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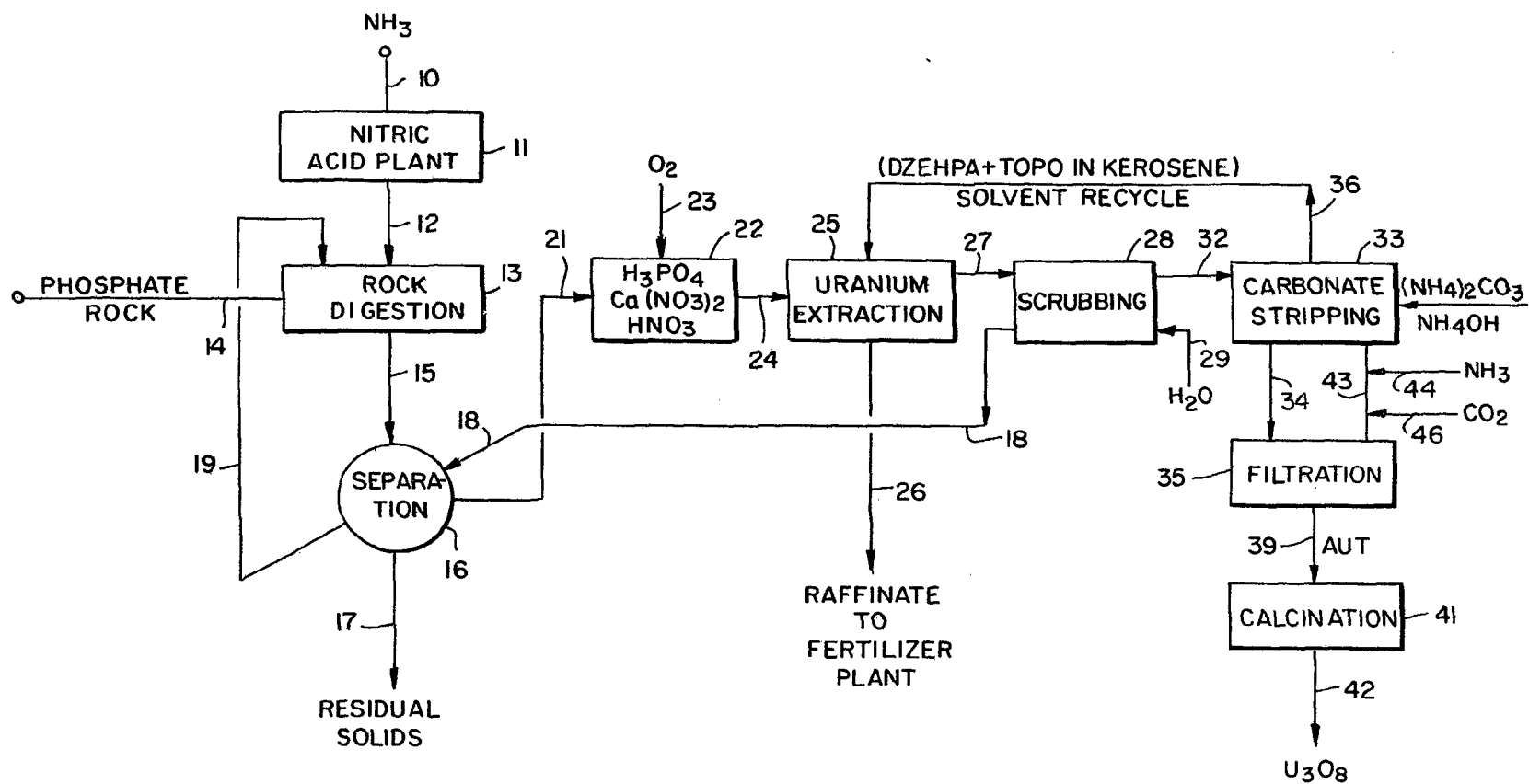
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(54) **Recovering phosphorus and uranium values from phosphate rock**

(57) Phosphate rock is acidulated with aqueous nitric acid to produce an aqueous solution containing phosphate values, calcium and uranium values. The aqueous solution is contacted with an extraction solvent for the uranium values; the extraction

solvent comprising a water immiscible organic diluent, a dialkyl phosphonic acid having at least 10 carbon atoms, and an organic phosphorus compound having the formula $R_1 R_2 R_3 P = O$ where R_1 , R_2 and R_3 are each either alkyl or alkoxy, the organic phosphorus compound having at least 10 carbon atoms. The uranium values are then recovered from the extraction solvent.

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SPECIFICATION

Improvements in or relating to a process for recovering phosphorus and uranium values from phosphate rock

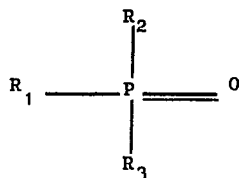
5 This invention relates to the treatment of phosphate rock, and more particularly to a process for recovering both phosphorus and uranium values from a phosphate rock.

10 Phosphorus values are conventionally recovered from phosphate rock by acidulation with sulphuric acid, which extracts the phosphorus values into the aqueous phase and produces a calcium sulphate residue. The acid is later converted to various forms of fertilizer products, such as diammonium phosphate and others.

15 It is known that the traces of uranium present in the phosphate rock are a valuable raw material for nuclear power plant fuel, and it has been proposed to extract such uranium values from the aqueous phosphoric acid produced in the acidulation. It has been found, however, that such a procedure is not completely effective in that uranium, which is contained in the solid calcium sulphate waste produced as a byproduct, is not extracted, and the radioactivity of the calcium sulphate waste creates an environmental problem.

20 The present invention seeks to provide a process for extracting and recovering phosphorus and uranium values from phosphate rock, without loss of any significant portion of the potential uranium values present in the phosphate rock in a solid phase.

25 According to the broadest aspect of this invention there is provided a process for recovering phosphorus and uranium values from phosphate rock, comprising: treating phosphate rock with aqueous nitric acid to produce an aqueous solution of phosphoric acid, calcium nitrate and uranium values present in the phosphate rock; extracting uranium values from the aqueous solution with an extraction solvent comprising a water immiscible organic diluent, a dialkyl phosphoric acid having at least 10 carbon atoms, and an organic phosphorus compound having the structural formula;



30 wherein R_1 , R_2 , and R_3 are each selected from the group consisting of alkyl and alkoxy, and wherein the organic phosphorus compound has at least 10 carbon atoms, said dialkyl phosphoric acid and organic phosphorus compound being dissolved in the water immiscible organic diluent; and recovering uranium values from the extraction solvent.

35 Thus, in a preferred process in accordance with the present invention, phosphate rock is acidulated with aqueous nitric acid to produce an

aqueous solution containing the phosphate, calcium and uranium values present in the phosphate rock. Such aqueous solution is then contacted with an extraction solvent selective for the uranium present in such aqueous solution, whereby the uranium values are effectively separated from the phosphate and calcium values.

40 The uranium is then recovered from such extraction solvent. It has been found that by employing a combination of nitric acid acidulation with uranium extraction it is possible to improve the recovery of the uranium values originally present in the phosphate rock, in comparison with prior proposed processes.

45 More particularly, phosphate rock, which may be any one of the varieties conventionally employed in the art for recovery of phosphate values, which may be employed in the acidulation in the calcined or uncalcined state, in ground form, is acidulated with aqueous nitric acid to produce water soluble calcium nitrate and water soluble phosphoric acid, with such aqueous portion also including uranium values originally present in the rock. In general, such acidulation is conducted at a temperature in the order of from about 38°C (100°F) to about 93°C (200°F) with nitric acid having a concentration in the order of from about 50 to about 70% by weight. The nitric acid is generally employed in an amount which is from about 10 to about 20% in excess of that required to convert all calcium in the rock to calcium nitrate. As a result of the use of such nitric acid for the acidulation, a major portion, if not all of the uranium, is in the aqueous phase in the hexavalent state. Insoluble materials such as stones, clays, etc. are separated from the aqueous acid solution by filtration, and the filter cake is washed with a small amount of water.

50 In a preferred process in accordance with the present invention, the uranium is subsequently recovered from such aqueous acid solution by an extraction solvent which extracts uranium in the hexavalent state. As a result, in the event that any of the uranium present in such aqueous acid solution is not in the hexavalent state, such uranium must be oxidized to the hexavalent state. In general, such oxidation may be conveniently conducted by the addition of hydrogen peroxide, sodium chlorate, ammonium persulfate and similar oxidizing agents at temperatures ranging from 37°C (100°F) to 93°C (200°F). In fact, given sufficient time, air can be used to accomplish the oxidation at 60°C (140°F) to 76°C (170°F).

55 The aqueous acid solution which contains uranium in the hexavalent state, as well as calcium ions, is then contacted with an extraction solvent for selectively extracting the uranium therefrom. It has surprisingly been found that uranium extraction solvents previously employed in the art for extracting uranium from acid solutions could be effectively employed in the present invention, notwithstanding the fact that the acid solution includes calcium ions. The preferred organo phosphorus used in the

extraction solvent has three identical alkyl groups.

The organic diluent is generally a hydrocarbon, with kerosene being particularly preferred.

5 A particularly preferred uranium extraction solvent is comprised of di(2-ethylhexyl) phosphoric acid and triocetylphosphine oxide in an organic diluent; in particular, kerosene.

10 In employing the extraction solvent, in general, the ratio of the dialkyl phosphoric acid to organo phosphorus compound is in the order of from about 2 to 1 to about 6 to 1, and preferably from about 3.6 to 1 to about 4.4 to 1. In general, the two compounds are employed in the organic diluent in a concentration in the order of from about 0.375 molar to about 1.0 molar.

15 The extraction may be conducted at temperatures in the order of from about 21°C (70°F) to about 71°C (160°F) with the temperature being preferably above 26°C (80°F) generally in the order of from about 26°C (80°F) to 49°C (120°F) in that phase separation is improved at such higher temperatures. Thus, at such higher temperatures, there is a suitable liquid viscosity and in addition crystallization of calcium nitrate is avoided.

20 In the presently preferred procedure, the extraction is conducted in several stages as a counter-current extraction with a continuous organic phase. In employing such an extraction procedure, at the extraction temperature, the phase ratios and contact times are selected to provide for extraction of the uranium values into the organic phase, with substantially all of the phosphate values remaining in the raffinate phase. Thus, for example, the extraction may be conducted with organic to aqueous phase ratios in the order of from 2 :1 to 0.25 :1. Any small amounts of phosphate which are extracted into the organic phase may be effectively recovered by the use of a water wash, which can be recycled to the washing of the filter cake from the nitric acid acidulation.

25 The aqueous raffinate recovered from the extraction includes the phosphorus and calcium values, which may be processed by procedures known in the art to produce fertilizer products.

30 The organic extract, including the extracted uranium values, may then be treated in order to recover such uranium values. Thus, for example, uranium can be recovered from such organic extract by contacting the organic extract with an aqueous carbonate solution, to give the soluble ammonium uranyl tricarbonate complex in the aqueous phase. The solubility of uranium is inversely dependent on the ammonium salt concentration, and as a result, by employing an excess amount of ammonium salt in the recovery procedure, yellow crystals of ammonium uranyl tricarbonate can be obtained upon standing. Such crystals can be recovered by filtration, and then decomposed by calcination to yield a relatively high-grade U₃O₈ product.

35 In employing ammonium carbonate (ammonium carbonate generically refers to the carbonate and/or bicarbonate) for recovering

40 uranium from the organic extraction solvent, in general about 1.0 M ammonium carbonate is sufficient to precipitate the ammonium uranyl tricarbonate (AUT), although about 1.5 M to about 2.5 M ammonium carbonate is preferred. The ratio (by volume) of aqueous solution to organic solvents is preferably about 0.5 to about 5.

45 The recovered AUT can be calcined in an oven at about 350°C to about 900°C to recover uranium oxide. If a reducing atmosphere is employed, the uranium is recovered as UO₂ and if an oxidizing atmosphere is employed, such as oxygen, U₃O₈ is obtained.

50 It has been found that by proceeding in accordance with the present invention, it is possible to recover at least 80% of all the uranium values originally present in the phosphate rock, and in most cases the uranium recovery is 85% or better. The invention also relates to phosphorus and uranium recovered by the described process.

55 In order that the invention may be more readily understood, and so that further features thereof may be appreciated, the invention will now be described by way of example, with reference to the accompanying drawing which is a simplified schematic flow diagram of an embodiment of the present invention.

60 Referring now to the drawing, ammonia in line 10 is introduced into a nitric acid plant, schematically generally indicated as 11, wherein the ammonia is oxidized and converted to nitric acid by procedures known in the art.

65 Such nitric acid, in line 12, is then employed for the digestion (acidulation) of phosphate rock, schematically indicated as 13, with the phosphate rock being provided to such acidulation through line 14.

70 The effluent from such acidulation, in line 15, is introduced into a suitable separator, schematically generally indicated as 16, in order to separate insoluble materials such as stone, clays, etc. Such separation may be conveniently conducted by a suitable filtration procedure, with the residual solids being recovered in line 17. Prior to recovery of such solids, such solids are washed with a wash liquor introduced through line 18, and obtained as hereinafter described.

75 The wash liquor, containing any dissolved phosphate or uranium values is recycled to the digestion through line 19.

80 The acid solution from which the residual solids have been separated, containing calcium nitrate, phosphoric acid, and nitric acid, as well as dissolved uranium values, primarily in the hexavalent state, flows through line 21, and may be subjected to oxidation in zone 22 by oxygen or another oxidant introduced through line 23, if required, in order to convert any uranium values to the hexavalent state.

85 The aqueous solution in line 24 is then introduced into the uranium extraction zone, schematically generally indicated as 25, wherein the aqueous solution is contacted with a uranium extraction solvent, of the type hereinabove described. As hereinabove described, such

extraction may be effected in one or more stages, with the extraction preferably being conducted in a plurality of stages by counter-current extraction.

5 An aqueous raffinate, containing soluble phosphorus and calcium values is withdrawn from the extraction through line 26.

An organic extract, containing dissolved uranium values, withdrawn from the extraction 25 through line 27, is introduced into a water scrubbing zone, schematically generally indicated as 28, wherein the extract is scrubbed with water, introduced through line 29, in order to recover any phosphorus values which may have been dissolved in the organic phase. Such water, 15 recovered from the scrubbing operation in line 18, may then be employed for washing the solids in separator 16, as hereinabove described.

The extract recovered from the scrubbing in line 32 is then introduced into the uranium recovery zone, schematically generally indicated as 33, wherein uranium is recovered from the extract by use of aqueous ammonium carbonate, as hereinabove described. As hereinabove described, the ammonium carbonate is employed in a 25 manner such that the uranium is recovered as solid crystals of AUT.

Crystallized AUT in an aqueous phase is recovered from zone 33 through line 34 for introduction into a filtration zone, schematically 30 generally indicated as 35. Organic extraction solvent is recovered from zone 33 through line 36 for re-use in extracting the uranium values from the aqueous acidulation effluent, as hereinabove described.

35 AUT crystals, recovered from the filtration zone 35 in line 39 is introduced into a calcination zone, schematically generally indicated as 41 to calcine AUT to U_3O_8 , which is recovered through line 42.

Filtrate recovered from filtration zone 35 40 through line 43 is provided with makeup ammonia and carbon dioxide in lines 44 and 45, respectively, and recycled to the uranium recovery zone 33.

The invention will be further described with 45 respect to the following examples:

EXAMPLE 1

A 1000 g Mobil Florida phosphate rock (Table 1 and 2) containing, by weight, 32.35% P_2O_5 , 47.51% CaO, 1.18% Fe_2O_3 , 5.59% SiO_2 , 3.45% F 50 and 0.013% uranium was charged to a reactor. It was reacted with 2090 g of nitric acid, 61.4% concentration by weight. This amount of acid represents a 20% excess of what is required to convert all calcium in the rock to calcium nitrate. 55 The reaction was completed in about 1/2 hour, during which time the temperature rose from ambient to about 51 °C (125 °F). The product was then filtered; the insoluble materials were washed by two portions of water, 150 g each. A combined 60 liquor of about 3015 g (digestion acid + wash water) was obtained. The solid residue of 208 g was discharged to waste.

The 3015 g of liquor thus obtained contained 10.6% by weight of P_2O_5 , 15.5% CaO and 0.044%

65 uranium. A certain amount of nitrate, iron and aluminium are also present in the liquor. (See Table 3.)

Table 4 gives the composition of insoluble solids. The recovery of P_2O_5 , CaO and uranium 70 were 98%, 97% and 97.7% respectively in the nitric acid acidulation step. Following the scheme outlined in Perry's Chemical Engineers' Handbook p. 14—43, a multiple stage batchwise simulated countercurrent extraction was then made, using 75 0.5 M di(2-ethylhexyl)phosphoric acid (D2 EHPA) + 0.125 M triocylphosphine oxide (TOPO) in kerosene (AMSCO-460) to recover uranium from the phosphoric acid-calcium nitrate-nitric acid mixture. The solvent was placed first in a 80 separatory funnel. The aqueous acid mixture with 0.044% uranium (obtained from digestion as described above) was introduced slowly into the solvent phase. The phase ratio of organic solvent to acid was about 0.5 to 1.0 (on volume). The 85 separatory funnel was shaken at ambient temperature for about 10 minutes. After settling, the phases were separated, the raffinate and extract were analyzed for their uranium contents via a colorimetric method. The raffinate and 90 extract then entered the next stage for further extraction. After 5 stages, 93% of the uranium was recovered.

TABLE 1

Mobil Floride Phosphate Rock Compositions
Moisture 0.8% after drying

	Wt %
Phosphorus pentoxide (P_2O_5)	32.35
iron oxide (Fe_2O_3)	1.18
Aluminum oxide (Al_2O_3)	1.05
Calcium oxide (CaO)	47.51
Magnesium oxide (MgO)	0.42
Fluorine	3.45
Silica (SiO_2)	5.59
Sodium oxide (Na_2O)	0.56
Potassium oxide (K_2O)	0.14
Sulphite (SO_3)	1.08
Carbon dioxide (CO_2)	2.86
Organic carbon	0.05
Arsenic oxide (As_2O_3)	0.001
Uranium (U_3O_8)	0.013

TABLE 2

*Phosphate Rock Size Analysis
Wt % Collected on the Sieve*

Sieve No.	Floride Rock Mobil Chemical
+35	0.20
+60	1.76
+70	1.62
+100	6.32
+200	44.12
+325	33.78
Pan	12.20
Total	100.00

TABLE 3

Mobil Phosphate Rock Digestion Liquor

	Wt %
Phosphorus Pentoxide (P ₂ O ₅)	10.58
Calcium oxide (CaO)	15.47
Iron oxide (FeO ₃)	0.29
Aluminum oxide (Al ₂ O ₃)	0.26
Nitrate (NO ₃)	16.93
Fluorine	0.94
Uranium (U ₃ O ₈)	44 ppm

TABLE 4

*Mobil Phosphate Rock Residual Solid Main
Compositions
Amount of residue 208 gms*

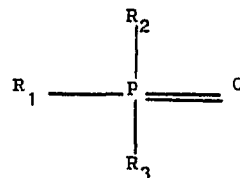
	Wt %
Phosphorus pentoxide (P ₂ O ₅)	3.04
Calcium oxide (CaO)	6.76
Uranium (U ₃ O ₈)	15 ppm

The present invention is particularly
5 advantageous in that it permits effective recovery
of phosphorus values from phosphate rock, while

simultaneously providing for high recovery of
uranium values. Thus, by utilising the present
invention, it has been found possible to recover at
10 least 80% and most generally at least 85% of the
uranium values present in the phosphate rock.
This is an improvement over prior art procedures
in which uranium recoveries were lower as a result
of uranium loss in calcium sulphate byproduct.
15 Thus the present invention has enabled high levels
of uranium recovery to be achieved, not
withstanding the presence of calcium loss ions
(calcium nitrate) which would have been expected
to interfere with uranium recovery.

20 CLAIMS

1. A process for recovering phosphorus and
uranium values from phosphate rock, comprising:
treating phosphate rock with aqueous nitric acid
to produce an aqueous solution of phosphoric
25 acid, calcium nitrate and uranium values present
in the phosphate rock; extracting uranium from
the aqueous solution with an extraction solvent
comprising a water immiscible organic diluent, a
dialkyl phosphoric acid having at least 10 carbon
30 atoms, and an organic phosphorus compound
having the structure formula:



- wherein R₁, R₂ and R₃ are each selected from the
group consisting of alkyl and alkoxy, and wherein
35 the organic phosphorus compound has at least 10
carbon atoms, said dialkyl phosphoric acid and
organic phosphorus compound being dissolved in
the water immiscible organic diluent; and
recovering uranium values from the extraction
40 solvent.

2. A process according to claim 1 wherein the
nitric acid concentration is from 50% to 70% by
weight.

3. A process according to claim 1 or claim 2
45 wherein the nitric acid is employed in an amount
of from about 10% to 20% in excess of that
required to convert all calcium in the rock to
calcium nitrate.

4. A process according to any one of the
50 preceding claims wherein the ratio of dialkyl
phosphoric acid to organic phosphorus compound
is from 2 : 1 to 6 : 1.

5. A process according to any one of the
preceding claims wherein the extracting is
55 conducted at a temperature of above 26°C
(80°F).

6. A process according to any one of the
preceding claims wherein the uranium is
recovered from the extraction solvent as
60 ammonium uranyl tricarbonate by contact with
aqueous ammonium carbonate.

7. A process according to any one of the

preceding claims wherein the extraction solvent is di(2-ethylhexyl) phosphoric acid and trioctylphosphine oxide dissolved in kerosene.

5 8. A process according to claim 7 wherein at least 85% of the uranium present in the rock is recovered.

9. A process according to claim 7 or claim 8 wherein the ratio of di(2-ethylhexyl) phosphoric acid to trioctylphosphine oxide is from 2 :1 to 6 :1.

10 10. A process according to any one of the preceding claims including the step of recovering phosphorus from said aqueous solution after said

solvent extraction of uranium values.

15 11. A process substantially as herein described with reference to the accompanying drawing.

12. A process substantially as herein described in the example.

13. Phosphorus whenever recovered by a process according to claim 10.

20 14. Uranium whenever recovered by a process according to any one of claims 1 to 12.

15. Any novel feature or combination of features disclosed herein.