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PROCESS FOR THE FIXATION OF HIGH LEVEL RADIOACTIVE WASTES

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ABSTRACT OF THE DISCLOSURE

This invention relates to a method in which radioactive waste solutions can be incorporated into silicate-type minerals via a thermite reaction. Nitrate solutions of radioactive materials are treated with sulfuric acid, evaporated to form a sulfate mass which is then reacted with silicon or silicon dioxide as a thermite mixture to form a polysilicate mass highly insoluble to water leaching.

Background of the invention

With the devolpment of nuclear reactors for power generation and the continued production of fissionable material, the problems encountered in the handling, treating, and ultimate safe storage of the resulting liquid radioactive wastes are becoming increasingly important.

Presently, liquid radioactive wastes are disposed of by storage in underground steel tanks. This method requires extremely large installations in view of the great quantities of liquid wastes which must be stored and further requires constant surveillance of the storage tanks. The costs of such operations are high, and thus there is need for a less costly means of disposal and one which does not require large storage units nor elaborate surveillance provisions.

Suggestions have been made that the radioactive wastes could be converted to a dry mass thus negating the necessity of storage tanks. This invention is concerned with the conversion of liquid radioactive wastes to a dry mass which is self-fixing in respect of the radioactive substances, insoluble to water leaching and which can be stored for extended periods with a minimum of safety precautions.

Summary of the invention

The instant invention comprises a process for the fixation of radioactive waste substances. According to the art, spent atomic fuel elements are normally conveyed to a spent fuel processing center. The spent fuel elements are usually cladded with a metal such as aluminum, zirconium, or stainless steel, and the first step in reprocessing is to remove the cladding material from the fuel. This may be accomplished by stripping or by acid leaching, depending on the cladding material itself. After the cladding is removed the fuel is dissolved, usually in nitric acid to recover uranium and plutonium and to obtain separation of waste fission products therefrom.

When the cladding material is aluminum metal, the entire spent fuel element may be dissolved in nitric acid. After separation of the uranium and plutonium, the residual waste acid solution will contain large amounts of aluminum nitrate together with smaller quantities of fissionable materials such as strontium-90, cesium-137, promethium-147, ruthenium-106 and cerium-144, all in the nitrate form.

In any event, the instant invention encompasses the formation of a solution wherein the radioactive waste fission products are present in cationic form.

The radioactive solution containing the fission products is then treated with a high boiling acid to convert the waste fission products to a less volatile form. Sulfuric acid is preferred, but acid such as phosphoric and perchloric may be used under appropriate conditions. The amount of high boiling acid used must be sufficient to convert all of the materials present to the less volatile salt.

The solution now containing the less volatile salts is then evaporated to remove water and the lower boiling acid originally used to dissolve the fuel, and to form a salt mass which is then employed in a thermite reaction as will be explained in more detail. In the case of sulfuric acid a sulfate mass will be formed. The term "mass," as used in connection with the evaporation concentrate, may include a dry condition of the concentrate, but preferably the concentrate comprises a melt or a highly concentrated slurry of the salts. There is some greater hazard involved in further processing powders of fissionable waste materials, and dangers are minimized when a melt or a highly concentrated slurry is employed.

The acid mass containing the waste fission products is then mixed with silicon and, if desired, also with silicon dioxide, to form a thermite mixture. The thermite mixture is then evaporated to dryness, if necessary, and ignited in a controlled manner. As a result of the exothermic thermite reaction a polysilicate mass is formed, which upon solidification may be stored for long periods, the polysilicate mass containing the radioactive fission products being highly insoluble to water leaching.

Description of the preferred embodiment

Typically, the starting material for use according to the instant invention may be a nitric acid solution containing radioactive fission products as hereinbefore described and which may also contain substantial quantities of cladding material, as for example aluminum, in nitrate form. Such nitrate solution is generally stored for extended periods of time prior to being treated by the instant process.

The nitrate solution is placed in a suitable vessel and admixed with sufficient sulfuric acid so as to convert all of the nitrate values to sulfates. The resulting solution is then fed to appropriate evaporating apparatus and heated for sufficient time and at high enough temperatures to drive off water and nitrogen values as nitric acid and nitrogen oxides. The off gases of the evaporation step are collected, scrubbed, and filtered to reduce any possible radioactivity to acceptable standards. The sulfates, being much less volatile than the corresponding nitrates or oxides which derivate from the decomposition of the nitrates, will remain in the evaporator as a sulfate mass. Aliquot portions of the sulfate mass are then subsequently used in a thermite reaction as will be described in more detail.

The thermite reaction involves the preparation of a suitable reaction mixture. Typically, the thermite reaction may be indicated by the following equation:

$2Al_2(SO_4)_3+9Si \rightarrow 2Al_2O_3+9SiO_2+6S+1000$ Kcal.

The thermite reaction vessel is typically a metal container of closed configuration and lined with a castable high temperature refractory. The vessel has appropriate exhausting means and inlet means for charging the thermite mixture and for introducing oxygen as may be required to burn sulfur to sulfur dioxide. Preferably the vessel is capable of being externally heated.

The thermite mixture employed according to this process consists of a predetermined amount of the aforementioned sulfate mass and silicon. If desired, silicon dioxide may also be present. Silicon dioxide is added for two reasons—first to act as a coolant during the thermite reaction and prevent too great a temperature rise—second to assist in the formation of the polysilicate end product, the polysilicate being particularly insoluble with respect to water leaching.

There must be a source of oxygen to support the thermite reaction. This may be supplied from an external source, however, when large quantities of $Al_2(SO_4)_3$ are present, much of the oxygen may be obtained from the sulfate portion.

When the sulfate mass is in the form of a highly concentrated slurry when admixed with the silicon and silicon dioxide, it will be necessary to dry the mixture prior to ignition. This may be done by application of heat from an external source.

The thermite reaction mixture must be ignited by one means or another. Ignition may be by a fuse or igniter such as a sparking mechanism or by other means as known to those familiar with such operations.

The heat of the thermite reaction leads to fusion of the mass and incorporation of the fission products and other metallic ions, if present, into the polysilicates structure.

In the dried thermite mixture ruthenium and cesium volatization will not ordinarily occur during the practice of this process because of the stability of the sulfate forms. The sulfate salts of these two fission products will also react with the silicon and thus be chemically incorporated in the silicate matrix.

The off gases of the thermite reaction, sulfur dioxide and some traces of nitrogen oxides are collected and may be utilized elsewhere in the overall process.

When the thermite reaction has been completed the entire reaction apparatus, i.e. the metal vessel containing the polysilicate mass is cooled to a temperature dictated by fission product containment and removed to a convenient storage area.

The polysilicate matrix, like most high silica content rocks and sands, is highly resistant to leaching by ground water or sea water. Thus, this type of matrix affords maximum protection against natural or other induced water inundation of storage sites. The metallic shell and refractory lining of the thermite reaction vessel becomes an integral part of the solid mass which is ultimately stored as contemplated herein.

The fission products are fixed or chemically bonded in the form of silicates. According to this process there is less metal content in the polysilicate structure, as contrasted with the use of iron or other metals, thus improving insolubility. The glass-like structure of the polysilicate also minimizes surface area thus restricting leachability.

In order to demonstrate the chemistry of the instant process a typical simulated radioactive waste solution is prepared comprising a solution of aluminum nitrate containing trace amounts of non-radioactive cations, strontium and cesium.

For each six grams of aluminum nitrate

$$Al(NO_3)_3 \cdot 9H_2O$$

used in preparing the solution, approximately 1.6 ml. of concentrated sulfuric acid is used to convert the

nitrates to sulfates. This is done by mixing aliquot portions of the aforementioned nitrate solution with the concentrated sulfuric acid and evaporating to a highly concentrated slurry or sulfate mass as aforedescribed.

An aliquot portion of the concentrated sulfate slurry is then admixed with two grams of silicon metal. The resulting mixture is heated to dryness and then ignited. A vigorous thermite reaction occurs resulting in the formation of a polysilicate.

Alternatively the thermite reaction is repeated, but a small amount of silicon dioxide (1 gram) is also added to the thermite mixture. Upon drying and ignition a somewhat less vigorous thermite reaction occurs, showing the tempering effect of the silicon dioxide on the overall reaction. Nevertheless, a polysilicate structure is still obtained.

Analysis of both end products establishes the existence of a polysilicate with the cations of the aluminum, cesium, and strontium fixed or chemically bonded within the polysilicate matrix. Extended attempts to leach the polysilicate mass with water shows it to be highly insoluble.

We claim:

1. A process for fixation of radioactive waste products comprising the steps of:

(1) forming a solution wherein the radioactive waste products are present in the form of nitrates,

(2) adding a high boiling point acid selected from the group consisting of sulfuric acid, phosphoric acid and perchloric acid to said solution in amount sufficient to convert all the waste products to less volatile acid salts,

(3) evaporating the resulting solution to remove water and non-radioactive volatiles and to form an acid salt mass,

(4) admixing the acid salt mass with silicon to form a thermite mixture,

(5) igniting said mixture and continuing ignition to form a polysilicate mass containing said radioactive waste products and being highly insoluble to water leaching.

2. Process according to claim **1** wherein said acid salt mass is admixed with silicon and silicon dioxide.

3. Process according to claim **1** wherein said thermite mixture is dried before igniting same.

4. A process for fixation of radioactive waste fission products comprising the steps of:

(1) forming a solution of said waste fission products by dissolving them in nitric acid,

(2) adding sulfuric acid to said solution in amount sufficient to convert all of the nitrates in said solution to sulfates,

(3) evaporating the resulting solution to remove water and nitrates and to form a sulfate mass,

(4) admixing said sulfate mass with silicon to form a thermite mixture,

(5) igniting said mixture and continuing ignition to form a polysilicate mass containing said radioactive fission products and being highly insoluble to water leaching.

5. Process according to claim **4** wherein said sulphate mass is admixed with silicon and silicon dioxide.

6. Process according to claim **4** wherein said thermite mixture is dried before igniting same.

7. In the art of recovering uranium and plutonium from spent fuel elements having an aluminum cladding thereon wherein the spent fuel elements are dissolved in nitric acid to form a nitrate solution, the uranium and plutonium separated therefrom, leaving a waste nitrate solution containing aluminum and radioactive waste fission products, the improvement for fixation of said radioactive waste fission products comprising the steps of:

(1) adding sulfuric acid to said waste nitrate solution in amount sufficient to convert all the nitrates in said solution to sulfates,

(2) evaporating the resulting solution to remove water and nitrates and to form a sulfate mass,

(3) admixing said sulfate mass with silicon to form a thermite mixture,

(4) igniting said mixture and continuing ignition to form a polysilicate mass containing said radioactive fission products and aluminum as metal polysilicates and being highly insoluble to water leaching.

8. Process according to claim **7** wherein said sulfate mass is admixed with silicon and silicon dioxide.

9. Process according to claim **7** wherein said thermite mixture is dried before igniting same.

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