



(11) (A) No. **1 187 293**

(45) ISSUED 850521

(52) CLASS 53-211

(51) INT. CL. ³C22B 60/02

(19) (CA) **CANADIAN PATENT** (12)

(54) Measurement of the Oxidation-Extraction of Uranium
from Wet-Process Phosphoric Acid

(72) Lawes, Bernard C.,
U.S.A.

(73) Granted to du Pont (E.I.) de Nemours and Company
U.S.A.

(21) APPLICATION No. 392,992

(22) FILED 811222

(30) PRIORITY DATE U.S.A. (220,824) 801229

No. OF CLAIMS 4 - NO DRAWING

Canada

TITLE

Measurement of the Oxidation-Extraction
of Uranium from Wet-Process Phosphoric Acid

ABSTRACT OF THE DISCLOSURE

5 In the oxidation-extraction steps in the
reductive stripping process (e.g., DEPA-TOPO process)
for recovering uranium from wet-process phosphoric
acid, efficient use of oxidant is obtained using an
mv monitoring of the redox potential during a uranium
10 extraction step to determine an appropriate amount
and rate of addition of the oxidant.

TITLE

Measurement of the Oxidation-Extraction
of Uranium from Wet-Process Phosphoric Acid

BACKGROUND OF THE INVENTION5 Field of the Invention

The present invention relates to processes for the recovery of uranium from wet-process phosphoric acid and more particularly to the oxidation-extraction steps in the DEPA-TOPO process for such recovery. A more
10 efficient use of oxidant is obtained by monitoring the redox potential during the extraction step.

Prior Art

In the mining of phosphate rock to recover phosphate-containing fertilizer, the first step con-
15 sists of digesting the rock with sulfuric acid under carefully controlled conditions to produce a phosphoric acid solution and calcium sulfate. The crude phosphoric acid solution, called "wet-process" phosphoric acid, can be processed to remove valuable uranium values,
20 particularly if it can be economically justified. Removal of uranium from crude phosphoric acid not only provides an additional valuable energy source, but also removes an unwanted contaminant from the phosphoric acid, much of which is used to make fertilizer. It is
25 important, however, that chemicals used in uranium removal do not add any substantial contaminant burden to the phosphoric acid.

There are two types of processes used to recover uranium values from wet-process phosphoric acid:
30 oxidative stripping processes such as described in Schmitt, U.S. Patent 3,052,514 and Hurst et al., U.S. Patent 3,835,214, and a reductive stripping process such as described in U.S. Patent 3,711,591, also to Hurst et al.



In the oxidation step of the DEPA-TOPO [di-(2-ethylhexyl) phosphoric acid combined with trioctylphosphine oxide] reductive stripping process, uranium (IV) in the crude phosphoric acid solution is oxidized to the hexavalent state by an appropriate oxidizing agent. Many oxidizing agents have been described in the art, e.g., sodium chlorate, air, pure oxygen and hydrogen peroxide. Although sodium chlorate appeared to be the oxidizing agent of choice, chlorides resulting from this oxidizer are corrosive and also can carry over into fertilizer as undesirable impurities. Hydrogen peroxide even though more costly to use is becoming increasingly desirable as an oxidant since it does not contribute contaminants.

In the art of reductive stripping, the teaching is to oxidize the uranium and extract. To know if there is sufficient oxidant for the uranium extraction, the redox potential of the acid solution is measured before the uranium is extracted by an organic DEPA-TOPO solution; however, the measurement of the acid stream before extraction is not a sensitive enough measurement to determine the sufficiency of oxidant to be used for the uranium extraction.

The present invention is an improvement in the reductive stripping process allowing for the more accurate determination of the uranium value and more efficient use of the oxidizing agent.

SUMMARY OF THE INVENTION

According to the present invention, there has been found in a reductive stripping process for recovering uranium values from a phosphoric acid solution wherein uranium in the solution is oxidized to uranium (VI) oxidation state and extracted from the solution, the improvement which comprises measuring the redox

potential of the system during an extraction step,
including during a simultaneous oxidation and extrac-
tion step. Specifically, it has been found that by
monitoring redox potential during the extraction step
5 one can better predetermine the amount of oxidant to add
to the phosphoric acid to extract uranium by the DEPA-
TOPO process. It has also been found that when the
oxidant is added simultaneously during the extraction
stage, redox potential monitoring during that stage can
10 be used to determine the oxidant requirement.

In summary, it has now been found that the
process can be operated at a desired level of oxidant
to give more efficient use of oxidant and more
efficient recovery of uranium.

15 DETAILED DESCRIPTION OF THE INVENTION

The detailed process conditions for the over-
all DEPA-TOPO process are well-known to those skilled
in the art and need not be repeated here. The process
is described in the aforesaid U.S. Patent 3,711,591
20 and in a paper presented by copatentee Hurst at the
AIME (American Institute of Mining Engineers) Annual
Meeting, Las Vegas, Nevada, February 22-26, 1976,
available as Preprint Number 76-B-66 of Society of
Mining Engineers of AIME in Littleton, Colorado 80123.

25 The state of the art as revealed in these
references does not disclose that there are constraints
or qualifications as to how to best determine an oxi-
dant for use during the first oxidation step. This is
not surprising since the purpose of the oxidation is
30 basically a simple inorganic oxidation reaction, the
conversion of any uranium in the uranium (IV) state into
the uranium (VI) state so that it can be extracted from

the phosphoric acid solution. Although the oxidation can be represented by a direct reaction of hydrogen peroxide with uranium (IV) to obtain uranium (VI), the exact mechanism of the conversion may be more complicated. As one example, ferric ion produced by oxidation of ferrous ion by hydrogen peroxide can also be acting as an oxidant for uranium (IV). For purposes of the invention, however, the specific mechanism of the oxidation of uranium (IV) to uranium (VI) in the presence of hydrogen peroxide is not relevant.

Irrespective of the simplicity or complexity of the determinant reactions, controlling factors for inorganic reactions are those relating to kinetics, equilibria, and, of course, relative concentrations of reactants. If kinetics and equilibrium constants are especially favorable, it would be expected that merely adding a stoichiometric amount of oxidant would suffice to convert essentially all the uranium (IV) to uranium (VI). Considering a typical crude phosphoric acid solution containing 100-200 ppm of uranium, this would correspond to about 15 to about 30 ppm of hydrogen peroxide. Of course, ideality associated with large equilibrium constants and fast kinetics is not always achieved, even in inorganic reactions. Furthermore, the presence of impurities that can occasion side reactions with oxidant is another factor that could lead to larger-than-stoichiometric quantities of oxidant being used. As a practical matter, then, oxidant is not added to conform to theoretical stoichiometry predicted by an equation. Rather, an attempt is made to use the minimal quantity of oxidant required to achieve substantially complete conversion (greater than 90%, preferably greater than 95%) of uranium (IV) to uranium (VI) prior to extraction. In actual practice

this means adding sufficient oxidant so that the oxidation level will be maintained not only during the oxidation step but to the end of the succeeding extraction step, i.e., till after phase separation of the aqueous acid and the organic extractant phases. If a proper oxidizing level is not so maintained to the end of phase separation, some of the uranium (IV) already oxidized to uranium (VI) can be reduced back to uranium (IV) depending at which point and to what extent the oxidation level becomes insufficient. This would have the effect of decreasing the quantity of extractable uranium. There are contaminants in the phosphoric acid phase that can be expected to waste some oxidant in side reactions and the preferred oxidant, hydrogen peroxide, is particularly sensitive to such side reactions. Surprisingly, as disclosed in applicant's copending Application Serial No. 392 994, filed 1981 December 22, the combining of oxidation and extraction steps will not itself exacerbate loss of oxidant by additional reactions between the oxidant and chemicals in the organic extracting phase. However, the efficient use of oxidant is compromised, regardless of whether these two process steps are separate or combined, because there are not sufficiently sensitive monitoring means to measure the oxidation level.

In the state of the art, the measuring of the redox potential is either on the aqueous phosphoric acid solution before or during the addition of oxidant to the aqueous solution, or on the aqueous phosphoric acid solution after phase separation following extraction. In the former processes it can be appreciated that the tendency would be to overfeed oxidant to compensate for potential losses from independent decomposition reactions. The situation is complicated

if the incoming phosphoric acid solution to be oxidized and extracted has a varying level of oxidant-destroying contaminants. In the latter process there would still be a tendency to overfeed because of the time lapse
5 factor inherent in downstream measurements.

In the oxidation step in the DEPA-TOPO process, the measurement of solution redox potential is often used to indicate whether uranium is completely oxidized. In work done by Hurst et al. in "Solvent Extraction of
10 Uranium for Wet-Process Phosphoric Acid," ORNL-TM-2522, April, 1969, the adequacy of 0.6 volts has been demonstrated. Thus, in practical operation, sufficient oxidant must be added so that the redox potential will not drop below an adequate value prior to the time that
15 the uranium is to be extracted from phosphoric acid. If insufficient oxidant is added, then uranium that is not converted to the uranium (VI) state will not be extracted from the crude phosphoric acid, with the consequence that unextracted uranium will represent an economic loss as
20 well as a residual contaminant in the phosphoric acid.

The actual time period during which the redox potential must be maintained at an adequate value may vary for individual processes depending upon such factors as the length of storage time before extraction, the
25 transfer time in conduits, and even the time of extraction. In the context of the present invention, a specific numerical redox potential is not critical per se because there are many factors known to affect the numerical value of this potential, e.g., temperature.
30 In the final analysis, empirical data obtained from a particular process on the completeness of uranium extraction as a function of solution redox potential is the true practical measure as to what constitutes a relevant reading. Temperature and pH were held
35 constant for the various experiments to remove

experimental bias that could otherwise arise.

It has now been found that in the reduction stripping process for the extraction of uranium from phosphoric acid solution, measurement of the redox potential of the acid solution during the extraction by the DEPA-TOPO solution is an improved measurement of the oxidizing level. Measurement of the oxidizing level before extraction is no guarantee that the oxidizing level will, in fact, have been high enough throughout the extraction stage as might be indicated by a measurement of the separated acid phase after extraction. The unsatisfactory alternatives of measuring before extraction are either using excess oxidizing agent to compensate for the drop in oxidation potential during processing, or reduced yield of extracted uranium. The unsatisfactory consequence of using after-extraction measurement as a control is that the lag thus introduced does not allow accurate adjustment of oxidizing agent feed to compensate for variations in acid feed composition.

Surprisingly it has been found that the measurement of redox potential of the system during the extraction, including during a simultaneous oxidation-extraction step, by immersing a probe electrode directly into the two-phase system under agitation can be used to determine the amount and the rate of addition of the oxidant sufficient to maintain the redox potential at the desired level. The fact that the electrode in contact with both phases accurately measured the oxidation potential of only the aqueous phase was unexpected. Furthermore no fouling of the electrode by organics was experienced as shown in the examples below.

Furthermore, hydrogen peroxide need not be used in as high a concentration or for so long a period of time, hence is not as subject to decomposition. The decomposition of hydrogen peroxide according to the equation $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$ is at least one way decomposition can take place, if contaminants such as heavy metals are present. Such decomposition could occur whether the impurities exist as dissolved ions, or as part of detrital residue, even down to the size of sub-filterable and sub-visible colloids. Organic contaminants, such as humic acid debris, could be part of such detritus, and could conceivably, alone or in combination with metals, contribute to peroxide decomposition. If, as can be the case with many reactions of hydrogen peroxide, the rate of peroxide decomposition were to be dependent in some way on the concentration of hydrogen peroxide, then the mere fact that initial high concentrations have been used to achieve goal redox potential could be itself contributing to extensive, wasteful decomposition.

The hydrogen peroxide used can be any of the commercial grades available on the market. Commercial grades of hydrogen peroxide contain various types of stabilizers depending upon a particular end-use to which a particular grade is destined. For the present invention, none of the stabilizers in the commercial grades of hydrogen peroxide appear to have an adverse effect on the oxidation of uranium (IV) to the hexavalent state and the maintenance thereof prior to extraction.

The concentration of aqueous hydrogen peroxide solution used is not critical and appears to be more a function of convenience. For example, with small

volumes of phosphoric acid solution a more dilute hydrogen peroxide solution may be used, i.e., about 1-10 percent by weight. However, when used on a commercial scale to treat large volumes of phosphoric acid solution, hydrogen peroxide is more conveniently used at commercial concentrations, i.e., a strength of about 30-55 percent by weight, without dilution.

The extraction solvent composition comprises a reagent, generally dissolved in a hydrocarbon diluent such as kerosene. Uranium extractant solvents are standard and well known in the art.

As mentioned previously, it is important that the hydrogen peroxide used be added to the phosphoric acid in order to maintain the redox potential of the solution up until the time that hexavalent uranium is extracted from the solution. As will be apparent to one skilled in the art, the greater the time to extraction, the more hydrogen peroxide will be needed to maintain the redox potential. An initial amount of hydrogen peroxide is added which is just sufficient to raise the redox potential of the solution to an adequate level. The remainder of the hydrogen peroxide addition, up until extraction, can be either in periodic, slug additions at times when the redox potential decreases toward an inadequate level or by continuous additions in an amount sufficient to maintain the adequate level.

EXAMPLE A

The following is a summary of data obtained by procedures as described in Example B below comparing measurements of the redox potential during the one-phased oxidation step and measurements during a combined two-phased oxidation and extraction step. The data compare redox potential of phosphoric acid to which the oxidant has been added with a dispersed mixture comprising the same quantity of acid, the same quantity of oxidant, plus added extraction solvent.

The general dosing procedure was to add the appropriate quantity of 35% hydrogen peroxide solution to provide the quantity of hydrogen peroxide specified in the tables below as those figures are based on 100% hydrogen peroxide. For the one-phased oxidation procedure the hydrogen peroxide was added to a suitable, e.g., 50 cc phos-acid sample. The sample was first warmed to the desired reaction temperature with an infrared lamp. The temperature was maintained and the acid sample was stirred mildly, only enough to create a small vortex. The mv value reported in the table below was after a reasonably stable value was reached, generally after about 6 minutes.

For the combined two-phased oxidation and extraction procedure a 50 cc aliquot of phos-acid was added to a beaker containing 100 cc of extraction solvent preheated to about 40-45C. The Orion* electrode was inserted, and the mixture was agitated moderately under magnetic stirring. The mv values recorded in the table below were after a reasonably stable value was obtained, generally 3-5 minutes, although, for practical purposes a reasonably stable value was reached within about 3 minutes.

	Comparative Runs (g H ₂ O ₂ /l.)	mv during one-phased Oxidation	mv during two-phased Oxidation and Extraction
25	A - A' (0.26)	315	375
	B - B' (0.20)	292	335
	C - C' (0.24)	763	724
30	D - D' (0.10)	696	740

The data show that mv can be measured directly during an extraction even though the electrode in the agitated two-phased mixture is in contact with both phases.

* denotes trade mark

Measurement of mv during Extraction Stage

The following table gives some examples showing the change of mv with time for an agitated mixture of phos-acid (50 cc) and extraction solvent (100 cc) that had been dosed with varying quantities of hydrogen peroxide at the onset of agitation, and furthermore shows that the mv is not substantially different from the value measured in the separated acid phase following the agitation.

Run	g/l <u>H₂O₂</u>	mv After Minutes of Extraction						mv After phase Separation
		0	1	2	3	4	5	
F	0.26	274	356	371	<u>375</u>	375	376	366
G	0.20	300	<u>336</u>	336	335	332	331	326
H	0.24	308	500	550			<u>724</u>	720
I	0.11	333	477	486			503	541
J	0.10	348	677			<u>740</u>		701
K	0.05	360			755			780

The results therefore show that the organic solvents do not foul the electrodes or otherwise substantially interfere with the measuring or redox potential.

EXAMPLE BDIAGNOSTIC TEST FOR PEROXIDE REQUIREMENT

(Measuring Millivolts During Solvent Extraction)

To a 250 cc beaker, equipped with magnetic stirrer, add 100 cc of extraction solvent and warm to 40-45°C. Add 50 cc of "wet-process" phosphoric acid. Turn stirrer on to rapid but nonsplashing agitation and insert an Orion 96-78 electrode which incorporates

a silver/silver chloride and platinum reference in a single-sleeved unit. Using a graduated pipette, add dilute peroxide dosing solution (PDS) to just below the anticipated peroxide requirement (PR) and
5 observe mv rise over next 1-3 minutes. If value tends to level out substantially below 500 mv, add small increments of hydrogen peroxide to achieve a level of at least 500 mv. If the initial dosage causes a rapid rise to substantially above 600 mv, repeat starting
10 with a smaller peroxide dose.

An infrared heat lamp is especially convenient to warm up sample and to maintain temperature if needed.

Keep electrode maintenance solution sufficiently high in electrode to maintain hydrostatic head
15 (and prevent back migration of liquor into electrode). Also, do not keep electrode for extended times in solvent, as many solvents, e.g., kerosene, can cause plastic sleeve to gradually deteriorate.

Dosing can be done with any suitable dispenser
20 that accurately measures 0-2 cc, e.g., graduated pipette, lab syringe, or simply an eye-dropper calibrated as to drop volume.

All glassware used for contact with hydrogen peroxide should be treated for one hour with warm
25 (about 50°C) 1:1 nitric acid and rinsed well with deionized water before use with peroxide. Thereafter, this passivated glassware should be dedicated for peroxide use only.

A convenient peroxide dosing solution (PDS)
30 is made by diluting 35% commercial strength peroxide as follows: Pipette 10.0 cc of 35% hydrogen peroxide into a 100 cc volumetric flask, dilute to 100 cc mark with D.I. water. This dilute solution should be assayed daily as follows: Pipette 1.00 cc (using a calibrated

pipette) into a 125 or 250 ml Erlenmeyer flask. Add about 50-100 cc water, about 5 cc of a 4:1 $H_2O:H_2SO_4$ solution, a scoop (2-5 g) of potassium iodide crystals, 1-2 drops of a dilute ammonium molybdate solution (about 5 2% concentration). Titrate to a yellow or light orange color with 0.1 N sodium thiosulfate. Then add 1-5 cc of starch solution and titrate to the absence of dark color.

Normally maximum mv is attainable within about 10 5 minutes, but probably mv readings up till 10 minutes after dosing begins would be adequate for purposes of this test.

Computations:

Theoretical "Assay" of Peroxide Dosing Solution (PDS)
15 (made by diluting 10.0 cc of 35% hydrogen peroxide up to 100 cc):

$$\frac{10.0 \text{ cc} \times 1.133 \text{ sp. gr.} \times 0.35}{100} = 0.0396 \text{ g } H_2O_2/\text{cc}$$

Thus for PDS having an assay of 0.0396 g H_2O_2 /cc, each 20 1.00 cc of PDS theoretically provides to a 50 cc sample of "wet-process" phosphoric acid:

$$0.0396 \times 20 = 0.79 \text{ g } H_2O_2/1. \text{ of "wet" process} \\ \text{phosphoric acid}$$

Titrated Assay of PDS (Using 1.00 cc sample of PDS):

$$25 \quad H_2O_2 \text{ Assay} = \frac{\text{Titre of } 0.1 \text{ N } S_2O_3 \times 0.1 \text{ N} \times 17.01}{1000} =$$

$$0.0017 \times S_2O_3 \text{ titre} = \text{g } H_2O_2/\text{cc in PDS}$$

Note: On basis of theoretical assay of 0.0396, above, S_2O_3 titre should be 23.3 cc.

30 Peroxide Requirement (PR) of "Wet-Process" Phosphoric Acid

$$\text{Assay} \times \text{cc of PDS} \times 20 = \text{g of } H_2O_2/1 \text{ of "wet-process"} \\ \text{phosphoric acid}$$

Example: If it requires 0.45 cc of PDS to reach goal mv, for a dosing solution (PDS) having an assay of 0.0390 g H₂O₂/cc, then

$$PR = 0.0390 \times 0.45 \times 20 = 0.35 \text{ g H}_2\text{O}_2/1 \text{ acid}$$

5 Assuming PDS does not lose strength, an approximation of PR could be obtained using 0.04 as the approximate assay.

Then PR = 0.8 x cc of PDS.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a reductive stripping process for
5 recovering uranium values from a phosphoric acid
solution, wherein uranium in said acid solution is
oxidized to uranium (VI) oxidation state by addition
of an oxidant, and the uranium (VI) is extracted from
the oxidant-containing solution by contacting it with
10 an organic solvent and thereafter reductively strip-
ped from solution in said organic solvent, the
improvement which comprises measuring the oxidation
potential of the oxidant-containing solution during
the extraction step to determine an amount and rate
15 of addition of oxidant that would be sufficient to
maintain the oxidation potential at a desired level.

2. The process of Claim 1 wherein oxida-
tion and extraction of uranium are performed in a
single step.

20 3. The process of Claim 1 or 2 wherein
the oxidant is hydrogen peroxide.

4. The process of Claim 2 wherein the
oxidation potential is measured in a two-phase
system.

25

30

35



SUBSTITUTE
REPLACEMENT

there are NO DRAWINGS

il n'y a PAS DE DESSINS