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2,901,343

DISSOLUTION OF ALUMINUM JACKETS FROM URANIUM CORES BY NITRIC ACID CONTAINING MERCURIC NITRATE

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No Drawing. Application August 25, 1944
Serial No. 551,269

1 Claim. (Cl. 75-97)

The present invention is in connection with the problem of dissolving aluminum coatings, especially aluminum coatings or jackets on other metals such as uranium, when it is desired to also dissolve the uranium.

An object of the present invention is to facilitate the solution of metals, particularly uranium when enclosed in aluminum jackets.

Another object of the invention is to permit dissolving of aluminum jackets separately from uranium on neutron-bombarded uranium slugs encased in aluminum, so that the uranium solution obtained is substantially free from aluminum.

A further object of the invention is the use of a single solution of varying strength for dissolving both the aluminum jacket and the uranium in cases where the presence of aluminum will not interfere with further treatment of the uranium solution.

It is known that when uranium metal is bombarded with neutrons, radioactive fission products and certain transuranic elements are formed. It is often important to recover these fission products as well as other radioactive elements that are formed, for purposes of study and for other uses. In order to carry out the neutron bombardment under the best conditions with a minimum loss of valuable products and to minimize corrosion of uranium, the slugs are incased in aluminum jackets before being subjected to neutron bombardment. Following the neutron bombardment, the problem arises of removing the aluminum jackets in order to dissolve the uranium and the desired products.

Despite the fact that numerous solvents are known which are capable of dissolving aluminum, considerable difficulty has been encountered in development of a process by which the aluminum jackets may be dissolved from the uranium without encountering other difficulties. When uranium slugs which have been subjected to neutron bombardment are treated for the removal of the aluminum, the uranium usually contains such a substantial quantity of radioactive fission products that the slugs cannot be handled directly without injury to personnel, and therefore these slugs must be placed in a solvent wherein an effective removal of the aluminum may be secured with a minimum of hand operation. Certain solvents such as hydrochloric acid are not suitable since they attack process equipment, in which they are used, to an objectionable degree.

The problem of facilitating the solution of both the jacket and the uranium has been solved, in accordance with the present invention, by the discovery that the presence of small quantities of mercuric ion causes aluminum to dissolve readily in relatively dilute nitric acid not in excess of about 50 percent strength and preferably about 5 to 20 percent. Nitric acid of this strength attacks the uranium so slowly that substantially all of the aluminum may be dissolved and the solution removed before serious attack of the uranium can occur. After the aluminum jacket has been dissolved either the nitric acid solution can be made up to a sufficiently high strength to dissolve

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the uranium at a rapid or comparatively rapid rate by addition of stronger nitric acid, or the solution containing the dissolved aluminum can be removed and the uranium treated with a new solution of concentrated nitric acid sufficiently strong to dissolve the uranium within a short period of time. Thus the initial use of small amounts of mercuric ion facilitates fast dissolving of aluminum-jacketed uranium slugs, either in a single solution or in successive separate solutions of aluminum and uranium, respectively, in nitric acid and affords a means by which uranium may be put into solution without serious contamination or loss.

If the nitric acid concentration is above about 50 percent, the rate of solution of aluminum, even with mercuric ion present, is so slow as to make dissolving of aluminum with such concentrations of nitric acid impractical.

The use of small concentrations of mercuric ion is preferred, for instance, of the order of 0.1 percent. For example, mercuric nitrate, $\text{Hg}(\text{NO}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, equivalent to about 0.06 percent mercuric ion based on the weight of the entire solution may be used. The mercuric ion may be added to the nitric acid solution or the aluminum may be previously dipped in aqueous mercuric nitrate solution and thereafter immersed in nitric acid. Apparently sufficient mercury solution adheres to the aluminum surface by physical adhesion and/or sufficient metallic mercury is deposited thereon to be effective in accelerating the solution of the aluminum in nitric acid.

The preferred method, however, is to add the compound furnishing the mercuric ion directly to the nitric acid solution. Mercuric ion can be supplied by practically any mercuric salt, such as mercuric nitrate or mercuric chloride.

The concentration of mercuric compound present may be varied over a wide range, but is preferably above about 0.01 percent and is particularly useful between 0.05 percent and 1 percent, equivalent in the case of $\text{Hg}(\text{NO}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ to between 0.03 and 0.6 percent of mercuric ion by weight in solution. A larger amount of mercuric compound does not impair the operation insofar as the dissolution of aluminum is concerned but introduces additional quantities of a foreign substance, mercury, into the solution. Reduced percentages of the mercuric compound are less effective in increasing the rate of solution. Thus, less than about 0.1 percent mercuric nitrate hemihydrate in the dissolving solution produces a noticeably decreased effect on the rate of solution of aluminum as compared with higher concentrations.

The amount of nitric acid used to effect the dissolution of the aluminum should be sufficient to dissolve all or substantially all of the aluminum jacket and generally a small excess of the nitric acid over the theoretical amount required is used. During the dissolving process nitric acid is consumed and consequently the concentration of the solution gradually tends to decrease and the solution tends to become more and more dilute. Frequently, therefore, it is desirable to add fresh nitric acid to the solution as the process proceeds in order to build up the concentration to its initial value and thereby to maintain a reasonably rapid rate of dissolution of the aluminum.

The temperature of operation is capable of considerable variation, although it is found that in general the reaction proceeds at a more rapid rate when the temperature is high. Accordingly, it is usually most advantageous to conduct the process using boiling nitric acid solutions.

Following removal of the aluminum jacket from the uranium, it is found desirable to dissolve the uranium in a suitable solution. Where it is desired to avoid the presence of a substantial amount of aluminum in the uranium solution, the solution in which the aluminum

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has been dissolved may be removed after the aluminum has substantially completely dissolved and before substantial attack of the uranium occurs and the uranium washed or otherwise treated with water or dilute acids, such as dilute nitric acid, to remove occluded solution or residual sludge from the surface of the uranium. Thereafter the uranium is subjected to the action of a concentrated solution of nitric acid generally initially containing at least 50 percent of nitric acid and preferably about 60 to 90 percent of nitric acid. This process is usually conducted at an elevated temperature, for example, at or near the boiling point of the solution. During the reaction the consumption of HNO_3 may result in a substantial decrease in the concentration of HNO_3 , and not infrequently the solution may become quite dilute containing nitric acid in concentrations of nitric acid as low as 10 percent by weight or lower. Despite this reduction in concentration, however, substantially complete solution of the uranium may be secured if the nitric acid is concentrated initially although the rate of solution in the later stages may be rather slow due to the decrease in HNO_3 concentration of the solution. Consequently it is not necessary to replenish HNO_3 in order to build up the concentrations even though the concentration of HNO_3 may fall below 50 percent. However nitric acid may be added periodically during the operation in order to maintain the concentration of the solution at a sufficiently high value if a more rapid dissolution of uranium is desired and high acidity of the ultimate solution is not objectionable. Usually about 8 to 10 mols of nitric acid are required per mol of uranium to be dissolved in order to dissolve the uranium rapidly and completely. The uranium solution thus secured may be subjected to further treatment for isolation of the radioactive fission products and/or the transuranic elements and/or for other suitable purposes.

While the process may be advantageously conducted by removing the aluminum solution before attempt is made to dissolve the uranium, it may often be found that contamination of the ultimate uranium solution with aluminum is not objectionable and in such a case removal of the aluminum solution may be unnecessary. In such a case the concentration of the solution may be increased to a strength at which uranium may readily dissolve, for example 50 percent HNO_3 and above, by addition of highly concentrated HNO_3 after the aluminum is sufficiently well dissolved. Thereafter the uranium solution may be subjected to treatment for separation of the aluminum from the uranium by precipitation or by other means. The following examples are illustrative.

EXAMPLE 1

Neutron-irradiated uranium slugs having a coating of aluminum approximately 20 mil thick and containing approximately 200 milligrams of radioactive fission products and about 200 milligrams of element 94^{239} per ton of uranium were immersed in a solution of 10 percent nitric acid containing 0.1 percent mercury and the solution was boiled for 4 hours. During the period of boiling the concentration of nitric acid was made up to 10 percent concentration 3 times by an addition of the required amount of 60 percent HNO_3 . After solution of the aluminum was completed, the solution was separated and the slugs were cleaned first by heating for an hour with 10 percent sodium hydroxide solution and then by heating for three hours with 10 percent nitric acid solution. Only about 0.1 percent of the uranium in the slugs was dissolved during the dissolution of the aluminum. The slugs were then placed in boiling nitric acid solution containing 60 percent HNO_3 . The initial mol ratio of acid used to metal treated was 8.8 to 1. The reaction temperature was maintained at about 112°C . throughout and heating was continued for 16 hours after which all the uranium had gone into solution. The solution contained insignificant amounts of aluminum.

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EXAMPLE 2

Aluminum of 20-mil thickness was immersed in boiling 30 to 70 percent nitric acid. It was found to require 10 to 20 hours to dissolve the 20-mil sheet. However, when mercuric nitrate was present, the rate of solution was increased as shown in the following table:

Table I

EFFECT OF MERCURIC NITRATE ON THE RATE OF SOLUTION OF ALUMINUM IN BOILING 45% NITRIC ACID

Concentration of $\text{Hg}(\text{NO}_3)_2 \cdot \frac{1}{2} \text{H}_2\text{O}$ (percent)	Minutes required to dissolve 20 mil sheet
1.....	4
0.1.....	4
0.01.....	124

All percentages in the above table and elsewhere in this specification are by weight.

EXAMPLE 3

The process of Example 2 was repeated except that instead of adding the mercuric compound to the solution, the aluminum sheet was first immersed in aqueous mercuric nitrate and then in the dissolving solution. There was a noticeable reduction in time of solution of a 20-mil aluminum sheet compared to solution in nitric acid alone, as shown by the following table:

Table II

Concentration of aqueous $\text{Hg}(\text{NO}_3)_2 \cdot \frac{1}{2} \text{H}_2\text{O}$ (percent)	Minutes immersion of Al sheet in aqueous mercuric nitrate	Minutes then required to dissolve 20 mil sheet in boiling 45% HNO_3
0.1.....	5	223
5.....	5	205

EXAMPLE 4

Twenty-mil aluminum jackets were dissolved from around uranium slugs by immersion in boiling 45 percent nitric acid containing about 0.1 percent mercuric nitrate. After the aluminum was dissolved, the uranium was then dissolved by increasing the acid concentration to 60 percent in the boiling solution. The acid consumed in dissolving the aluminum under these conditions was determined to be 4.06 moles per mole of aluminum dissolved, i.e., the nitrogen oxides evolved are almost 100 percent NO , showing that the aluminum has been efficiently dissolved with a minimum use of nitric acid.

When mercuric ion is present, aluminum coatings may also be dissolved or at least converted to an aluminum compound by non-acid aqueous solutions having a high pH for example above 5 such as hot water alone. With alkaline solution the presence of mercuric ion increases the rate of solution of the aluminum. When hot water or alkaline mercuric nitrate solutions are used to dissolve aluminum coatings, a sludge of hydrated aluminum oxide (aluminum hydroxide) is produced. This hydrated aluminum oxide sludge is difficult to remove due to its gelatinous nature.

In order to remove the sludge from the dissolving vessel, sludge must be either dissolved in dilute nitric acid and the solution drained off, or the sludge must be slurried in one or more large batches of wash water, and the wash water containing the slurry drained from the dissolving vessel. Following removal of the hydrated aluminum oxide sludge by either of these methods, concentrated nitric acid is added and the temperature raised to the boiling point in order to dissolve the uranium.

I do not intend to limit my invention to any particular

theory of operation. The scope of my invention is to be limited only by the following claim.

I claim:

A process of dissolving aluminum jackets from uranium cores without substantial attack of said uranium cores, comprising immersing said aluminum-jacketed uranium cores into nitric acid having a maximum concentration of 50% and containing mercuric nitrate in a concentration of between 0.05 and 1% by weight of solution, bringing the nitric acid solution to boiling temperature while said jacketed uranium core remains immersed, whereby said aluminum is dissolved but said uranium remains substantially unaffected.

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