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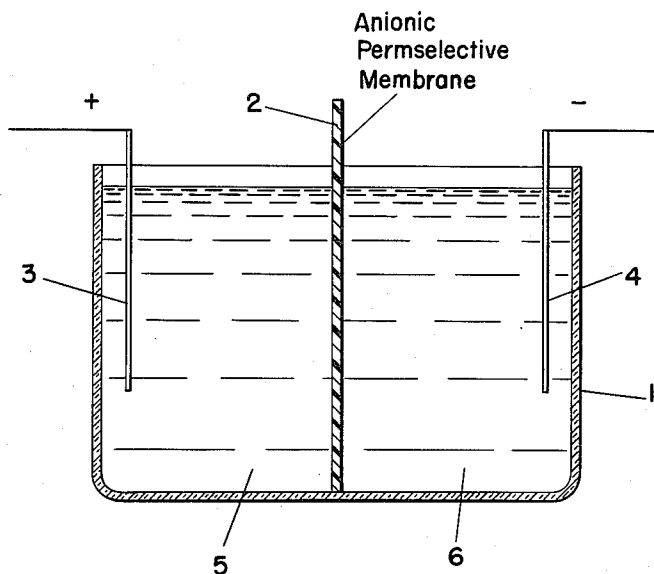
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RECOVERY OF URANIUM VALUES FROM PHOSPHORIC ACID

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2 Sheets-Sheet 1

Fig. 1



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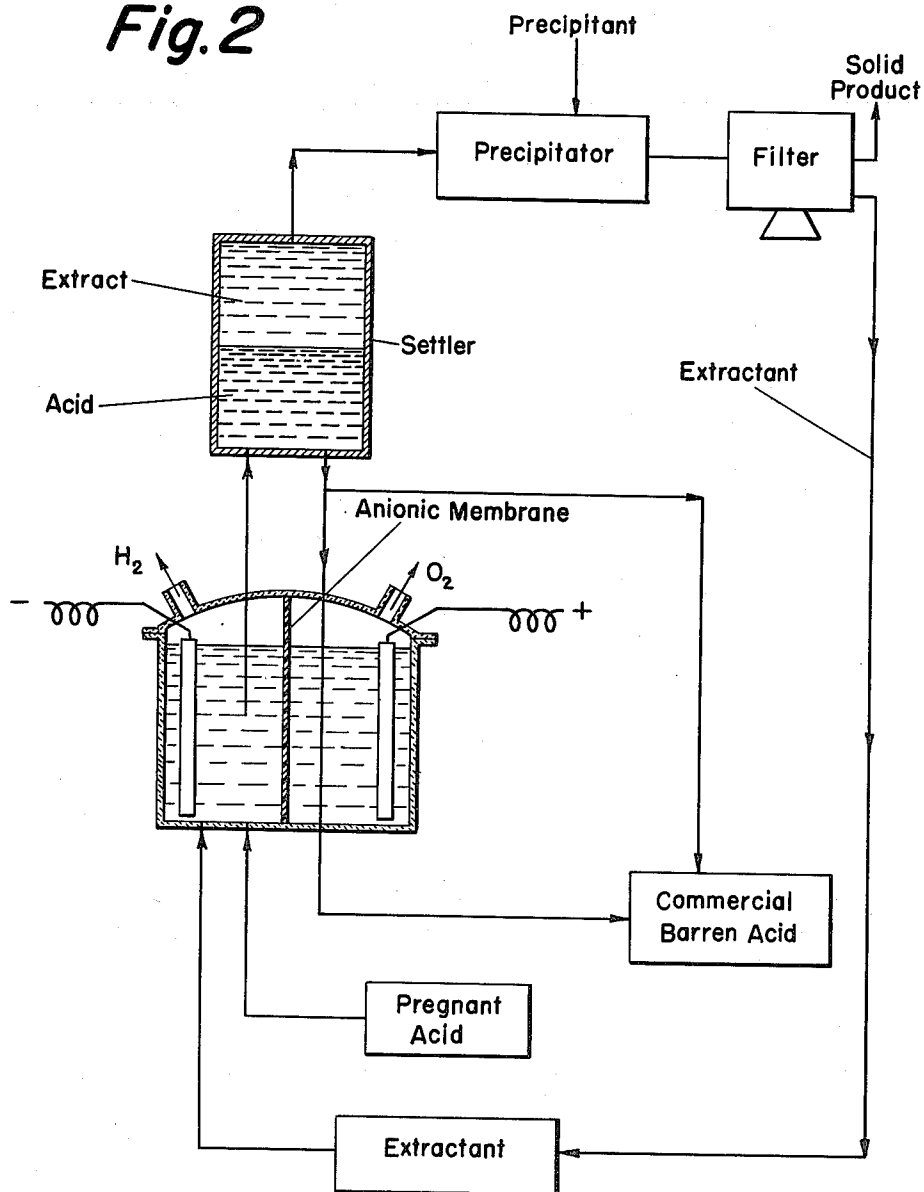
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Fig. 2



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RECOVERY OF URANIUM VALUES FROM PHOSPHORIC ACID

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1 Claim. (Cl. 204—90)

This invention relates to the recovery of uranium values from commercial phosphoric acid. More particularly, it relates to an electrolytic process wherein uranium values which are present in commercial phosphoric acid are reduced electrolytically and thereafter are extracted from the phosphoric acid.

The chief object of this invention is to provide an efficient and economical process for removing and recovering uranium values which are present in commercial phosphoric acid without otherwise altering the phosphoric acid.

It is already known that the uranium values which are present in low amounts in commercial phosphoric acid can be far more easily extracted from the acid when they are reduced in valency to a value of plus four. It is also most advantageous to reduce the iron, which is usually present in much larger quantities than the uranium, from the ferric condition to the ferrous condition since otherwise the ferric compounds are extracted together with the uranium. Heretofore, it has been customary to add metals such as iron, zinc, or aluminum to the acid in order to effect the reduction. The last two metals represent a major expense if they are thus employed. While iron is less expensive, its use is undesirable because the presence of iron interferes with the use of the acid in the manufacture of phosphate end-products such as superphosphate fertilizer.

By the process of this invention uranium and iron compounds in commercial phosphoric acid are reduced electrolytically. The uranium values, thus reduced, are readily extractable from the phosphoric acid by conventional methods, such as by extraction with a kerosene solution of octyl pyrophosphoric acid.

The process comprises passing pregnant phosphoric acid containing uranium values through the cathode compartment of an electrolysis cell which is divided into a cathode compartment and an anode compartment by means of an anionic permselective membrane containing an anion exchange resin. The anode compartment preferably contains phosphoric acid as the anolyte but a solution of another acid—or a solution of a salt—can be used equally well. All that is required is that an electrolyte be present in order to conduct the current through the anode compartment.

Fig. 1 is a diagrammatical representation of a typical cell which is divided into an anode compartment and a cathode compartment by means of a permselective membrane or diaphragm.

Fig. 2 is a flow sheet showing the steps in the preferred cyclic process of this invention.

Referring now to Fig. 1, the character 1 represents a container which is divided into two compartments, 5 and 6, by a permselective membrane, 2, which is described in greater detail below. Compartment 5 is an anode compartment by virtue of the presence there of the anode 3, while compartment 6 is a cathode compartment because it contains the cathode 4. When the cell is in

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operation, the electrodes are connected to a source of electric power not shown.

The cell which is employed in this invention can be varied as to size, shape, volumes of the individual compartments, vents, ports, exits, construction materials, controls, embellishments, means for admitting and removing the contents of the compartments, et cetera without departing from the spirit of this invention. What is essential is that the cell have two compartments, one containing the anode and the other containing the cathode, and that the two compartments be separated by a permselective membrane as defined herein.

The permselective membranes which divide the electrolysis cell into two compartments and which prevent diffusion of the anolyte and catholyte are anionic membranes. They allow the passage through them of anions but do not permit the passage of cations. The membranes contain anion exchange resins, and it is the presence of the ion exchange resins which imparts the property of permselectivity. While the compositions of the permselective membranes can vary within reasonable limits, it is important that they contain enough ion exchange resin as to have suitably high conductance when employed in the electrolysis cell. The permselective films which have proven to be most suitable for use in the process are those made by incorporating particles of an ion exchange resin in film-forming matrices such as polyethylene or vinyl resins. Such membranes are available commercially and are described in U. S. patent application Serial No. 205,413, now U. S. Patent No. 2,681,319, and in the corresponding Canadian Patent No. 493,563.

In the process of this invention the phosphoric acid containing the uranium values is electrolyzed in the cathode compartment and it is much preferred that the acid be passed through the cathode compartment continuously. It is important that the acid have good contact with the cathode since it is at the cathode that reduction in the valence of the uranium and the iron ions takes place. The use of an irregularly shaped cathode, such as a corrugated and perforated electrode is strongly recommended since it not only provides a large area of surface but also causes turbulence in the flow of the acid and, hence, better contact with the electrode. Alternatively, the cathode compartment can be equipped with baffles or agitators so as to promote contact of the acid and the cathode.

In one embodiment of this invention the phosphoric acid which has been electrolyzed in a cathode compartment is next treated with a solvent for the uranium values. Ordinarily these materials are alkyl phosphonates. They are made by reacting, for example, phosphorus pentoxide or phosphoric acid with an alkanol such as a butanol, hexanol, or octanol; and they are mono-, di-, or tri-esters of phosphoric acid or mixtures of the esters. Consequently, they are often referred to as "alkyl phosphoric acids." These materials and their use as extractants for uranium values are well known. They are best used in the form of diluted solutions in hydrocarbons such as gasoline, kerosene, benzene, toluene or the like.

Next, the extracted phosphoric acid and the extracting solution are allowed to settle and are then separated. The uranium-free phosphoric acid raffinate—or barren acid—is then ready for commercial utilization. The uranium-rich extract is then treated with hydrofluoric acid and the uranium is precipitated as UF_4 , which is separated and isolated by such conventional means as filtering or centrifuging.

In the preferred embodiment of this invention, as shown in Fig. 2, the reduction in valence of the uranium compounds in the phosphoric acid and the extraction of

the reduced uranium values are carried out simultaneously in the cathode compartment. Thus, a stream of pregnant phosphoric acid and a stream of an extractant, such as a 5% solution of octyl pyrophosphoric acid in kerosene, are introduced simultaneously and continuously into a cathode compartment of an electrolysis cell such as is described above. In the development of this invention the phosphoric acid and the extractant were mixed in the ratio of approximately ten volumes of the former to one volume of the latter although the ratio of the two may be varied. Agitation is provided and the uranium values are both reduced and extracted within the cathode compartment. The resultant mixture is removed and allowed to settle and separate, after which some or all of the barren acid is passed through the anode compartment to provide an anolyte. Finally, the barren acid is available for commercial utility. Meanwhile the extract is treated with hydrogen fluoride to precipitate the uranium values. After the uranium values are precipitated and removed from the solution of alkyl phosphoric acid, the latter is fed continuously to the cathode compartment of the cell together with more pregnant phosphoric acid; and the cycle of electrolytic reduction, extraction, and isolation of barren acid and uranium values is continued.

In the development of this invention, electrolytic cells of various sizes and shapes were used. All were made of polymethyl methacrylate (Plexiglas) and all contained a cathode compartment separated from an anode compartment of the same size and shape by means of an anionic permselective membrane. The membranes, which are commercially available (Amberplex A-1) were known to contain about 70% of a quaternary ammonium anion exchange resin dispersed in a matrix of polyethylene and were also known to have been made by the process of Canadian Patent No. 493,563 of June 9, 1953. The ion exchange resin, in turn, was known to have been made by aminating with a tertiary amine a cross-linked, chloromethylated copolymer of styrene and divinylbenzene. Both platinum and lead perforated electrodes were used with no apparent difference in efficiency. As indicated above, a corrugated and perforated cathode was the most satisfactory.

In some instances the pregnant acid alone was passed through the cathode compartment and was separately extracted with a kerosene solution of octyl pyrophosphate. In other cases the pregnant acid and the extractant solution were passed through the cathode compartment simultaneously. In every case, however, the uranium values were completely reduced and were completely removed from the phosphoric acid.

It is apparent that the amount of electric current and

hence the cost of the process depends upon the rate at which the pregnant acid is circulated through the cathode compartment and on the intimacy of the contact of the pregnant acid with the cathode and with the extractant. The electrolytic reductions were carried out with currents as low as 0.5 ampere and as high as 50 amperes and ranging in voltage from 2 to 6 volts. It was found, however, that the cost of reducing the uranium values in pregnant phosphoric acid ranged from about 1 to 10 kilowatt hours for every thousand gallons of acid thus treated. At a cost of one cent per kilowatt hour, this represents a cost of 1-10 cents per pound of U_3O_8 , since the average concentration of uranium is about 100 parts per million or about one pound, as U_3O_8 , for every thousand gallons of pregnant acid.

I claim:

A cyclic process for isolating uranium values which are present in pregnant commercial phosphoric acid which comprises continuously passing a mixture of said pregnant acid and a solution which is capable of extracting uranium values having a valence of plus four and is immiscible with phosphoric acid through the cathode compartment of an electrolysis cell, said cell containing said cathode compartment separated from an anode compartment containing phosphoric acid as the anolyte by means of an anionic permselective membrane comprising an anion exchange resin, electrolyzing the mixture in said cathode compartment while the components of the mixture are maintained in intimate contact with the cathode and with each other whereby said uranium values are electrolytically reduced in valence to a value of plus four and said values of valence plus four are extracted from the phosphoric acid, removing the resultant mixture from said electrolysis cell and separating the immiscible phosphoric acid and extract solution, precipitating the uranium values and separating them from said solution and returning said extractant solution to said cathode compartment together with additional pregnant acid and repeating the electrolysis operation and the distribution of the products of the electrolysis operation.

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