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

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TITLE

Oxidation-Extraction of Uranium From
Wet-Process Phosphoric Acid

ABSTRACT OF THE DISCLOSURE

- 5 The oxidation and extraction steps in the reductive stripping process (e.g., DEPA-TOPO process) are carried out simultaneously for recovering uranium from wet-process phosphoric acid.

TITLE

Oxidation-Extraction of Uranium From
Wet-Process Phosphoric Acid

BACKGROUND OF THE INVENTION5 Field of the Invention

The present invention relates to a process
for the recovery of uranium from wet-process phosphoric
acid and more particularly to a simultaneous oxidation-
extraction step in the DEPA-TOPO process for such
10 recovery.

Prior Art

In the mining of phosphate rock to recover
phosphate-containing fertilizer, the first step con-
sists of digesting the rock with sulfuric acid under
15 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, particularly if it can be economically
20 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 important, however, that chemicals
25 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: oxidative stripping processes such as
30 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.

CH 1102 35 In the oxidation steps 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 then extract it in two separate steps. The present invention is an improvement in the reductive stripping process utilizing simultaneous oxidation and extraction and hence a more efficient use of process. This combining of steps into a single step process in a commercial process scale would allow for considerable capital and operating costs savings. The combining of the steps also offers the advantage of being able to more closely monitor oxidation levels and indirectly oxidant feed, whether the redox potential is measured before or after extraction.

25 SUMMARY OF THE INVENTION

According to the present invention, there has been found an improvement in the DEPA-TOPO reductive stripping process whereby the two steps of oxidation and extraction are combined. The oxidant is added during the extraction step.

30 DETAILED DESCRIPTION OF THE INVENTION

The detailed process conditions for the overall DEPA-TOPO process are well known to those skilled in the art. The process is described in the aforesaid U.S. Patent 3,711,591 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.

5 Irrespective of the simplicity or complexity
of determinant reactions, controlling factors for
inorganic reactions are those relating to kinetics,
equilibria, and relative concentrations of reactants.
If kinetics and equilibrium constants are especially
10 favorable, it would be expected that merely adding a
stoichiometric amount of oxidant would suffice to con-
vert essentially all the uranium (IV) to uranium (VI).
Considering a typical crude phosphoric acid solution
containing 100-200 ppm of uranium, this would corres-
15 pond to about 15 to 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
20 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 mini-
25 mal quantity of oxidant required to achieve substanti-
ally complete conversion (greater than 90%, preferably
greater than 95%) of uranium (IV) to uranium (VI).

In the oxidation steps of the DEPA-TOPO
process, the measurement of solution redox
30 potential is often used to indicate whether uranium
is completely oxidized, and it has been determined by
Hurst et al. in "Solvent Extraction of Uranium for
Wet-Process Phosphoric Acid," ORNL-TM-2522, April,
1969, that this is done if the solution redox

35

potential (gold vs. saturated calomel) is + 0.600 volt or higher.

In the context of the present invention, a theoretical or predetermined specific numerical
5 voltage value is not critical per se because there are many factors known to affect the numerical value of redox potential, e.g., temperature (although the choice of the detecting electrode, gold or platinum, is not such a factor). In the final analysis empirical
10 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.

In the process of the invention the important
15 thing is not so much a millivolt (mv) reading per se but the use of the minimal amount of oxidant to maintain extractability of the uranium. In actual practice this means adding sufficient oxidant so that the oxidation level will be maintained not only during the
20 oxidation step but to the end of the succeeding extraction, i.e., till after phase separation of the aqueous acid and the organic extractant phases. If a proper oxidizing level is not maintained to the end of phase separation, some of the uranium (IV) already oxidized
25 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
30 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. Furthermore, this situation can be expected to be exacerbated if the oxidant were to be placed

in contact with the extracting phase, which is a mixture of organic chemicals that might themselves undergo oxidation and thus be wasteful of the oxidant.

It has now been found that in the reduction stripping process for the extraction of uranium from phosphoric acid solution, the oxidation and extraction steps can be combined and carried out simultaneously, using substantially the same quantity of oxidant as used in an uncombined process.

As mentioned previously, to determine if there is sufficient oxidant for the uranium extraction, the redox potential of the acid solution is measured. It has now been found that after observing the mv of the extracted phase of the acid stream and comparing with the mv of a combined oxidation and extraction phase, that the mv is similar. Based on these mv data, it has been determined that the oxidation and extraction steps can be combined. The combining of the two steps does not compromise the solution's maintaining its oxidizing capability.

The addition of the oxidant during the extraction phase is a method whereby the oxidation step of the reductive stripping process is always operated at desirable levels. A more efficient recovery of uranium is observed. Further, a more efficient use of oxidant is achieved in particular when hydrogen peroxide is used. Hydrogen peroxide need not be used in as high a concentration or for so prolonged 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 the major 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, along or in combination with metals, contribute to peroxide decomposition. Furthermore since peroxide decomposition is often concentration dependent; thus using initial high concentrations of hydrogen peroxide to achieve goal redox potential can contribute 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.

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 kerosene. Uranium extractant solvents are standard and well known in the art.

As mentioned previously, the hydrogen peroxide used is added in sufficient quantity to the phosphoric acid to maintain the redox potential at a level to ensure maximum conversion of uranium (IV) to uranium (VI) during oxidation and extraction. The Example shows the addition of the oxidant in a single addition slug in a batch reaction. Oxidant additions can also be in periodic slugs or continuous.

EXAMPLE

The following is a summary of data comprising separate oxidation and extraction steps with the combined process step. The comparative runs contained the same amounts of oxidant and acid. The data show that the redox potential (mv) of the separated acid phase in the combined process is essentially as high as the corresponding two-step process. The redox potential was measured with an Orion*96-78 electrode.

Comparative Runs (g H ₂ O ₂ /l)	mv After Extraction	
	Two-Step (Anal. Result)	One Step (Anal. Result)
A - A' (0.56)	625	680
B - B' (0.49)	430	490
C - C' (0.18)	310	300
D - D' (0.26)	348	335
E - E' (0.58)	633	639
F - F' (0.58)	532	521
G - G' (0.58)	450	450

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 table as those figures are based on 100% hydrogen peroxide. When running the two-step process, the first (oxidation) step was carried out as follows: The hydrogen peroxide was added from a graduated

* denotes trade mark

pipette to a suitable phos-acid sample, e.g., 50 cc under moderate magnetic stirring in a beaker. The sample was first warmed to the desired reaction temperature (38-40C) with an infrared lamp, and the
5 temperature was maintained during the reaction period, typically 5-6 minutes.

The second (extraction) step was as follows:
A 50 cc aliquot of phos-acid was pipetted from the sample under peroxide treatment immediately after the
10 oxidation reaction to a beaker containing 100 cc of extraction solvent which had been preheated to about 40-45°C. The mixture was stirred under vigorous magnetic stirring (just short of splashing) for a period (generally 5 minutes). At the end of this
15 extraction period the mixture was immediately transferred to a separatory funnel, allowed to separate (generally within two minutes), and as soon as the lower acid layer could be drawn off its oxidation potential was measured using the Orion electrode. It
20 generally took up to about two minutes with occasional stirring to get a stabilized mv reading. These readings are recorded above.

When running the one-step process the same amount of hydrogen peroxide was added to a stirred
25 mixture of 50 cc of phos-acid and the extraction solvent and mixed essentially under the same conditions as the extraction step for the two-step process.

CLAIMS

1. In a reductive stripping process for recovering uranium values from wet-process phosphoric acid solution, wherein uranium in the solution is
5 oxidized to uranium (VI) oxidation state and then extracted from the solution by contact with a water immiscible organic solvent, the improvement which comprises adding sufficient oxidant to obtain greater than
10 90% conversion of the uranium to the uranium (VI) oxidation state to the phosphoric acid solution and simultaneously extracting the uranium (VI).
2. The process of Claim 1 wherein the oxidant is hydrogen peroxide.
3. The process of Claim 2 wherein sufficient
15 oxidant is added to obtain greater than 95% conversion of the uranium (VI).



SUBSTITUTE

REPLACEMENT

SECTION is not Present

Cette Section est Absente