
(12) UK Patent Application (19) GB (11) 2 088 346 A

(21) Application No **8118140**
(22) Date of filing **12 Jun 1981**
(30) Priority data
(31) **160245**
(32) **17 Jun 1980**
(33) **United States of America (US)**

(43) Application published
9 Jun 1982

(51) **INT CL³**
B01D 11/04

(52) Domestic classification
C1A 326 D8 G12 G12D8
G36 G58 PD2B

(56) Documents cited
None

(58) Field of search
C1A

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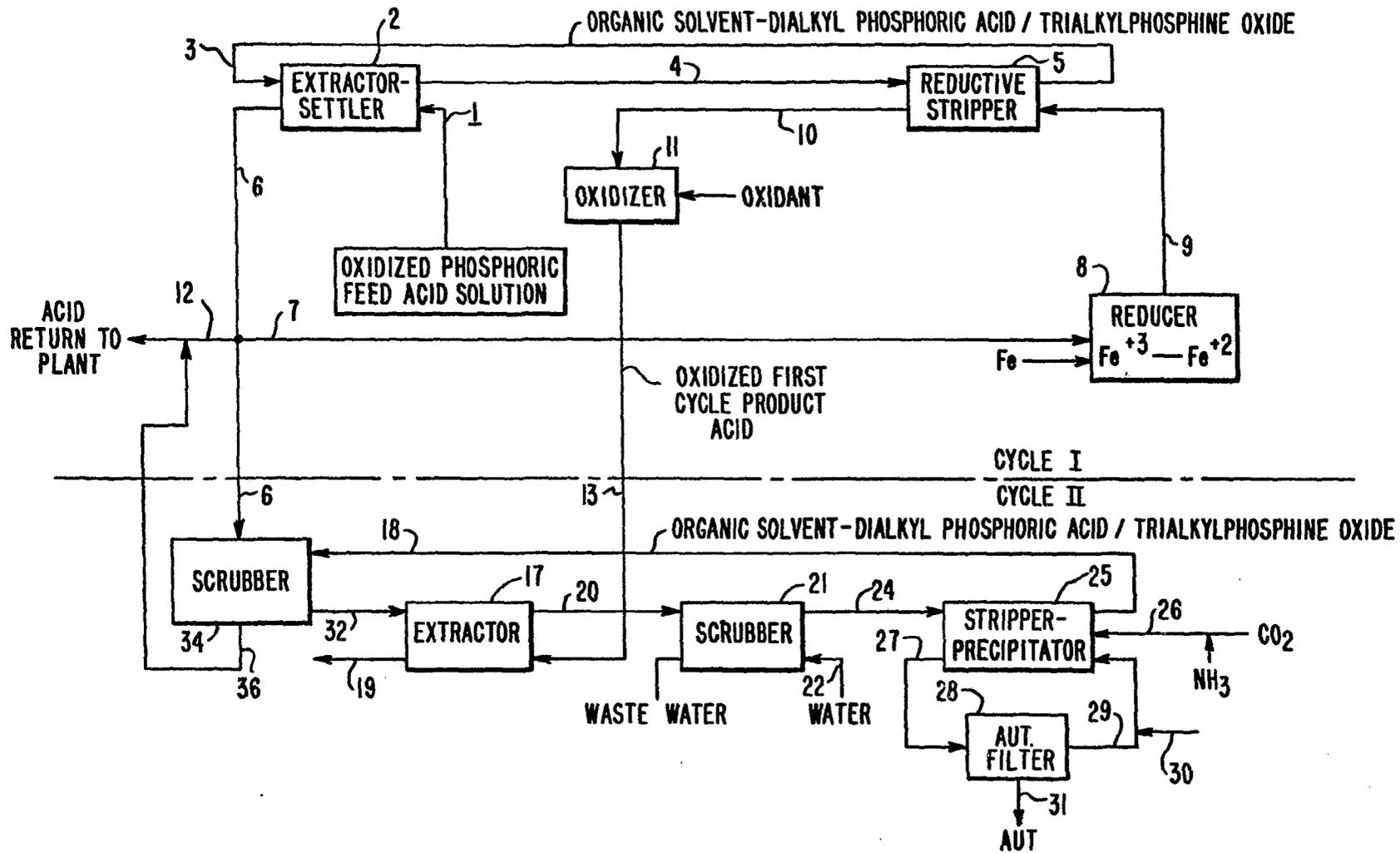
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(54) **Recovering Uranium from Phosphoric Acid**

(57) Precipitation of $\text{Fe}_3\text{HN}_4\text{H}_8(\text{PO}_4)_6$ is prevented in the second cycle extractor, in a two cycle uranium

recovery process, by washing ammonia laden organic solvent stream, from the second cycle stripper, with first cycle raffinate iron stream containing phosphoric acid, prior to passing the solvent stream into the second cycle extractor.

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SPECIFICATION

Method of Recovering Uranium from Phosphoric Acid.

This invention relates to a method of recovering uranium from phosphoric acid.

Presently, uranium is being recovered from phosphoric acid by solvent extraction. In the first cycle of preferred processes using a di-2-ethylhexylphosphoric acid/trialkylphosphine oxide (D2EHPA/TOPO) solvent mixture, the uranium is stripped from the solvent using phosphoric acid containing a high concentration of ferrous iron. The uranium can be recovered from this strip acid by first oxidizing the acid and then re-extracting the uranium, preferably with a D2EHPA/TOPO solvent mixture in a second cycle extraction. The uranium can be recovered from the second cycle solvent using an ammonium carbonate strip solution. This process is well known in the art, and is taught for example by Hurst et al., in U.S. Patent No. 3,711,591; Elikan et al., in U.S. Patent No. 3,966,873 and Sundar, in U.S. Patent No. 4,002,716.

In this second cycle operation, uranium stripped organic is recycled back to re-extract more uranium from the oxidized first cycle product acid. However, an iron-ammonium-phosphate precipitate is formed. The precipitate has been identified as primarily $\text{Fe}_3\text{NH}_4\text{H}_8(\text{PO}_4)_6$. Wiewiorowski et al., in U.S. Patent 4,105,741, dealing primarily with iron removal from phosphoric acid, also recognized this problem. Wiewiorowski et al. attempted to eliminate this precipitate, which interferes with uranium recovery, by washing the second cycle solvent with an outside stream of a purified acid selected from sulfuric, hydrochloric, nitric or iron-free phosphoric acid. However, this requires a large supply of expensive, pure acid, and requires a disposal of the partially neutralized acid. What is needed is an inexpensive means to eliminate the precipitate.

Accordingly, the present invention resides in a process of recovering uranium from an aqueous solution of wet process phosphoric acid feed, having first and second cycles, where phosphoric acid is passed through extractor means and stripper means in both cycles and where a phosphoric acid raffinate containing from 5 grams to 15 grams per liter of iron is produced in the first cycle; said process comprising treating a second cycle ammonia laden organic solvent stream to remove ammonia therefrom, after said solvent has passed through a second cycle stripper means and contacted ammonium compounds, said treating consisting of scrubbing said second cycle ammonia laden organic solvent stream with first cycle phosphoric acid raffinate containing from 3 grams to 15 grams per liter of iron, in an amount effective to remove ammonia, to provide an ammonia barren organic solvent stream which is then fed into the second cycle extractor means, where the volume ratio of the second cycle ammonia laden organic solvent stream: first cycle

iron containing phosphoric acid raffinate stream is from 1:0.2 to 0.5.

The above problems are thus countered by contacting the ammonia laden, organic, second cycle solvent stream with first cycle raffinate wet process phosphoric acid in a scrubbing means. This scrubbing will occur after the second cycle solvent exits the stripper means and before the second cycle solvent re-enters the extractor means. The washed, ammonia barren solvent can then be circulated to extract uranium from the oxidized acid in either but preferably in the second cycle extraction with minimum precipitation of $\text{Fe}_3\text{NH}_4\text{H}_8(\text{PO}_4)_6$. The partially ammoniated, first cycle raffinate acid may then be returned to the main acid stream where it is further processed to make fertilizer products. It has been found that the iron present in the raffinate does not hinder treatment of the second cycle solvent, and so allows use of the inexpensive unpurified phosphoric acid raffinate which is readily available in the uranium recovery system.

In order that the invention can be more clearly understood, a convenient embodiment thereof will now be described, by way of example, with reference to the accompanying drawing which shows a flow diagram, illustrating one example of a prior art process for first and second cycle stripping of uranium from a wet process phosphoric acid feed.

Referring to the drawing, in Cycle I, purified phosphoric feed acid from line 1 enters extractor-settler means 2, which may contain 1 to 6 stages. This feed from domestic phosphate is typically a 35°C to 50°C aqueous 5 to 6 M solution of wet process phosphoric acid having a pH of from 0.1 to 2.5, and containing from 0.1 to 0.5 g/l of uranium (as the uranyl ion, UO_2^{+2}), about 600 g/l of phosphate and about 3 to 15 g/l of iron. Some foreign phosphate deposits may provide a raffinate containing about 3 g/l of iron. In the process shown, the phosphoric acid may be oxidized by any suitable means, to ensure that the uranium is in the +6 oxidation state, i.e., uranyl ion. In the extractor-settler, the feed acid is contacted by mixing with a water-immiscible, organic extractant composition from line 3. The extractant solvent composition contains a reagent which extracts the uranyl ions to form a uranium complex soluble in the organic solvent. Typically, the solvent composition from line 3 is added in a 0.5 to 1 solvent to phosphoric feed acid ratio (by volume). The solvent composition from line 3 contains from 0.2 to 0.7 mole of a di-alkyl phosphoric acid additive having from 4 to 10 carbon atoms in each chain, preferably di-2-ethylhexyl phosphoric acid (D2EHPA) per liter of solvent. The solvent also contains from 0.025 to 0.25 mole of a synergistic additive agent well known in the art, for example, a trialkylphosphine oxide, where the alkyl chains are linear from C_4 to C_{10} , preferably tri-n-octylphosphine oxide (TOPO) per liter of solvent. These synergistic agents allow reduction of equipment size while increasing uranium extraction. The solvent is usually

kerosene. The use of the term "solvent stream" herein is meant to include such additives as described above. While the description herein is primarily directed to D2EHPA/TOPO mixtures, it is to be understood that broader di-alkyl phosphoric acid/trialkylphosphine oxides are included.

The solvent stream, containing complexed uranium, passes through line 4 to reductive stripper means 5, which may contain 1 to 4 stages, to strip uranium from the organic solvent. A portion of the raffinate from extractor 2 passes through line 7 to reducer 8 where iron (Fe^0) is added to reduced enough ferric ions to bring the ferrous ion concentration up to a level sufficient to reduce the uranyl ion to the U^{+4} ion. The ferrous ion enters reductive stripper 5 by line 9 and is oxidized there to the ferric ion, while reducing the uranyl ion to the quadravalent U^{+4} ion, which is transferred to the aqueous stream strip solution in line 10. The organic solvent leaving the stripper is then recycled through line 3 to extractor 2.

Finally, the U^{+4} ion in the strip solution in line 10 is oxidized to the uranyl ion in oxidizer 11, to enable the uranium to be extracted again in Cycle II. The product from Cycle I contains phosphoric acid and typically has a pH of about 0.1 to 2.5. It contains from 25 g/l to 40 g/l of iron, and from 3 g/l to 15 g/l of uranium. An appropriate portion of the first cycle raffinate acid is fed into Cycle II by line 6. The remainder of the raffinate exits by line 12.

Cycle II

The oxidized aqueous liquor solution in line 13 contains uranium in the hexavalent state i.e., the uranyl ion. The aqueous liquor passes through line 13 to liquid-liquid solvent extractor 17. The aqueous liquor is mixed with a water-immiscible, organic solvent stream from line 32, which reacts with the uranyl ions in the liquid to form a complex soluble in the solvent. This second cycle solvent stream from line 18 is washed in scrubbing means 34, as described below, to prevent precipitation of $\text{Fe}_3\text{NH}_4\text{H}_8(\text{PO}_4)_6$ in the extractor 17.

This solvent stream 32 is generally the same as that of feed line 3, i.e., preferably from 0.2 to 0.7 mole of di-alkyl phosphoric acid additive, well known in the art, having 4 to 10 carbon atoms in each chain, preferably di-2-ethylhexyl phosphoric acid (D2EHPA) per liter of solvent. The solvent stream also contains about 0.025 to 0.25 mole of a synergistic additive agent well known in the art, for example, a trialkylphosphine oxide, where the alkyl chains are linear from C_4 to C_{10} , preferably tri-n-octylphosphine oxide (TOPO) per liter of solvent. Ammonia present in the solvent stream of line 18 will be removed in scrubbing means 34, as described below, to provide the ammonia barren stream 32. Typically, the volume ratio of solvent stream:aqueous liquor of line 16 fed into the second cycle extractor is about 1:4 to 1.

The organic solvent stream, containing complexed uranium leaves extractor 17 through line 20. The organic solvent-acid in line 20 may

be scrubbed with water in scrubber 21 to remove any acid entrainment which would increase the ammonia consumption in the stripper-precipitator 25. Water enters scrubber 21 by line 22 and waste water leaves by line 23. The organic solvent then passes through line 24 to stripper 25.

In the stripper 25, the organic solvent stream is stripped with an aqueous solution containing enough ammonium compounds, such as ammonium carbonate, ammonium bicarbonate, or a mixture thereof from line 26 to precipitate a uranium complex from the organic phase. The preferred uranium complex is AUT as it is easy to filter. The organic solvent stream is recycled through line 18. The aqueous slurry containing the precipitated AUT passes through line 27 to AUT filter 28 where AUT is filtered off.

The filtrate is recycled through line 29 to stripper-precipitator 25. A 0.5 M ammonium carbonate solution is added to line 29 as needed from line 30 to make up for water losses. The precipitated AUT can be calcined in an oven at from 350°C to 900°C which drives off carbon dioxide and ammonia. If the calcining is done in a reducing atmosphere, such as a hydrogen-nitrogen mixture, UO_2 is obtained and collected. If the calcining is done in an oxidizing atmosphere, such as air, the mixed oxide U_3O_8 is obtained and collected.

In the second cycle organic solvent-dialkyl phosphoric acid/trialkylphosphine oxide wash step, central to this invention, an ammonia laden second cycle solvent stream from line 18, i.e., uranium barren solvent-dialkyl phosphoric acid/trialkylphosphine oxide contacted with ammonium carbonate, and containing from 5 to 10 grams per liter of ammonium ion, is washed in scrubber means 34, with first cycle raffinate, iron-containing phosphoric acid from line 6. The volume ratio of the ammonia laden second cycle solvent cycle solvent stream:first cycle raffinate acid is from about 1:0.2 to 0.5. Over 0.5 and the system will start to become acid continuous instead of organic continuous and an emulsion will form hindering extraction. Under 0.2 and the ammonia will not be effectively neutralized. This range is critical to providing substantially ammonia barren organic solvent-D2EHPA/TOPO, feed into the extractor.

In the scrubber means 34, the ammonia passes from the organic solvent stream to the aqueous acid phase, transferring to the phosphoric acid raffinate. The organic phase, which is immiscible in the aqueous phase, is then fed into the extractor. In this invention, wet process phosphoric acid raffinate is used, containing from 5 to 15 grams per liter of iron, rather than chemically pure phosphoric acid. It has been found that the iron present does not hinder washing the second cycle solvent stream and allows use of inexpensive raffinate already in the system. The washed second cycle solvent stream exits as line 32, which can then be used in the extractor 17, without forming any substantial

amounts of $Fe_3NH_4(PO_4)_6$ precipitate. The partially ammoniated first cycle acid exits as line 36 which is returned to the main acid stream where it is returned to the plant and further processed to make fertilizer. The use of first cycle raffinate is especially effective for this washing step since it is low in contaminating organics and low in uranium. It is effective to remove from 95 to 99 wt. % of the ammonium ions present in the ammonia laden solvent-dialkylphosphoric acid/trialkylphosphine oxide, preferably solvent-D2EHPA/TOPO, stream 18.

The invention will now be illustrated with reference to the following Example:

15 Example

The second cycle of a uranium recovery process was modified as shown in the drawing, so that second cycle extractant, comprising ammonia laden di-2-ethylhexylphosphoric acid and tri-n-octylphosphine oxide in kerosene solvent, fresh from the second cycle strip mixer settler, was piped into a scrubber tank. About 0.50 mole of D2EHPA and 0.125 mole of TOPO was present per liter of kerosene. The ammonia laden organic contained about 9 grams per liter of ammonium ion. In the scrubber tank, the second cycle organic extractant was mixed with first cycle raffinate phosphoric acid, containing about 10 grams per liter of iron, to provide ammonia free solvent-acid. The volume ratio of ammonia laden second cycle solvent-D2EHPA/TOPO: first cycle raffinate acid was 1:0.3. This, washed, ammonia free extractant was then fed into the second cycle extractor means, where it extracts uranium from the oxidized acid from Cycle I. The uranium was then stripped with ammonium-uranyl-tricarbonate.

Prior to installation of the separate scrubbing tank, the quantity of $Fe_3NH_4H_8(PO_4)_6$ precipitate formed in the second cycle extractor means averaged 60 lb./hr. After installation of the scrubbing tank, the quantity of $Fe_3NH_4H_8(PO_4)_6$ solids was reduced to about 10 lb./hr. for the same flow rates of all the materials. This indicated that very little ammonia was back extracted, that the iron in the raffinate did not hinder scrubbing, and that about 97 wt. % of ammonium ion was removed from the ammonia laden solvent-D2EHPA/TOPO in the ammonia neutralization scrubber.

Identification of Reference Numerals used in the Drawings

	Ref. No.	Figure
<i>Legend</i>		
55 Extractor-Settler	2	1
Reductive Stripper	5	1
Reducer $F^{+3} \rightarrow Fe^{+2}$	8	1
Oxidizer	11	1
Extractor	17	1
60 Scrubber	21	1
Stripper-Precipitator	25	1
AUT. Filter	28	1
Scrubber	34	1

Claims

65 1. A process of recovering uranium from an aqueous solution of wet process phosphoric acid feed, having first and second cycles, where phosphoric acid is passed through extractor means and stripper means in both cycles and
70 where a phosphoric acid raffinate containing from 5 grams to 15 grams per liter of iron is produced in the first cycle; said process comprising treating a second cycle ammonia laden organic solvent stream to remove ammonia therefrom, after said
75 solvent has passed through a second cycle stripper means and contacted ammonium compounds, said treating consisting of scrubbing said second cycle ammonia laden organic solvent stream with first cycle phosphoric acid raffinate
80 containing from 3 grams to 15 grams per liter of iron, in an amount effective to remove ammonia, to provide an ammonia barren organic solvent stream which is then fed into the second cycle extractor means, where the volume ratio of the
85 second cycle ammonia laden organic solvent stream: first cycle iron containing phosphoric acid raffinate stream is from 1:0.2 to 0.5.

2. A method according to claim 1, wherein the second cycle ammonia laden organic solvent stream contains 5 to 10 grams per liter of ammonium ion before scrubbing, said scrubbing being effective to remove from 95 to 99 wt. % of the ammonium ions.

3. A method according to claim 1 or 2, wherein the second cycle ammonia laden organic solvent stream contains a di-alkyl phosphoric acid having 4 to 10 carbon atoms in each chain and a trialkylphosphine oxide, where the alkyl chains are linear from C_4 to C_{10} .

100 4. A method according to claim 3, wherein the second cycle ammonia laden organic solvent stream consists of di-2-ethylhexyl phosphoric acid and tri-n-octylphosphine oxide in kerosene solvent.

105 5. A method according to any of claims 1 to 4, wherein there is included the step of feeding the ammonia barren organic solvent stream into a second cycle extractor, to contact a stream of oxidized phosphoric acid and ammonium-uranyl-tricarbonate mixture without forming any
110 substantial amounts of iron-ammonium-phosphate precipitate.

6. A method according to claim 5, wherein the volume ratio of the solvent stream: oxidized acid plus ammonium-uranyl-tricarbonate stream is from 1:0.5 to 1.

7. A process of recovering uranium from wet process acid by liquid-liquid extraction, wherein uranium values are stripped from an organic
120 extractant with an aqueous ammonium carbonate solution, said process comprising contacting said extractant after said stripping with a phosphoric acid solution containing at least 3 grams per liter of iron.

125 8. A process according to claim 7, wherein the phosphoric acid solution is raffinate wet process acid.

9. A process according to claim 8, wherein the

acid solution is a portion of the raffinate wet process acid from a first stage liquid-liquid extraction process.

5 10. A process according to claim 7, 8 or 9, wherein the organic extractant contains a dialkylphosphoric acid and a trialkylphosphine oxide.

11. A process according to claim 10, wherein

10 the dialkylphosphoric acid is di-2-ethylhexyl phosphoric acid and the tri-alkyl-phosphine oxide is tri-n-octylphosphine oxide.

15 12. A process of recovering uranium from an aqueous solution of wet process phosphoric acid feed as claimed in claim 1 and substantially as described herein with particular reference to the foregoing Example.