This invention deals with a process of pretreating or conditioning nitric acid solutions containing plutonium for the purpose of increasing the yield in the plutonium recovery by carrier precipitation.

When neutron-bombarded uranium is dissolved in nitric acid for processing and recovery of the individual components thereof, the nitric acid in these so-called dissolver solutions reacts and forms hydrazine. Hydrazine, it was found, greatly impairs the carrier precipitation of plutonium, for instance, on bismuth phosphate, one of the carriers preferred used, and the efficiency of the plutonium recovery process is thus greatly reduced. This proved particularly true when such solutions, from which the plutonium was to be recovered, contained great quantities of uranium which is always the case in dissolver solutions. The chemism of the deleterious reaction or reactions of the hydrazine is not known with certainty; studies showed that it is quite involved and that most likely a number of factors or reactions are responsible for the high plutonium losses in the presence of hydrazine. One essential factor, however, seems to be that hydrazine reduces plutonium to the trivalent state and holds it in this valence and that plutonium (III) is not very well carriable on bismuth phosphate, at least not as completely carriable as is the tetravalent plutonium. This, too, is particularly pronounced when uranium is present in relatively great amounts.

Frequently the plutonium in the solutions, prior to carrier precipitation, is secured in its tetravalent state by adding formic acid to the dissolver solution. Formic acid reacts with nitric acid and forms nitrous acid which reduces plutonium (VI) to plutonium (IV) and/or holds any tetravalent plutonium present in this state. Also this nitric acid-formic acid reaction was found to be inhibited by the presence of hydrazine.

Carrier precipitation processes have been carried out in which the hydrazine had been destroyed prior to processing by sodium nitrite. But the results of those experiments were highly erratic, and the plutonium losses were too high in most instances; the satisfactory results obtained in a few experiments were not reproducible.

It is object of this invention to provide a process for the recovery of plutonium values from aqueous solutions by carrier precipitation which has a high degree of efficiency.

It is another object of this invention to provide a process for conditioning nitric acid plutonium solutions for carrier precipitation whereby detrimental side products are eliminated.

It is still another object of this invention to provide a process for conditioning plutonium-containing nitric acid solutions for carrier precipitation whereby practically complete plutonium recovery is always obtained.

All of the above-described disadvantages are overcome and the objects of this invention are accomplished by treating the nitric acid plutonium solution to be processed with an oxidizing agent. The oxidizing agent obviously destroys the hydrazine but at the same time oxidizes at least some plutonium (IV) to plutonium (VI). Plutonium (VI) is not carriable, for instance, on bismuth phosphate so that a subsequent reducing step for the conversion of the hexavalent plutonium to the plutonium (IV), the so-called prereducing, is often advisable, although not always necessary, to make the solution ready for carrier precipitation with bismuth phosphate.

Many substances are suitable as oxidizing agents for the process of this invention; however, potassium dichromate, sodium dichromate and potassium permanganate are preferred. The concentration in which the oxidizing agent has to be present in the solution is dependent upon the composition of the solution; however, a concentration ranging between 0.001 N and 0.03 N was found suitable in all cases tested. The optimal concentration range is that between 0.02 and 0.03 N. It is advisable to use elevated temperature for the oxidation in order to accomplish complete destruction of the hydrazine. For instance, heating to from 75° to 100° C. for about one hour proved sufficient, a temperature of 75° C. representing the best conditions.

There are also a great many substances that are suitable as the prereducing agent to be added after the preoxidation step. Sodium nitrite or a mixture of oxalic acid and a manganous ion-containing substance, e.g., manganous nitrate, is the preferred reducing agent for securing the plutonium in the tetravalent state. The concentration of the reducing agent may vary widely, but a concentration of about 0.1 M for the sodium nitrite and of about 0.03 M and 0.01 M for the oxalic acid and the manganous ion, respectively, have proved best. Hydroxylamine in a concentration of about 0.1 M has also given satisfactory results.

It was found advantageous to carry out the prereducing step in the presence of sulfuric acid in order to avoid reduction of the plutonium to the trivalent state. A concentration of about 0.5 M sulfuric acid is sufficient for this purpose. The function of the sulfuric acid is probably a complexing reaction with the tetravalent plutonium.

Elevated temperatures are also advisable for the prereducing step, and heating for one hour at about 75° C. represents the preferred condition.

In the following a few examples of the process of this invention are given for the purpose of illustrating the improvement obtained thereby without the intention to have the invention limited to the details given therein.

Example I

To a 20% aqueous uranyl nitrate hexahydrate solution containing 25 mg. of plutonium per liter of solution and being 1 N in nitric acid and 0.001 M in hydrazine were added 2.5 mg. of bismuth per ml of solution in the form of bismuth subnitrate; the solution was heated for four hours at 75° C. Thereafter 75% phosphoric acid was gradually added within two hours in a quantity to obtain a concentration of 0.6 M. The solution was then "digested" by holding it at 75° C. for one hour. The precipitate formed was removed by centrifugation and analyzed for its plutonium content. It was found that 40.3% of the plutonium originally present had remained in the solution.

A parallel experiment was carried out using the same solutions and conditions except that potassium permanganate was added to the solution prior to the four-hour heating in a quantity to obtain a concentration of 0.03 N. The subsequent precipitation, carried out as described above, yielded a 99% removal of plutonium by carrying on bismuth phosphate.

Example II

A simulated dissolver solution was made up by dissolving uranium metal in nitric acid, adding, during dis-
solving, inactive fission product elements and diluting the solution so as to obtain a concentration of 22.5% uranyl nitrate hexahydrate. Thereafter, there were added sulfuric acid to obtain a concentration of 1.1 N and tetravalent plutonium to obtain a concentration of 25 mg/liter of solution. The nitric acid concentration of the solution was 0.25 N. These concentrations correspond to those present in actual radioactive dissolver solutions. Nine 10-ml aliquots were used for nine parallel tests. Hydrazine was incorporated in seven of these aliquots, in each case in a quantity to obtain a concentration of 0.001 M, while the two other aliquots were used without hydrazine. The solutions were heated wherever all of the plutonium in the hydrazine-containing samples was found to be present in the trivalent state.

Precipitation tests were carried out on each of the 10-ml aliquots. The precipitation conditions used were practically identical with those described in Example I. Various kinds of pretreatment, however, preoxidation and/or prereduction, were applied prior to precipitation. The conditions of pretreatment used in these nine experiments are shown in the table below together with the results obtained thereby.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>NaH₂O₂ M</th>
<th>Preoxidation Treatment</th>
<th>Prunning Treatment</th>
<th>Percent Pu Loss</th>
<th>Percent Material Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.005</td>
<td>KMnO₄ (0.01 M), 1 hr., 75° C.</td>
<td>H₂O₂ (0.05 M), MnO₂</td>
<td>4.5</td>
<td>105.7</td>
</tr>
<tr>
<td>2</td>
<td>0.005</td>
<td>KMnO₄ (0.01 M), 1 hr., 75° C.</td>
<td>H₂O₂ (0.05 M), MnO₂</td>
<td>4.5</td>
<td>104.3</td>
</tr>
<tr>
<td>3</td>
<td>0.005</td>
<td>KMnO₄ (0.01 M), 1 hr., 75° C.</td>
<td>H₂O₂ (0.05 M), MnO₂</td>
<td>3.3</td>
<td>103.8</td>
</tr>
<tr>
<td>4</td>
<td>0.001</td>
<td>KMnO₄ (0.01 M), 1 hr., 75° C.</td>
<td>H₂O₂ (0.05 M), MnO₂</td>
<td>2.1</td>
<td>105.7</td>
</tr>
<tr>
<td>5</td>
<td>0.001</td>
<td>KMnO₄ (0.01 M), 1 hr., 75° C.</td>
<td>H₂O₂ (0.05 M), MnO₂</td>
<td>37.1</td>
<td>108.0</td>
</tr>
<tr>
<td>6</td>
<td>0.001</td>
<td>KMnO₄ (0.01 M), 1 hr., 75° C.</td>
<td>H₂O₂ (0.05 M), MnO₂</td>
<td>40.6</td>
<td>104.1</td>
</tr>
<tr>
<td>7</td>
<td>0.001</td>
<td>KMnO₄ (0.01 M), 1 hr., 75° C.</td>
<td>H₂O₂ (0.05 M), MnO₂</td>
<td>42.1</td>
<td>104.6</td>
</tr>
<tr>
<td>8</td>
<td>0.001</td>
<td>KMnO₄ (0.01 M), 1 hr., 75° C.</td>
<td>H₂O₂ (0.05 M), MnO₂</td>
<td>49.5</td>
<td>104.5</td>
</tr>
<tr>
<td>9</td>
<td>0.001</td>
<td>KMnO₄ (0.01 M), 1 hr., 75° C.</td>
<td>H₂O₂ (0.05 M), MnO₂</td>
<td>1.6</td>
<td>103.5</td>
</tr>
</tbody>
</table>

It will be obvious from this table that with no preoxidation, with or without prereduction, the plutonium loss amounted to approximately 40%. The plutonium losses were reduced to from 2.1 to 4.5% by the preoxidation treatment according to this invention, potassium dichromate showing slightly superior results to those obtained with potassium permanganate. In experiments 8 and 9 for which hydrazine-free solutions were used, the plutonium losses were as low as 1.5 and 1.6 with and without oxidization, respectively.

It will be understood that this invention is not to be limited to the details given herein but that it may be modified within the scope of the appended claims.

What is claimed is:

1. A process of improving plutonium precipitation on bismuth phosphate from an aqueous plutonium-

2. The process of claim 1 wherein the oxidizing agent is hydrazine-containing nitric acid solution, consisting in adding an oxidizing agent selected from the group consisting of alkali metal dichromate and potassium permanganate to said solution; digesting said solution with the oxidizing agent at a temperature of between 75 and 100° C.; adding sulfuric acid to said solution; adding also at about 75° C. a reducing agent selected from the group consisting of sodium nitrite, oxalic acid plus manganous nitrate and hydroxylamine to said solution whereby the plutonium is secured in the tetravalent state; and then precipitating a bismuth phosphate carrier in said solution.

3. The process of claim 2 wherein the oxidizing agent ranges between 0.02 to 0.03 N.

4. The process of claim 1 wherein the reducing agent is sodium nitrite and wherein it is present in the solution in a concentration of about 0.1 M.

5. The process of claim 1 wherein the reducing agent is a combination of oxalic acid and manganous nitrate which are present in respective concentrations of about 0.03 M and 0.01 M.

6. The process of claim 1 wherein the reducing agent is hydroxylamine and wherein it is present in a concentration of about 0.1 M.

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