

1

3,737,513

RECOVERY OF URANIUM FROM AN ORGANIC EXTRACTANT BY BACK EXTRACTION WITH H₃PO₄ OR HF

Tadeusz Karol Wiewiorowski, New Orleans, and David James Miller, Gretna, La., assignors to Freeport Minerals Company, New York, N.Y.

Filed July 2, 1970, Ser. No. 51,947

Int. Cl. B01d 11/00; C01g 56/00

U.S. Cl. 423-8

8 Claims

ABSTRACT OF THE DISCLOSURE

A process for the recovery of uranium values from uranium carrying extractants containing a dialkylphosphoric acid and a trialkylphosphine oxide dissolved in an organic solvent is described. The process involves liquid-liquid extraction of the extractants with an aqueous solution containing divalent iron and a complexing agent which may be either phosphoric acid, hydrofluoric acid or mixtures thereof.

BACKGROUND OF THE INVENTION

(1) Field of the art

This invention relates to the recovery of uranium values from organic extractants used in solvent extraction processes.

(2) Description of the prior art

Phosphate rock can contain from 100 to 400 parts per million (p.p.m.) by weight of uranium (expressed as U₃O₈), depending on its type and origin. A major portion of this uranium becomes solubilized during the acidulation of phosphate rock and ends up as a component of the phosphoric acid. It is estimated that at the present time, over 4 million pounds of uranium per year are so processed in the United States without being recovered. Organic extractants capable of removing the uranium from the phosphoric acid are presently available. The recovery of uranium values from such organic extractants is an essential step in any overall system for uranium recovery from phosphoric acid by solvent extraction.

The presence of uranium in phosphate rock and in phosphoric acid has been recognized for many years. Consequently, a process as described in "Uranium Recovery From West Process Phosphoric Acid" by B. F. Greek, O. W. Allen, and Donald E. Tynan, *Industrial and Engineering Chemistry*, vol. 49, No. 4, page 608 (1957), was developed and utilized for the recovery of uranium from phosphoric acid produced by treatment of Florida phosphate rock with sulfuric acid. The commercial application of this process was short-lived, however, due primarily to the technical and economic disadvantages which made uranium recovery by this process unattractive as compared to direct uranium production from uranium ores. The major disadvantages of this process included the chemically unstable nature of the extracting reagent, the poor phase separation in the solvent extraction circuit and the expensive pretreatment of the phosphoric acid requiring the use of elemental iron.

Recognizing the disadvantages of prior art, a research team at the Oak Ridge National Laboratory developed a new solvent extraction system which does not suffer from the shortcomings referred to above. In this system as reported in "Solvent Extraction of Uranium From Wet-Process Phosphoric Acid, by F. J. Hunt, D. J. Crouse, and K. B. Brown, Oak Ridge National Laboratory, Technical Manuscript 2522, April 1969, the uranium was extracted from phosphoric acid with an organic solution containing a dialkylphosphoric acid and a trialkylphosphine oxide. The uranium-containing organic solution was then sub-

2

jected to a washing step to remove phosphoric acid and to a stripping step, utilizing an aqueous ammonium hydroxide-ammonium carbonate stripping solution, to concentrate and recover the uranium values. In the stripping operation, the uranium values were transferred from the organic to the aqueous phase. Since the organic solution contained a dialkylphosphoric acid, ammonia values were absorbed into the organic phase from the stripping solution to form the corresponding ammonium salt of this acid. After the stripping operation, the ammonia-carrying organic solvent was returned to the uranium extraction circuit for contact with fresh phosphoric acid. The absorption of the ammonia values by the phosphoric acid resulted in ammonia losses and in undesirable contamination of the phosphoric acid.

This new system had certain other distinct disadvantages, namely high ammonia consumption costs resulting from the selection of an aqueous ammonium hydroxide-ammonium carbonate stripping solution, and phosphoric acid losses encountered in the washing step of the solvent extraction circuit.

THE INVENTION

It is an object of this invention to provide a new, convenient, and useful process for recovering uranium values from an organic extractant containing a dialkylphosphoric acid and a trialkylphosphine oxide.

It is another object of this invention to provide a new and useful process for recovering uranium values from organic extractants containing a dialkylphosphoric acid and a trialkylphosphine oxide which employs an acidic aqueous stripping solution, rather than an alkaline stripping solution.

It is a further object of this invention to eliminate disadvantages of prior art solvent extraction systems for recovering uranium values from phosphate rock and from phosphoric acid.

It is another object of this invention to provide a new and useful process of obtaining uranium values from organic extractants containing a dialkylphosphoric acid and a trialkylphosphine oxide in which process the dialkylphosphoric acid does not become neutralized to form a salt, but is retained in its free-acid form.

It is a further object of this invention to provide a new and useful process of obtaining uranium values from organic extractants which can be incorporated into an overall solvent extraction scheme for uranium recovery from phosphoric acid.

A further object of this invention is to provide a new and useful process of obtaining uranium values from an organic extractant containing a dialkylphosphoric acid and a trialkylphosphine oxide dissolved in an organic solvent.

We have found that uranium values can be obtained from an organic extractant containing a dialkylphosphoric acid and a trialkylphosphine oxide by using an acidic aqueous stripping (removal) solution, containing:

- (1) a dissolved divalent iron salt, and
- (2) a complexing agent selected from the group consisting of phosphoric acid, hydrofluoric acid and mixtures thereof.

In the process of this invention any dialkylphosphoric acid and trialkylphosphine oxide can be employed. The ratio employed of the two compounds is not critical. Illustrative of such compounds are dihexylphosphoric acid, dioctylphosphoric acid, didecylphosphoric acid, tributylphosphine oxide, trihexylphosphine oxide and tridecylphosphine oxide. In the process any divalent iron salt capable of dissolving in the aqueous stripping solution can be used. These include ferrous sulfate FeSO₄, ferrous chloride FeCl₂, ferrous bromide FeBr₂, ferrous