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RECOVERY OF URANIUM FROM PHOSPHORIC ACID

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This invention relates to a process for the recovery of uranium values and more particularly to a process for the recovery of uranium values from phosphoric acid.

Phosphate rock of marine origin contains a small concentration of uranium. Because of the huge reserves of this rock and the large tonnages that are mined each year, phosphate rock is a promising source of uranium. One of the important fertilizer chemicals produced from phosphate rock is monoammonium phosphate which is made by treating raw rock with sufficient sulfuric acid to produce phosphoric acid and calcium sulfate. The insoluble calcium sulfate is removed by filtration, the phosphoric acid is concentrated by heat, partially neutralized with ammonia, and the monoammonium phosphate solution is evaporated to recover the dry product. The phosphoric acid, which is an intermediate product, contains almost all of the uranium originally present in the rock.

An object of this invention is to provide a process for recovering uranium from phosphoric acid. A still further object is to provide a process for recovering uranium from phosphoric acid solution as one phase of the production of monoammonium phosphate. A still further object of this invention is the provision of a simple, economic process for the recovery of uranium and vanadium from phosphoric acid solutions. Other objects will appear hereinafter.

In accordance with the present invention, the phosphoric acid is first treated with a reducing agent such as metallic iron, zinc or aluminum to reduce the uranium therein to the uranous form, which is then precipitated when ammonia is added to form monoammonium phosphate. The uranium-bearing precipitate can be filtered readily from the monoammonium phosphate solution which is then evaporated to produce solid monoammonium phosphate. The uranium precipitate can be upgraded by proper techniques to give a product suitable for further use.

The phosphoric acid used in the present invention is obtained by the action of sulfuric acid on phosphate rock. Some such phosphoric acid of a concentration of about 27° Bé. has been found to contain about 0.09 gram of U₃O₈ per liter of acid. It was found that more than 98% of the U₃O₈ present in the phosphoric acid was precipitated by the present procedure. It is preferable to use phosphoric acid of not higher than about 30° Bé. concentration when practicing this invention in as much as difficulties are encountered at higher H₃PO₄ concentrations by the crystallization of ammonium phosphate.

EXAMPLE I

A series of tests was run in which a stock solution of phosphoric acid containing about 55 mg./liter of U₃O₈ was subjected to the reducing action of various forms of different metals for different times. These tests were carried out at a temperature of around 23° C., the samples being agitated during the reduction period. Neutralization was accomplished by the addition of aqueous ammonia. The pH was determined by a MacBeth line-operated meter.

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After neutralization, the precipitates were filtered, dried, weighed and analyzed. Results of these tests are presented in Table I.

Table I

REDUCTION OF URANIUM WITH VARIOUS REAGENTS PRIOR TO PRECIPITATION

Reducing Agent	Quantity	Time, Minutes	Final pH	Percent U ₃ O ₈ Precipitated
None			3.1	3.97
None			3.0	8.33
Liq. Zn Amalgam	50 ml/l.	5	3.7	99.77
Zn Metal	Excess	10	3.1	97.82
Iron Powder	4 g./l.	30	3.1	99.8
Iron Wire	4 g./l.	1,440	3.0	97.5
Al turnings	Excess	10	3.4	98.12

The object in treating the phosphoric acid with a reducing agent is to have all of the uranium present in the tetravalent form, which is more readily precipitated from the acid solution. It has been found that after reaching a pH of about 2.0, each subsequent addition of ammonia results in some precipitation and a rise in the pH of the solution. Table II is presented to show the relationship between the pH of the solution and the degree of precipitation. In the tests tabulated in Table II, aqueous ammonia was added to solutions of phosphoric acid containing less than 20% P₂O₅ which had been reduced with liquid zinc amalgam. When the desired pH was reached, the solution was agitated for 30 minutes and then filtered.

Table II

RELATION OF pH TO PERCENTAGE OF TOTAL U₃O₈ PRECIPITATED

pH	Percent of Total U ₃ O ₈ Precipitated
2.0	27.4
2.2	54.4
2.4	60.3
2.6	69.7
3.5	98.9

The U₃O₈ content of the precipitate was found to decrease as the pH at which the precipitate was obtained increased. Consequently, if the precipitation is to be done in a single step, it is desirable to obtain the precipitate at the lowest pH permissible, considering the degree of recovery desired.

In general, the heat of reaction between the ammonia and the acid is sufficient to maintain the temperature of the solution at about 80° C. or higher. The precipitate obtained from a heated solution is of somewhat higher grade than that obtained from a cooled solution under otherwise similar conditions. The advantages gained in this respect, however, are not believed to be sufficient to justify the application of artificial heat to the reaction vessels.

Vanadium, as well as uranium, is recovered from phosphoric acid according to the present process. At a pH of 2.8 about 75 percent of the vanadium in the acid reports in the precipitate. Increasing the pH to 3.5 gives recovery of more than 85 percent of the vanadium.

EXAMPLE II

An apparatus was assembled for conducting the reduction and ammonia addition steps in a continuous manner by placing a vertical glass column 4 cm. in diameter and 50 cm. long adjacent to two glass precipitator vessels having over-flow arms near the top. The glass column was filled with 10d iron nails and connections were made so the phosphoric acid feed was introduced at the bottom of the column, and the reduced acid overflowed from the

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top of the column to the first precipitator vessel. Here anhydrous ammonia was introduced, and the pulp overflowed through a side arm to a second vessel. Frequent pH readings were obtained. Two vessels were used to prevent short circuiting of unprecipitated solution. The overflow from the second vessel went directly to a filtration apparatus. The flow rate was arranged so as to give a maximum retention time of one hour. A series of runs was made with this apparatus, and the results are given in Table III. In each run the precipitate was filtered with the aid of suction and washed with water. After the removal of the precipitate the ammonium phosphate solution was evaporated to obtain a dry salt suitable as fertilizer material. In the lower pH range (2.2 to 3.0) a dry product was not obtained, probably due to the presence of too much free phosphoric acid. At a pH of 3.5-4.0 a dry, granular, easily pulverized product resulted.

Table III

CONTINUOUS PRECIPITATION AND OPERATION TESTS

Run No.	1	2	3	4	5
Washed Precipitate:					
Assay U_3O_8 , Percent	0.136	0.158	0.150	0.168	0.112
Percent of Total U_3O_8	97.6	97.6	93.0	90.1	96.5
Assay V_2O_5 , Percent	3.7	4.0	3.7	3.6	3.3
Percent of Total V_2O_5	94.4	84.0	81.0	72.9	68.0
Filtrate:					
Assay g./l. U_3O_8	0.003	0.005	0.003	0.008	0.003
Percent of Total U_3O_8	1.6	3.0	3.0	6.1	2.4
Operating Data:					
$^{\circ}B\acute{e}$. of acid	40.0	27.0	32.2	28.9	29.9
ml./min. feed	26.0	49.0	49.0	48.0	51.0
g./l. Fe	1.3	2.0	3.6	3.3	3.3
Average pH	4.1	3.5	3.8	2.8	3.7
Aver. Reduction Temp., $^{\circ}C$..	27	27	28	28	27
Aver. Temp. # 1 Vessel, $^{\circ}C$..	99	94	96	94	92
Aver. Temp. # 2 Vessel, $^{\circ}C$..	95	96	98	94	90

The uranium and vanadium may be recovered from the low grade precipitate by any suitable procedure. One satisfactory method has been found to consist of sodium carbonate leaching of the roasted precipitate. Following roasting at an elevated temperature, the calcine is leached with sodium carbonate solution. The residue is then leached again under the same conditions. In general, the vanadium present is leached to approximately the same extent as the uranium.

While certain aspects of my invention have been described in detail, it is to be understood that my invention is not to be limited to the precise procedures described. For example, instead of using ammonia as a neutralizing and precipitating agent in the present process potassium hydroxide or calcium hydroxide may be used. The disclosed invention is furthermore applicable to either a batch or a continuous process for recovering uranium

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and vanadium from phosphoric acid. Other modifications will be apparent to those skilled in the art.

The process of the present invention for the recovery of uranium is very economical because it requires the addition of only two simple steps to the present flow-sheets for the production of monoammonium phosphate: a reduction step and a filtration step. In addition, if vanadium is present in the phosphoric acid, the vanadium is obtained in the uranium precipitate and can be recovered therefrom. It may thus be seen that the present invention makes possible the recovery of low-grade uranium precipitates from phosphoric acid. Having described my invention, what I claim is:

1. A process for recovering uranium values from phosphoric acid containing the same comprising the steps of treating the phosphoric acid with a reducing agent to place the uranium in the uranous state, and then precipitating the uranium by adding a base to the reduced solution.

2. A process for recovering uranium and vanadium values from phosphoric acid containing the same comprising the steps of treating the acid with a reducing agent and then adding a base to the reduced solution to precipitate the uranium and vanadium values.

3. A process for recovering uranium values from phosphoric acid containing the same comprising the steps of contacting the phosphoric acid with metallic iron to reduce the uranium therein to the uranous state, and then precipitating the uranium by adding ammonia to the reduced solution.

4. A process for recovering uranium and vanadium values from phosphoric acid containing the same comprising the steps of contacting the phosphoric acid with a reducing agent, adding a base to the reduced solution to precipitate the uranium and vanadium values therein, separating the uranium and vanadium-containing precipitate from the solution, and recovering the uranium and vanadium from said precipitate.

5. A process for recovering uranium from a solution of phosphoric acid containing the same comprising the steps of treating the phosphoric acid with a reducing agent to place the uranium in the uranous state, adding a base to the reduced solution to precipitate the uranium and separating the precipitate from the solution.

6. In the production of monoammonium phosphate from phosphoric acid containing uranium values, the improvement which comprises treating the phosphoric acid with a reducing agent to reduce the uranium therein to the uranous state, adding ammonia to the reduced solution to precipitate the uranium, separating the uranium-containing precipitate from the solution, and thereafter evaporating the solution to obtain monoammonium phosphate.

No references cited.