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"The Precipitation of Uranium Peroxide in the Presence of Fluorides."

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The large-scale recovery of uranium from materials which also contained great quantities of fluorides did not give a product which had a low enough fluoride content to be treated satisfactorily by the ether extraction process. The objective of the investigations carried out in this laboratory was a method of reducing the amount of fluoride which accompanied the uranium.

The material from which the uranium was recovered in the industrial process was a slag containing (in addition to uranium) magnesium fluoride, calcium and dolomitic limes, crucible dross, and other waste products from the reaction of magnesium metal and uranium hexafluoride. Most of the fluoride was removed from this mixture by heating the roasted and ground slag with sulfuric acid. The residue was mixed with water and much of the calcium sulfate and fluoride, magnesium fluoride, and hydrated ferric oxide and alumina was precipitated by reducing the acidity. After filtering off the precipitate, ammonium sulfate was added to the solution and uranium peroxide ($UO_4 \cdot 2H_2O$) was precipitated by addition of hydrogen peroxide. The pH of the solution was maintained between 3.0 and 3.5 during the precipitation by addition of sodium hydroxide. The uranium peroxide, even after washing, contained between 2 and 3% fluoride. The

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percentage of fluoride could be reduced to 0.5% by precipitating the peroxide from a more acidic solution but this required the use of much larger amounts of hydrogen peroxide.

Discussion

Small-scale preliminary experiments, which need not be reported in detail, indicated that uranium peroxide precipitated from a solution of uranyl sulfate which also contained sodium fluoride and magnesium, calcium, and ammonium sulfates was contaminated with as much as 0.8% of fluoride. If the uranium peroxide stood in contact with the solution for ten hours before being filtered off, the fluoride content of the precipitate increased to as much as 2%. These results indicate considerable adsorption of fluoride and post-precipitation of insoluble fluorides, such as those of calcium and magnesium. A reduction in the concentration of fluoride ion in the solution should cause a decrease in the amount adsorbed or post-precipitated. The desired reduction in concentration of fluoride ion may easily be secured by addition of a metal ion, such as ferric or aluminum, which forms a stable complex ion with the fluoride. Therefore, precipitation of uranium peroxide in the presence of these ions was investigated.

Ferric ion was found to be unsuitable because it was impossible to maintain a large excess of the ion in solutions of the prescribed pH values. Aluminum ion was found to be satisfactory because its hydrated oxide normally does not precipitate in solutions as acidic as those encountered here and its fluoride complex ion is very stable. As a result of the experiments described below it was found that the fluoride content of uranium peroxide precipitates can be reduced to less than 0.1% when the precipitation is done in the presence of at least one gram ion of

aluminum for every two of fluoride.

Experimental

The fluoride content of the uranium peroxide was determined by the following procedure. A weighed sample of the dried peroxide was treated with perchloric acid according to the method of Willard and Winter.(1) To the distillate (a solution of hydrofluosilicicacid) there was added 20 g. of solid sodium nitrate, 25 ml. of 95% ethyl alcohol, and a measured volume of methyl red indicator for each 75 ml. Then 4% sodium hydroxide solution was added until the solution was just basic to methyl red. This neutralization was inconveniently slow at room temperature but proceeded rapidly at 50° C. The solution was then titrated with N/4 or N/16 aluminum chloride solution until acidic to methyl red.(2) The use of a permanent color standard prepared by blending solutions of sodium dichromate and cobaltous chloride ensured a reproducible end-point. For the larger samples the accuracy of this titration compared favorably with that of acid-base titrations involving solutions of the same concentration. Much better results were obtained than from titrations of fluorides with ferric chloride solution using thiocyanate as the indicator. The aluminum chloride solutions were standardized against sodium fluoride treated by the above procedure.

In the first series of experiments uranium peroxide was precipitated from 125 ml. portions of a solution which was 0.10 M in uranyl sulfate, 0.0762 M in sodium fluoride, and 2.00 M in magnesium sulfate and also contained 10 g. of ammonium sulfate and varying amounts of aluminum sulfate. All chemicals were of reagent quality. The precipitate was either filtered off immediately or first allowed to stand in contact with the solution for ten hours. The results are given in Table I.

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Table I.

The Effect of Aluminum Sulfate Upon the Fluoride Content of Uranium Peroxide Precipitates.

Experiment Number	Gram-ion ratio Al:F	Hours standing	% F in Precipitate
A-1	0	0	0.98
A-2	1:6	0	.60
A-3	2:6	0	.23
A-4	3:6	0	.08
A-5	6:6	0	.06
A-6	0	10	.90
A-7	3:6	10	.12

These results show that if there is to be less than 0.1% of fluoride in the peroxide the gram-ion ratio of aluminum to fluoride in solution must be at least 3:6. Since one aluminum ion combines with six fluoride ions to give the complex ion, a 3:6 ratio corresponds to a three-fold excess of aluminum. The use of a smaller amount of ammonium sulfate (3 g.) with the three-fold excess of aluminum did not cause any significant increase in fluoride content. The peroxide which analyzed 0.08% fluoride was found to contain small amounts of aluminum, estimated to be only a few hundredths of a per cent. The alizarin spot test[3] was used; all other qualitative tests gave negative results for aluminum.

In an experiment similar to those described above a three-fold excess of ferric sulfate was substituted for the aluminum sulfate. Most of the iron precipitated as the hydrated oxide when the pH was adjusted. This was removed before the peroxide was precipitated. Since the peroxide precipitate so obtained was 0.75% fluoride, iron was clearly shown

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to be inferior to aluminum as the complexing agent.

The second series of experiments was designed to determine the effect of the presence of calcium ion on the effectiveness of aluminum in removing fluoride. A solution was prepared which was 0.13 M in uranyl sulfate, 0.13 M sodium fluoride, 2.00 M in sulfuric acid, and 2.50 M in magnesium sulfate. After heating this solution to 50° C, calcium hydroxide was added, 55.5 g. for each liter of solution. The pH of the mixture was raised to 3.5 by addition of 20% sodium hydroxide solution. One portion was filtered immediately and the filtrate reserved for Experiment B; the other was kept at 50.0° C for 14 hours and then filtered for Experiment C. The two filtrates contained 0.151 and 0.153 grams of fluoride per 100 ml. of B and C respectively. On the basis of these analyses aluminum sulfate was added to 200 ml. aliquots of these filtrates to give the prescribed aluminum to fluoride gram-ion ratios. A white precipitate which formed in the solution for Experiment C was filtered off prior to addition of the aluminum sulfate. Six grams of ammonium sulfate was added to each aliquot and uranium peroxide was precipitated in the usual manner. Some of the precipitates were filtered off immediately, some after ten hours of standing. The results are summarized in Table II.

Table II.

The Effectiveness of Aluminum in Removing Fluoride in the Presence of Calcium

Experiment Number	Gram-ion ratio Al:F	Hours Standing	% F in Precipitate
B-1	1:6	0	0.41
B-2	1:6	10	2.32
B-3	3:6	0	0.062
C-1	3:6	0	.056
C-2	3:6	10	.056

The high result in Experiment B-2 can doubtless be attributed to post-precipitation of calcium fluoride. Comparison of the results in Tables I and II leads to the conclusion that the presence of calcium does no harm provided that excess calcium fluoride is allowed to deposit before precipitation of the uranium peroxide.

Summary

The fluoride content of uranium peroxide precipitated from solutions which also contain magnesium sulfate and sodium fluoride can be reduced below 0.1% by addition of aluminum sulfate. There should be at least one gram ion of aluminum for every two gram ions of fluoride. The presence of calcium ion does no harm provided excess calcium fluoride is removed before precipitation of the peroxide. Ferric sulfate cannot be substituted for aluminum sulfate.

References

(1) Willard, H. H. and Winter, O. B., Ind. Eng. Chem., Anal. Ed. 5, 7-10 (1933).

(2) Geyer, R., Z. anorg. Chem. 252, 42-55 (1943).

(3) Feigl, F., "Spot Tests", p. 116, Nordemann Publishing Co., New York (1937).