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PROCESSES FOR THE DISSOLUTION OF URANIUM IN NITRIC ACID

Filed June 4, 1963

2 Sheets-Sheet 1

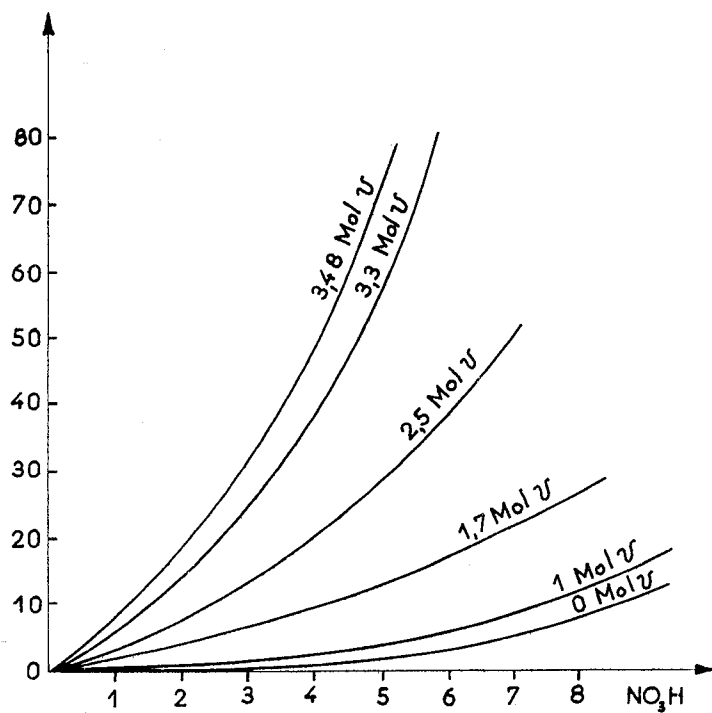


FIG. 1

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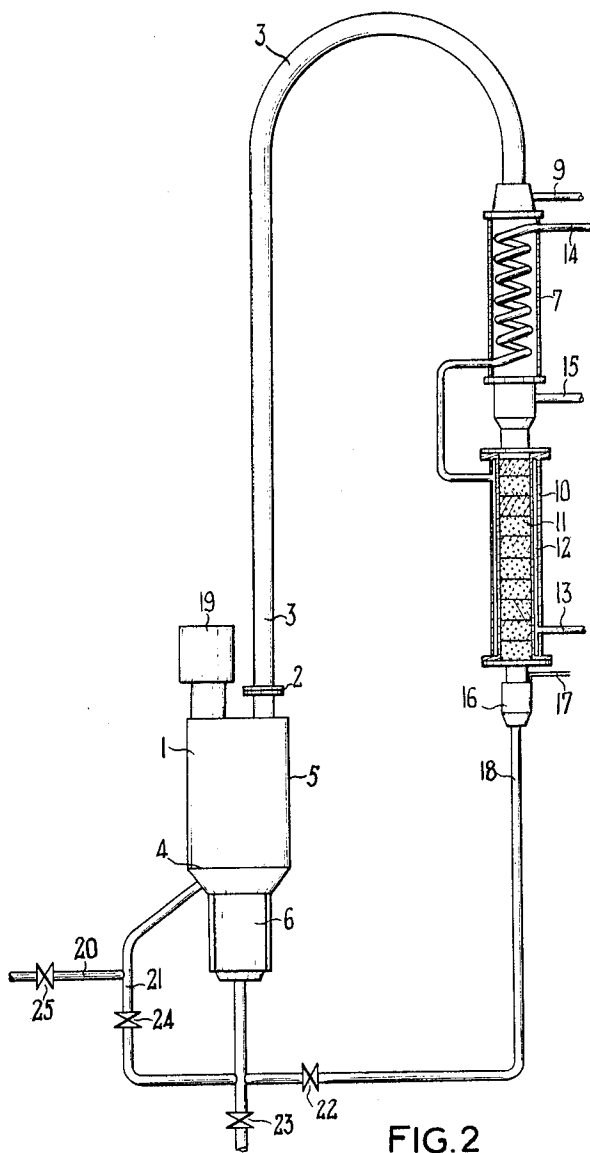


FIG. 2

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PROCESSES FOR THE DISSOLUTION OF URANIUM IN NITRIC ACID

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7 Claims. (Cl. 23-14.5)

The present invention relates to an improvement in processes for the dissolution of uranium in nitric acid.

A process for the dissolution of uranium is already known, which consists in operating in a discontinuous manner by placing metallic uranium, in the form of rods for example, in a receptacle containing nitric acid maintained at the boiling point and in effecting complete dissolution of the metal under these conditions. The disadvantage of such process is that, for the same velocity of penetration of the acid into the metal, overall velocity of dissolution, in proportion to the metal surface exposed to the acid, decreases progressively as the surface decreases. In consequence, the velocity becomes very low at the end of the attack on the metal by the acid, which involves undesirable immobilisation of the material.

A so-called "continuous" process is also known, which consists in supplying both fresh acid and metal to the receptacle in a regular manner, in order to obtain a substantially constant velocity of dissolution. The reaction can be favoured by increasing the temperature, but this expedient is limited by the complication which is necessarily involved in maintaining a suitable pressure, for example equal to the atmospheric pressure, inside the receptacle. It is also possible to increase the concentration of the attacking acid in nitric ions, but tests show that this concentration has only a minor effect upon the velocity of attack at least at the onset of the reaction. It has in fact been found that the velocity of attack is substantially higher if what is dissolved is not pure uranium, but alloys of uranium, particularly a uranium/molybdenum alloy.

The present invention relates to a process which allows a velocity of attack by nitric acid to be attained with uranium which is at least as high as that which is obtained ordinarily with uranium/molybdenum alloys.

This process consists in attacking metallic uranium with a nitric solution containing a quantity of uranium previously dissolved in state of uranyl nitrate, the concentration of uranyl ions in the solution being maintained at a constant elevated value.

Other characteristics of the process together with the advantages which they produce, will appear more clearly from the following description of a particular example.

Referring to the accompanying drawings:

FIG. 1 shows a set of graphs plotted on a coordinate system having, as abscissae, the free acidity of the attacking solution and, as ordinates, the velocity of dissolution, thus showing the effect of the concentration of uranyl ions in the solution;

FIG. 2 is a diagram illustrating one embodiment of a dissolver which operates according to the process of the invention.

It is suitable first of all to note that, by its own definition, the process relates particularly to an operation carried out continuously by using predetermined quantities and proportions of an attacking liquor constituted by nitric acid and uranyl nitrate. In these circumstances, it is found that the velocity of attack, that is to say, the weight of uranium dissolved with respect to the reactable surface presented by the metal, is considerably increased when the concentration of the liquor in uranyl ions is

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large, as is also shown by the following table in which the velocity of attack of the uranium is given in mg. per sq. cm. and per minute, using an acid containing 4.5 moles of free HNO_3 per litre, as a function of the quantity of uranyl nitrate present in the solution.

Concentration of attacking solution in uranyl nitrate (moles litre)	Velocity in mg./sq. cm./minute
0	1.5
1	3.0
1.7	10
2.52	24
3.27	45
3.5	57.5

The curves of FIG. 1 allow the above figures to be verified and it is consequently possible to deduce the preponderant influence of the concentration of uranyl ions in the solution upon the velocity of attack.

Referring now to FIG. 2, the process can be carried out as a continuous operation in a dissolver which itself is of the standard type.

This apparatus, of stainless steel, comprises a dissolution tank 1 of generally cylindrical form connected by a flange joint 2 to a column 3. The lower part 6 of the dissolution tank 1 is provided with a perforated plate, at the level indicated at 4, serving to support uranium rods to be dissolved, and is surrounded by a lateral jacket 5 provided with a standard heating system. The column 3 is connected at its other extremity to an assembly comprising a condenser and an absorber. The condenser is intended to cool the vapours produced during the dissolution of the uranium by the acid inside the dissolver and to condense the water vapour. The absorber serves to recombine the nitrous vapours in order to reintroduce them for a further cycle through the dissolver tank.

The condenser 7 is connected at one end to the pipe forming the column 3 and includes an inlet 9 for the admission of oxygen to the inside of the condenser, in order to oxidise the vapours circulating in the pipe 3 to effect their recombination as acid. The absorber 10 includes a column provided inside with a stack of Raschig rings 11 and is cooled externally by a double jacket 12 where a current of water circulates, which is admitted through an inlet pipe 13 and removed through an outlet pipe 14. At the upper part of the absorber, an inlet 15 is also provided for fresh acid and, at the lower part, a gas separator 16 which allows the incondensable gases to be removed through an outlet pipe 17 which have successively passed through the condenser 7 and the absorber 10. The outlet 18 from the separator 16 is connected to the lower part of the dissolver tank 1, in order to obtain a simple gravity feed of fresh acid and to produce the attack on the bars of fuel which are contained therein. The dissolver also comprises an inlet lock 19 for the introduction of metallic uranium and also an outlet pipe 20, to permit removal of uranyl nitrate in solution, which communicates with a pipe 21 acting as a thermosyphon and allowing the operation to proceed continuously with a homogeneous attacking solution. The pipes 20 and 21 are provided with valves 22, 23, 24 and 25, the valve 23 being provided for draining the apparatus and being closed during attack of the metal with the acid. The above-described apparatus is thus constructed to carry out the continuous dissolution in nitric acid of rods of either natural or enriched metallic uranium or alloys of uranium, such as uranium/molybdenum and uranium/chromium alloys, and also compounds of uranium and uranium cermetes. This dissolution takes place with permanent recombination, by oxidation and absorption, of the vapours evolved. The solution of nitrate obtained

flows from the dissolver through the outlet pipe 20, so providing a constant level inside the dissolver.

According to the invention, the attacking solution used is a liquor containing per litre, for example, about 4 to 5 moles of free nitric acid and about 3 to 3.5 moles of uranyl nitrate. The nitrate solution leaving the dissolver is more concentrated in uranyl nitrate than the solutions at present used. This feature is not critical however and it is possible subsequently to dilute this in the desired proportion in order to obtain the usual concentration.

Another of the important advantages of the process of the invention resides in the considerable reduction in the reserve of uranium, usually called the "hold-up," which is necessary to maintain permanently within the dissolution tank.

The following examples all relate to the attack of uranium cylindrical rods 100 mm. in length and 25 mm. in diameter. By the standard procedures for obtaining a solution of uranyl nitrate of 1.7 moles of uranium per litre with a free acidity of 1.6 N, it is necessary for continuous production of 1 kg. of uranium per hour, to provide a reserve or hold-up of about 55 kg. of uranium in the receptacle. The velocity of penetration of the acid into the metal is very low, its value only being of the order of 0.08 mm. per hour.

On the contrary, according to the process of the invention, it becomes possible to prepare for example a solution containing 3.5 moles of uranium per litre with a free acidity of 4.5 N. For such a concentration and for an overall velocity of dissolution of 1 kg. of uranium per hour, the uranium hold-up in the receptacle is not more than 2.8 kg. The velocity of penetration of the acid into the metal is then of the order of 1.5 mm. per hour, that is to say relatively very high. The attack takes place under a pressure which is substantially the same as atmospheric pressure and at a temperature of about 114° C.

According to another example and again for an overall velocity of dissolution equal to 1 kg. of uranium per hour, a solution of uranyl nitrate was continuously prepared containing 2.6 moles of uranium per litre with a free acidity of 4.5 N and using a uranium hold-up of only 4 kg. in the dissolution tank, the velocity of penetration of the metal by the acid being 0.8 mm. per hour. The attack also took place under atmospheric pressure, but at a temperature of about 110° C.

Comparison of the two latter examples, both effected in accordance with the process of the invention, shows that, with the same nitric acidity and for the same overall velocity of dissolution, the velocity of penetration of the acid into the metal is considerably increased if the concentration of the attacking solution in uranyl nitrate is increased.

In this connection, it may be mentioned by way of example only that the concentration of the attacking solution should preferably be from 2 to 5 moles of uranium per litre. In return, the concentration of the solution in free nitric acid, from a given threshold value, has a much less marked influence upon the velocity of penetration of the acid (see FIG. 1). This concentration can be selected within the range from 1 N to 11 N nitric acid, but generally it is desirable to operate in the range from 3 N to 5 N. Nitric acid losses caused during the dissolution are low and generally less than 5%.

The process according to the invention thus allows a considerably increased velocity of attack under continu-

ous conditions (at least by 10 times), with respect to standard processes, at constant rates of introduction of uranium and nitric acid into the dissolver, which velocity of attack is maintained at a substantially constant value.

Operation of the process takes place simply and economically, as it is not necessary to make use either of high pressure or of elevated temperatures, which consequently considerably diminishes the corrosion of the constructional materials. Also, because of the considerable decrease in hold-up, the volume of the apparatus can also be considerably reduced for the same overall velocity of dissolution. This reduction in volume, which is appreciable in any case, has a particular advantage in the case of dissolution of enriched uranium, because the risks of criticality are thus also diminished.

It will be understood that the invention is not limited in its application to the examples given; it embraces all variants.

I claim:

1. A process for the continuous dissolution of uranium containing articles comprising continuously subjecting said article to a homogenous nitric acid solution containing a constant elevated amount of from 2 to 5 moles of uranyl nitrate per liter, said solution being introduced at a constant rate and uranyl nitrate being continuously removed to provide said homogenous solution.

2. A process according to claim 1 in which the homogenous concentration of said nitric acid solution is maintained by continuously introducing uranium metal and nitric acid to said solution.

3. A process according to claim 2 in which the homogenous nitric acid solution contains 3 to 3.5 moles of uranyl nitrate and 4 to 5 moles of free nitric acid per liter.

4. A process according to claim 1, in which the nitric acid concentration is from 1 N to 11 N.

5. A process according to claim 4, in which the nitric acid concentration is from 3 N to 5 N.

6. A process for the continuous dissolution of an uranium containing article as uranyl nitrate comprising continuously subjecting said article at atmospheric pressure and at a temperature of about 114° C. to a constant feed consisting essentially of nitric acid and uranium as a homogenous solution of 3.5 moles of uranium metal per liter of solution having a free nitric acidity of 4.5 N and continuously removing an uranyl nitrate solution, the speed of penetration of said solution into said article being about 1.5 mm. per hour.

7. A process according to claim 6 wherein the nitrous vapors resulting from said dissolution reaction are removed, condensed and reoxidized to nitric acid, which is returned to the dissolution stage of the process.

References Cited by the Examiner

UNITED STATES PATENTS

2,897,047 7/1959 Schulz ----- 23—14.5

OTHER REFERENCES

"Reactor Fuel Processing," vol. 1, No. 4, October 1958, Atomic Energy Commission, page 4, TK 9001 R43.

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