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Courier Press, Leamington Spa, England.

Description

This invention relates to recovering uranium from an aqueous calcium fluoride slurry.

U.S. Patent Specification No. 2,965,440 discloses the recovery of uranium from an ore containing iron. The ore is ground to a suitable particle size and is then roasted to produce a uranium-iron complex. In view of the presence of iron in the complex, the complex can then be magnetically separated from the remainder of the ore.

In an ammonium diuranate conversion process for the preparation of uranium oxide powder, a waste stream is produced which contains uranium, fluoride, ammonium, and nitrate ions. To recover the ammonia and lower the fluoride levels, a calcium hydroxide or lime slurry is added which precipitates calcium fluoride. The ammonium diuranate waste stream is processed in an ammonia stripping column, and the calcium fluoride slurry which is produced is sent to a settling lagoon where excess water is decanted and run off. Some of the uranium remains in the calcium fluoride slurry as insoluble calcium uranate. This calcium uranate waste not only creates an expensive disposal problem but also represents a loss of a valuable resource. While other processes, such as that disclosed in Japanese Patent 48-38320, can be used to remove some of the uranium from the waste stream prior to the precipitation of the calcium fluoride, these processes are of no use in recovering the uranium which is present in vast ponds of calcium fluoride slurry which already exist.

Accordingly the present invention provides a method of recovering uranium from an aqueous calcium fluoride slurry containing less than 100 ppm of iron characterized in that a magnetic field of at least 10 Kilogauss is applied to the slurry in a high gradient magnetic separator comprising two magnetic poles between which is a porous ferromagnetic intermediate through which the slurry passes, and separated calcium uranate is removed from the porous ferromagnetic intermediate.

This procedure is simple, reasonably inexpensive, does not require large amounts of capital, and can produce a uranium product which can be added directly to already existing uranium processes.

In order that the invention can be more clearly understood, convenient embodiments thereof will now be described, by way of example, with reference to the accompanying drawings in which:

Figure 1 is a block diagram illustrating a uranium recovery process using a carbonate leach and an ion exchange column.

Figure 2 is a block diagram of an alternative uranium recovery process using a nitric acid wash.

Referring to Figure 1, a dispersant in line 1 is added to a calcium fluoride slurry in line 2. The slurry passes through ball mill 3 which grinds up any large particles which may be present, then pump 4 forces the slurry into cyclone separator 5 which separates the slurry into large particles which are recycled in line 6 and finer particles which are passed through line 7 and valve 8 to high gradient magnetic separator 9. The magnetic separator comprises an iron box 10 containing poles 11 and 12 of an electromagnet between which is a porous ferromagnetic intermediate 13. As the calcium fluoride slurry passes through the separator, the uranium in the slurry adheres to the porous ferromagnetic intermediate. The remaining slurry goes to detector 14 which provides a signal when the separator has become saturated with uranium so that the uranium now passes through the separator. The slurry then passes through valve 15 to sludge dewaterer 16 which removes some of the water. The remainder of this slurry becomes waste sludge. When the detector indicates that the separator is saturated with uranium, valves 8 and 15 are turned so that carbonate leach solution in line 17 now passes into the separator, dissolving the uranium which adheres to the porous ferromagnetic intermediate. The carbonate leach solution containing the uranium passes through valve 15 and line 18 to filter 19 which removes any large particles which may be present. The dissolved uranium passes through line 20 into ion exchange column 21 where the uranium is exchanged onto the ion exchange column. Pump 22 provides the pressure for this flow cycle. When the carbonate leach is finished and valves 8 and 15 have been turned to permit the calcium fluoride slurry to again flow into the separator, filter 19 can be washed clean by pumping water from sludge dewaterer 16 through the filter using pump 23.

In another embodiment of the invention, nitric acid is used to remove the uranium from the separator and two separators are used to provide a continuous batch operation. In Figure 2, the calcium fluoride slurry passes through line 30 through valve 31 in the separator 32 through valve 33 and line 34 to a storage pond. While that is occurring, nitric acid in line 35 passes through valve 36 into separator 37 dissolving uranium on the porous ferromagnetic intermediate of that separator. The dissolved uranium passes through valve 38 and line 39 where it is sent to a solvent extractor. When separator 32 has become saturated, valves 31, 33, 36, and 38 are closed and valves 40, 41, 42, and 43 are opened. The nitric acid now passes through line 35 through valve 40, dissolves the uranium in separator 32, then passes through valve 41 and out line 39. The calcium fluoride slurry now passes through valve 42 into separator 37 through valve 43 and out line 34.

The initial calcium fluoride slurry may contain 1 to 10 percent solids, of which at least 95 percent by weight is calcium fluoride, and the rest is water, and from 1 to 1000 ppm uranium, usually in the form of some type of calcium uranate. The uranium in these slurries may be enriched in uranium 235, making it particularly valuable.

Generally, the invention will work with any liquid slurry of calcium fluoride which contains an insoluble uranium compound. This slurry must have less than 100 parts per million of iron present because the iron is dissolved with the uranium and would contaminate it in the subsequent processes. Such contamination would make it necessary to reprocess the uranium in the form of uranium hexafluoride in order to separate it from the iron. In the absence of iron, however, the product of this invention can be directly fed into the solvent extraction process.

A dispersant may be added to the calcium fluoride slurry to aid in breaking up the larger size particles. The dispersants include detergents such as sodium sulfurate of a naphthalene-formaldehyde condensation product, 5 to 8 percent sodium sulfate in a condensed organic acid, and complex polymerized organic salts of sulfuric acids of alkyl-aryl type. The preferred dispersant is a sodium sulfurate of a naphthalene-formaldehyde condensation product sold by Stepan Chemical Company as "Stepantan A". From 0.01 to 0.02 percent by weight of a dispersant may be used if desired.

The ball mill or other means of reducing the particle size in the slurry is necessary only if large particles are present. Preferably, the particles in the slurry should be no larger than about 5 μm.

Unlike normal magnetic separation, where particles are pulled out of a slurry with a strong magnet as they pass under the magnet on a belt, the process of this invention requires the use of a high gradient magnetic separator. In a high gradient magnetic separator, two poles of a magnet are spaced less than about 7.6 cm (three inches) apart, and the spacing between them is filled with a porous ferromagnetic intermediate. The separator must have a magnetic field of at least 10 kilogauss in order to remove the uranium particles, which are only very weakly magnetic. Generally greater than 75 kilowatts of power are required and the magnet should have a coil diameter of less than 40 centimeters. A separator can typically take up to 2.72 tonnes (3 tons) per hour of solids throughput. The separator traps the calcium uranate, for example, $CaUO_4$, particles on the intermediate, which should have a porosity of greater than 50%. If nitric acid is not used the intermediate can be made of steel wool, but if nitric acid is used stainless steel wool is needed as ordinary steel wool is attacked by nitric acid.

The calcium fluoride slurry is run through the separator until a detector indicates that the separator has become saturated and uranium is now passing through the separator. A suitable detector can be a Geiger counter or similar device, but a fluorimetor is preferred as they are the most sensitive to uranium. The flow rate through the separator should be less than about 37.9 litres (10 gallons) per minute as higher rates may wash the uranium off the intermediate.

The uranium can be removed from the intermediate in the separator by a variety of means. For example, almost any carbonate solution which is from 2 to 5 molar will dissolve the uranium in the separator. While sodium or any other alkali metal carbonate can be used, ammonium carbonate is preferred as it is more compatible with subsequent processes. The preferred method of removing the uranium, however, is to back wash with an aqueous solution of nitric acid. The nitric acid wash should have a pH of greater than about 2 in order to avoid dissolving the calcium fluoride and should have a pH of less than about 3 or it will not dissolve the uranium.

If nitric acid is used the leachate can be sent directly to a solvent extraction system using, for example, di-2-ethylhexyl phosphoric acid-trioctyl phosphine oxide (DEPA-TOPO) in an organic solvent such as kerosene, as is well known in the art. If a carbonate solution is used, the uranium can be removed from the carbonate solution on an ion exchange column as is also well known in the art. The uranium can then be removed from the ion exchange column with a solution of nitric acid which is then sent to a solvent extraction process. Thus, the extra step of extraction on an ion exchange column is avoided when nitric acid is used to remove the uranium from the separator.

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

Example

An aqueous calcium fluoride solution containing 2 percent solids and 15 parts per million uranium as calcium uranate can be passed through a separator as shown in Figure 1 containing a stainless steel wool intermediate. The separator can have a field of 20 kilogauss, a power of 150 kilowatts, and a coil diameter of 30 centimeters. 1.81 tonnes (two tons) per hour of slurry can be passed through the separator. When a fluorimeter indicates that uranium is no longer being detained on the intermediate, the calcium fluoride flow is terminated and the intermediate is washed with a 10% solution of nitric acid. The uranium in the nitric acid is then extracted using the DEPA-TOPO extractant.

Claims

1. A method of recovering uranium from an aqueous calcium fluoride slurry containing less than 100 ppm of iron characterized in that a magnetic field of at least 10 kilogauss is applied to the slurry in a high gradient magnetic separator comprising two magnetic poles between which is a porous ferromagnetic intermediate through which the slurry passes, and separated calcium uranate is removed from the porous ferromagnetic intermediate.

2. A method according to claim 1, characterized in that the calcium uranate is removed from the separator by washing with an aqueous solution of nitric acid having a pH between 2 and 3.

3. A method according to claim 2, characterized in that the uranium in the aqueous solution of nitric acid is solvent extracted using di-2-

ethylhexyl phosphoric acid-trioctyl phosphine oxide.

4. A method according to claim 1, characterised in that the calcium uranate is removed from the separator by leaching with an aqueous carbonate solution.

5. A method according to claim 4, characterized in that the carbonate solution is from 2 to 5 molar ammonium carbonate.

6. A method according to claim 4 or 5, characterized in that the uranium in the carbonate solution is removed on an ion exchange column.

7. A method according to claim 6, characterized in that the uranium on the ion exchange column is removed therefrom with an aqueous solution of nitric acid.

8. A method according to any of claims 1 to 7, characterized in that the magnetic poles are less than 7.6 cm (3 inches) apart and have a coil diameter of less than 40 cm.

9. A method according to any of claims 1 to 8, characterized in that the porous ferromagnetic intermediate is stainless steel wool having a porosity greater than 50%.

Revendications

1. Procédé pour la récupération d'uranium à partir d'une bouillie aqueuse de fluorure de calcium contenant moins de 100 p.p.m. de fer, caractérisé en ce que l'on applique sur cette bouillie un champ magnétique d'au moins 10 kilogauss dans un séparateur magnétique à gradient élevé comprenant deux pôles magnétiques entre lesquels se trouve un élément intermédiaire poreux ferromagnétique que traverse la bouillie et que l'uranate de calcium séparé est extrait à partir de cette élément intermédiaire ferro-magnétique poreux.

2. Procédé suivant la revendication 1, caractérisé en ce que l'uranate de calcium est extrait du séparateur par lavage avec une solution aqueuse d'acide nitrique ayant un pH de 2 à 3.

3. Procédé suivant la revendication 2, caractérisé en que l'uranium qui se trouve dans la solution aqueuse d'acide nitrique est extrait avec un solvant en utilisant une combinaison acide di-2-éthylhexyl-phosphorique/oxyde de trioctyl-phosphine.

4. Procédé suivant la revendication 1, caractérisé en ce qui l'uranate de calcium est extrait du séparateur par lavage avec une solution aqueuse de carbonate.

5. Procédé suivant la revendication 4, caractérisé en ce que la solution de carbonate est consitée par du carbonate d'ammonium de 2 à 5 fois molaire.

6. Procédé suivant l'une quelconque des revendications 4 ou 5, caractérisé en ce que l'uranium passé dans la solution de carbonate est extrait sur une colonne à échange d'ions.

7. Procédé suivant la revendication 6, caractérisé en ce que l'uranium est repris sur la colonne échangeuse d'ions avec une solution d'acide nitrique.

8. Procédé suivant l'une quelconque des revendications 1 à 7, caractérisé en ce que les pôles magnétiques sont éloignés de moins de 7,6 cm et ont un diamètre de bobinage inférieur à 40 cm.

9. Procédé suivant l'une quelconque des revendications 1 à 6, caractérisé en ce que l'élément intermédiaire ferro-magnétique poreux est fait de laine d'acier inoxydable dont la porosité est supérieure à 50%.

Patentansprüche

1. Ein Verfahren zur Wiedergewinnung von Uran aus einer wässrigen Kalzium-Fluoridaufschlämmung, die weniger als 100 ppm Eisen enthält, dadurch gekennzeichnet, daß ein Magnetfeld von zumindest 10 Kilogauss in einem Magnetseparator mit hohem Gradienten auf die Aufschlämmung einwirkt, welcher Separator zwei Magnetpole umfaßt, zwischen denen sich ein poröses ferromagnetisches Zwischenglied befindet, durch welches die Aufschlämmung passiert, und daß abgetrenntes Kalzium-Uranat von dem porösen ferromagnetischen Zwischenglied entfernt wird.

2. Ein Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Kalzium-Uranat von dem Separator durch Waschen mit einer wässrigen Lösung von Salpetersäure, die einen pH-Wert zwischen 2 und 3 besitzt, entfernt wird.

3. Ein Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß das Uran in der wässrigen Lösung der Salpetersäure mittels eines Lösungsmittels extrahiert wird, unter Verwendung von Di-2-Äthylhexyl-Phosphorsäure-Trioctyl-Phosphin-Oxid.

4. Ein Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Kalzium-Uranat von dem Separator durch Auslaugen mit einer wässrigen Karbonatlösung entfernt wird.

5. Ein Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß die Karbonatlösung 2- bis 5-molariges Ammonium-Karbonat ist.

6. Ein Verfahren nach Anspruch 4 oder 5, dadurch gekennzeichnet, daß das Uran in der Karbonatlösung auf einer Ionenaustauschersäule entfernt wird.

7. Ein Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das Uran auf der Ionenaustauschersäule von dieser mit einer wässrigen Lösung von Salpetersäure entfernt wird.

8. Ein Verfahren nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß die Magnetpole weniger als 7,6 cm (3 Zoll) voneinander entfernt sind und einen Spulendurchmesser von weniger als 40 cm aufweisen.

9. Ein Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß das poröse ferromagnetische Zwischenglied rostfreie Stahlwolle mit einer Porösität von mehr als 50% ist.

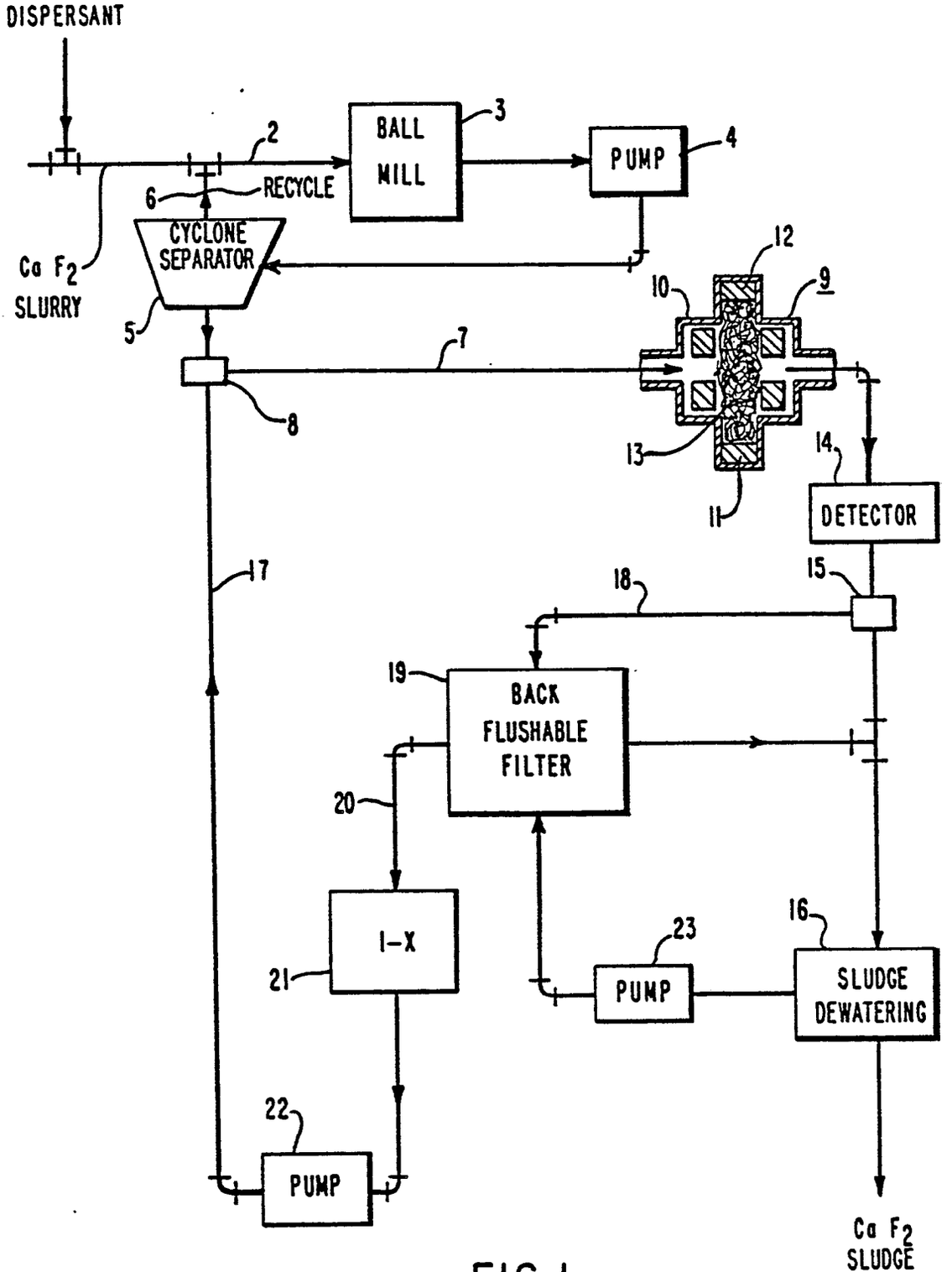
DISPERSANT
2
BALL MILL
3
PUMP
4
RECYCLE
6
CYCLONE SEPARATOR
Ca F2 SLURRY
5
12
10
9
7
8
13
14
11
DETECTOR
17
18
15
19
BACK FLUSHABLE FILTER
20
1-X
21
23
16
PUMP
SLUDGE DEWATERING
22
PUMP
Ca F2 SLUDGE

FIG. 1

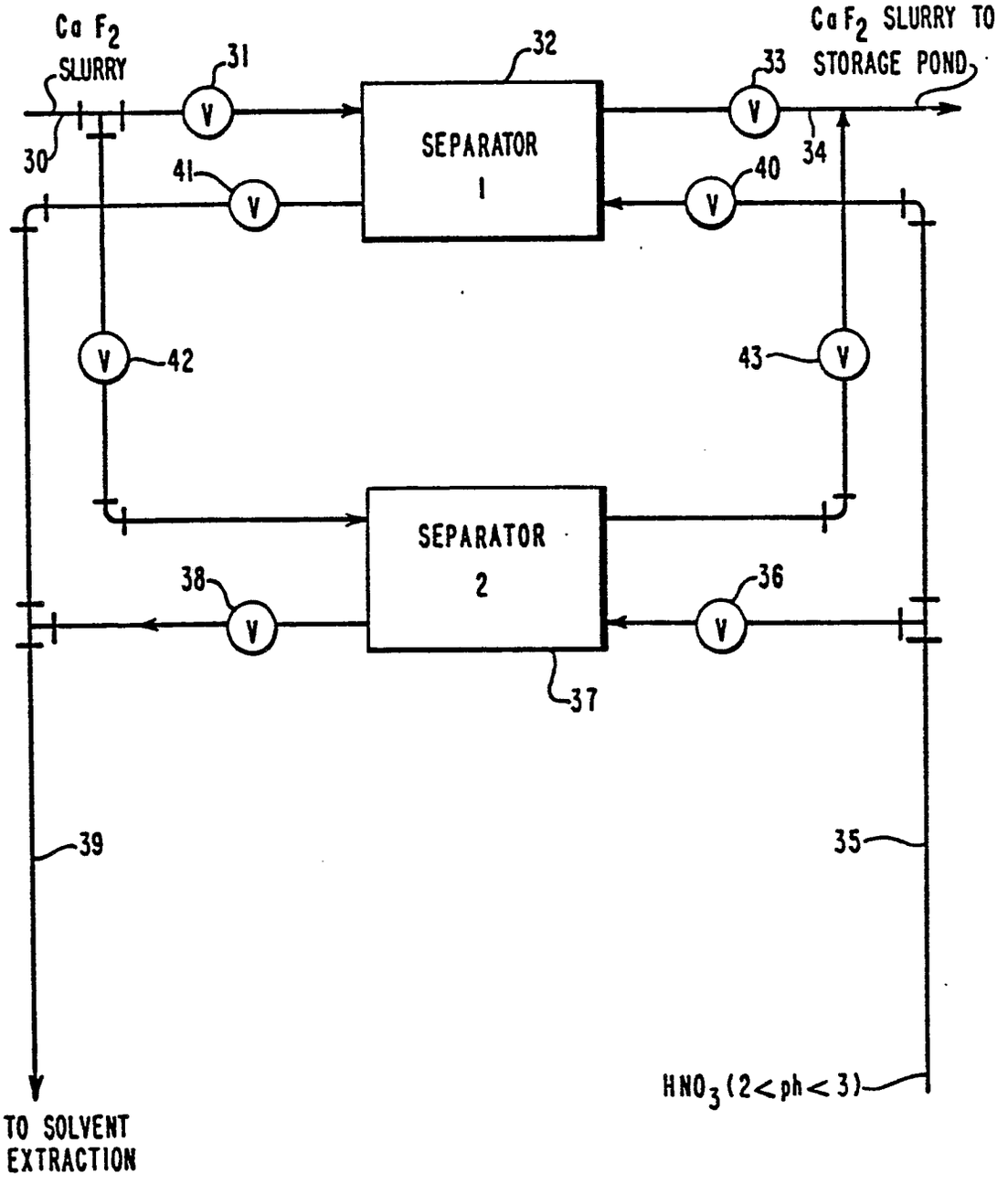
Ca F2 SLURRY
31
32
33
Ca F2 SLURRY TO STORAGE POND
30
SEPARATOR 1
34
41
40
42
43
SEPARATOR 2
38
36
37
39
35
TO SOLVENT EXTRACTION
HNO3 (2<ph<3)

FIG. 2