	73.8

An attempt was also made to use regular uranium dioxide in this process. A mixture was prepared in the usual fashion, but remained quite fluid even after forty-eight hours at 150°C. After standing at room temperature for one week, it hardened and assayed approximately eighty-six per cent uranous sulfate. It was felt that the rate of reaction was too slow to be practical.

3. The Recrystallization of Uranous Sulfate

In order to prepare a purified, crystalline uranous sulfate, approximately forty-five pounds of the crude material was added to fifty gallons of distilled water at room temperature in a glass-lined tub and stirred with a rubber-covered stirrer for about twenty minutes. The insoluble residue was allowed to settle for ten minutes and the solution was then

filtered through a heavy canvas filter cone lined with filter paper and a light canvas cone. The clear filtrate was concentrated to about one third its original volume in a seventy-gallon, glass-lined, steam-jacketed pan. The crystals, which did not cake on the bottom of the pan, were whirled dry in a centrifuge and dried on trays at 50°C. A yield of twenty-eight pounds of dull, dark-green crystals was obtained. These crystals were found to have a very limited solubility in water, which was in marked contrast to the ready solubility of the crude material. Analyses of some of the crude and purified preparations were made to determine the reason for the decreased solubility after crystallization. The results are shown in Table 3.

TABLE 3

Analyses of Crude and Recrystallized Uranous Sulfate

	<u>% SO₄</u>	<u>% Total U</u>	<u>% Excess SO₄ Based on Total U Content</u>
Recrystallized	33.4	54.2	-30.8
	35.4	53.7	-22.3
Crude	44.3	51.5	+ 6.3
	43.0	50.1	+ 5.8

The analyses of Table 3 show that the recrystallized uranous sulfate has a 22-30% deficiency of sulfate, whereas the crude salt has five to six per cent excess of sulfate. By treating

the recrystallized salt with an excess of concentrated sulfuric acid, its water solubility was improved. These results indicated that a large excess of sulfuric acid was required during the recrystallization if hydrolysis of the uranous sulfate was to be avoided.

A second recrystallization was performed, about seventy-five pounds of crude uranous sulfate being dissolved in sixty gallons of distilled water containing thirty-six pounds of concentrated sulfuric acid. Following the procedure outlined above, a yield of sixty-two pounds of crystals having a twelve per cent excess of sulfate was obtained. This material was soluble in water to the extent of 9.5% at 22°C.

4. The Preparation of Uranyl Sulfate

After several preliminary experiments in dissolving uranium trioxide in the equivalent quantity of sulfuric acid, the laboratory procedure was enlarged to the following method:

To 48.5 gallons of distilled water in a seventy-gallon, glass-lined pan was added 111 pounds of A.R. concentrated sulfuric acid. To the acid solution was added 312 pounds of ground uranium trioxide which dissolved readily to give a fairly clear, yellow solution having a Baume of 61° at 40-50°C. This solution was filtered through double, lightweight cone sacks lined with double layers of Reeve Angel No. 204 filter paper. The volume of filtrate was approxi-

mately sixty gallons. Fifty gallons of the filtrate was concentrated to a thin mush of crystals in a steam-jacketed, glass-lined pan. After cooling overnight, the resultant crystals were centrifuged and placed to dry on plastic trays at 60-70°C. The mother liquor, which had a volume of about fourteen gallons, 70°C at 25°C, was combined with the remaining ten gallons of original solution and concentrated to yield a second crop of crystals. A third crop of crystals was obtained from these mother liquors by further concentration. Analyses showed that 71.3% of the uranium was converted to uranyl sulfate, 22.5% remaining in the mother liquor, while 6.2% reached the recovery system in the form of residues and wash water from the equipment used. The analyses of the three crops of crystals obtained are given in Table 4.

TABLE 4

Analyses of Uranyl Sulfate Crystals

	<u>1st Crop</u>	<u>2nd Crop</u>	<u>3rd Crop</u>
Weight of dried salt	161 lbs.	93 lbs.	67.5 lbs.
% U	57.73	57.40	57.61
% SO ₄	23.16	23.51	23.38
% NO ₃	0.015	L 0.015	L 0.015
% Fe	0.0002	0.001	0.001
% H ₂ O-insoluble	0.03	0.003	0.001
Mol ratio, U/SO ₄	1.006	0.985	0.994

From the results of Table 4, the water content of the uranyl sulfate is calculated to be 11.3%, corresponding to a mixture of the di- and trihydrates.

IV. SUMMARY

1. A process for the preparation of uranous sulfate has been described in which micro-pulverized uranium dioxide is reacted at 100°C with a ten per cent excess of concentrated sulfuric acid in the presence of sufficient water to form the tetrahydrated salt. The reaction mixture is baked for approximately sixteen hours at 150-160°C. Conversions of uranium dioxide to uranyl sulfate of the order of 80-95% are obtained. At 28°C, the salt is soluble in water to the extent of 12.5%.
2. A study of the rate of reaction of micro-pulverized uranium dioxide with concentrated sulfuric acid at 160°C showed that at least an eighty per cent conversion to uranyl sulfate should be obtained in seven to ten hours of heating.
3. The use of regular, granular uranium dioxide in the preparation of uranous sulfate was found to be impractical because of its slow rate of reaction with sulfuric acid.
4. It was found necessary to recrystallize uranous sulfate in the presence of a large excess of sulfuric acid in order to avoid hydrolysis and the formation of an insoluble salt.

5. A process for the preparation of uranyl sulfate by reacting the stoichiometric quantities of ground uranium trioxide and 21.5% sulfuric acid has been described.

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