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RADIOACTIVE MATERIALS OF LOW SURFACE AREA

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This application is a continuation-in-part of application Serial No. 134,143, filed August 28, 1961, now U.S. Patent No. 3,213,031.

This invention relates to a process for the preparation of complex compounds having low surface area and containing radioactive elements. Another aspect of this invention relates to radioactive waste disposal and more specifically, to a process for the incorporation of radioactive waste materials in an improved water-unleachable solid.

The rapid expansion of nuclear power production has catalyzed the urgent need to devise safer and more economical methods for the disposal of fission by-products or radioactive waste materials. The most troublesome wastes are those derived from the chemical processing of fuel elements since these contain elements of high level radioactivity in aqueous solutions of aluminum and zirconium nitrate. The present day method of storing liquid radioactive wastes in underground tanks is not satisfactory from the standpoint of bulk and the uncertainty of container durability. Therefore, it has been the aim of development engineers in this field to provide a method by which these radioactive by-products can be stored in concentrated form, preferably as solids, and in a "package" which will not allow the radioactive elements to escape to ground water, atmosphere, or the surrounding area. The criteria of acceptability for the solid package containing radioactive elements is a high degree of water-unleachability in the solid mass.

Several methods of incorporating radioactive elements in solid matrices have been proposed and have been found to be advantageous in that in radioactive waste solutions can be concentrated to present a compact package for disposal in a relatively confined area. However, one of the major difficulties with most of the solid fixation processes is that a high temperature installation, such as that used in the glass or ceramic manufacturing plants is required. This type of high temperature operation, which must be carried out over prolonged periods, presents both maintenance and volatility problems which mitigate against the commercial acceptance of these processes.

In a copending patent application Serial No. 839,067, filed September 10, 1959, now U.S. Patent No. 3,110,557, the radioactive material is incorporated into a complex oxide having a remarkably low water leach rate, for example, about 1.0×10^{-5} grams per square cm. per year in boiling water and from 100 to 1,000 times less in water at 25° C.

For the purposes of the present invention, the terms "leach rate" and "leachability" are defined as follows. Leach rate is the erosion or solution of a solid matrix in terms of weight (g.) per area (cm.^{2}) per time (year). Leachability is the percentage of a solid matrix eroded or dissolved in a solution per unit of time. This is expressed as percentage loss per year under a given set of conditions. However, it has now been discovered that the leachability can be even further reduced and, it is well accepted that the lower the leachability, the more desirable the product for disposal.

Accordingly, it is an object of the present invention to overcome the disadvantages of previous processes while greatly reducing water leachability of the disposable product and providing an economically feasible and

commercial process for the safe disposal of radioactive wastes.

Another object of the present invention is to chemically incorporate radioactive elements in a complex compound having low surface area and greatly reduced water leachability.

Another object of this invention is to provide a method of treating radioactive waste for its fixation in relatively abundant and inexpensive materials.

Another object of this invention is to provide a process for the disposal of radioactive wastes employing a minimum of utilities and fixed plant equipment, thus simplifying the fixation process.

These and other objects will become apparent to one skilled in the art from the accompanying description and disclosure.

According to the present invention an improved matrix is provided for the exothermic fixation of radioactive materials, preferably radioactive waste materials containing cesium^{137} and strontium^{90} obtained from an atomic reactor, to provide an improved product having a critical surface area. The matrix of this invention is a mixture of inorganic materials comprising iron oxide and silicon or aluminum or mixtures thereof wherein the oxide portion of the mixture is present in a weight excess of at least 2.5:1 with respect to the aluminum and/or silicon. The ratio of this mixture is critical in the preparation of the improved products of the present invention which have a surface area of less than 0.01 square meter per gram. It has now been discovered that products of the type herein described, having this critical surface area, display water leachability at 25° C. of one of the most leachable of the radioactive components (Cs^{137}) of less than about 0.0001 percent of the product mass per year.

Generally, the radioactive waste derived from an atomic reactor contains between about 1.5 and about 2.5 molar aluminum nitrate, between about 0.9 and about 1.5 molar nitric acid, between about 0.3 and about 0.9 molar sodium nitrate, between about 0.02 and about 0.003 molar mercuric nitrate and radioactive components such as cesium, strontium and ruthenium, also in the form of nitrates. When zirconium cladding agents are used, the waste will also contain a zirconium salt. In the following Table I, the radioactive components which may be present in the waste are reported together with the probable and approximate accumulation of these components in waste mixtures.

TABLE I.—ACCUMULATION AND DECAY OF FISSION PRODUCTS

Nuclide Present	Half-life (yr.)	Accumulation [1] (μc./ml.)	Residual [2] (μc./ml.)	0.1 MPC [3] (μc./ml.)
Sr^{89}	0.148	21.1×10^4	>0.1 MPC	7×10^{-6}
Sr^{90}	28	3.0×10^4	2.3×10^4	8×10^{-8}
Y^{91}	0.159	26.4×10^4	>0.1 MPC	2×10^{-2}
Zr^{95}	0.178	30.0×10^4	>0.1 MPC	
Nb^{95}	0.096	30.0×10^4	>0.1 MPC	4×10^{-4}
Ru^{103}	0.110	13.6×10^4	>0.1 MPC	
Ru^{106}	1.0	1.4×10^4	14	10^{-2}
Te^{129}	0.090	1.6×10^4	>0.1 MPC	10^{-3}
Cs^{137}	30	2.5×10^4	2.0×10^4	1.5×10^{-4}
Ba^{140}	0.035	30.0×10^4	>0.1 MPC	2×10^{-4}
Ce^{141}	0.088	28.2×10^4	>0.1 MPC	
Pr^{143}	0.038	28.2×10^4	>0.1 MPC	4×10^{-2}
Ce^{144}	0.780	24.7×10^4	35	4×10^{-3}
Nd^{147}	0.032	12.2×10	>0.1 MPC	
Pm^{147}	2.6	6.9×10^4	4.8×10^4	0.1
Sm^{151}	80	0.005×10^4	49	0.02
Pu*	2×10^4	3	3.0	1.5×10^{-7}
U*	7×10^8	5.3×10^{-3}	5×10^{-3}	7×10^{-6}

[1] Accumulation in ten years by power program starting at 2,000 MW and increasing to 30,000 MW. Expressed as microcuries per milliliter assuming a waste volume 1.5×10^6 gallons.

[2] Microcuries per milliliter after an additional ten-year decay of the ten-year accumulation

[3] Ten percent of Handbook 52 maximum-permissible values for concentration in water.

*Assuming 1 percent losses for arbitrary operating conditions.

It is to be understood, however, that the concentration of these components can be higher or lower depending upon prior treatment and that all of the radioactive components shown in Table I are not necessarily present in waste mixtures suitable for treatment; although, ruthenium and cesium are components of most waste mixtures and are present in the waste mixtures of the present invention. It is also to be understood that the components of the radioactive mixture may be initially present in a form other than nitrates, e.g., oxides, sulfates, chlorides, fluorides, etc., depending upon the conditions employed in the atomic reactor and fuel reprocessing cycle.

In the non-radioactive matrix, suitable for incorporating the radioactive mixture, the iron oxide must be present in a weight excess of at least 2.5:1 with respect to the elemental portion and the weight ratio of the iron oxide to the elemental portion of the mixture is preferably at least 4:1. The iron oxide can be in the ferrous, ferric or ferro-ferric state as a pure compound, or in admixture with impurities found in iron ores. Thus, magnetite or haematite, for example, can be used as the iron oxide. The above weight ratio of oxide to elemental component is critical for producing the improved products of the present invention having a surface area less than 0.01 square meter per gram. It has been found that for smaller ignition charges, an iron oxide excess of at least 8:1 with respect to the elemental components is preferred. However, as the size of the charge increases, for example a 5 or 10 pound matrix mixture, the weight excess of the iron oxide can be lowered for example, to between about 3 to 6:1, if desired. A weight excess of iron oxide radioactive wastes of up to about 25 weight percent or higher based on the amount required to react with the elemental component or components, can be used, if desired in a matrix which has been impregnated with radioactive wastes. However, in most operations, since such a large excess does not enhance the operation, it is usually avoided.

In addition to the above-described essential ingredients in the matrix mixture, one or more of the following additives can be admixed in order to provide still more improved hardness and better affinity for cesium in the product. Suitable additives are oxides of metals such as aluminum, zirconium, calcium, magnesium, titanium, boron and strontium. These additives when used are admixed with the non-radioactive matrix solids in an amount not exceeding 10 percent, preferably not exceeding 5 percent, of the total matrix mixture.

As discussed above the matrix mixture is a system which includes in its composition aluminum or silicon, which upon ignition and reaction, are converted to the respective oxides. By reason of this circumstance, the aluminum nitrate or oxide in the radioactive waste materials can be tolerated and may well be advantageous in the fixation reaction since metal alumino silicates are generally less leachable than silicates alone. Heretofore, fixation processes depending on ion exchange, have had a low tolerance for the products resulting from the cladding agents such as aluminum oxide and zirconium oxide and it has been necessary to remove these materials which saturate the exchange medium, thus reducing the capacity for cesium and strontium sorption. In the present process weight ratios of metal oxides which do not enter into the initial exothermic reaction, for instance Al_2O_3 and SiO_2, may be tolerated up to a weight ratio of 1:1 with respect to the elemental material. Since the present process not only tolerates, but also utilizes the reactivity of these oxides, one of the significant objects and advantages of the present invention is accomplished, namely that of reducing the number of manipulative operations necessary to concentrate waste before the incorporation of the radioactive materials in a solid matrix. Thus a simplified, more economical method of fixation is provided.

The amount of charge used (matrix and radioactive waste) in the description of this invention is about 3 to 5 pounds; however, equally good results are achieved with charges up to 25 pounds. For commercial operation, 1,000 pound charges are suitable; although, it is to be understood that 10,000 and 50,000 pound charges can be employed. The difficulty of dealing with radioactive heat generated during storage is minimized due to the high melting points of the products of this invention. The minimum size of the charge is determined by the amount required to achieve a desired reaction temperature for a given composition to maintain the solids in the matrix mixture above their melting temperatures for a time sufficient to permit their coalescence. In addition, the size of the charge may also be limited by the amount and concentration of radioactive components to be diffused in the mixture. The concentration of radioactive components in the matrix can be as high as about 30 percent, but is preferably between about 1 percent and about 15 percent of matrix.

The products of the present process possess low surface areas of less than 100 $cm.^2$ per gram and as a result, have low water leachability, below 0.0001 percent per year in water under ambient conditions.

Aside from the disposal problems to which this application is primarily directed, the radioactive crystalline compositions produced are, themselves, useful in biological research and can also be employed in certain commercial installations as sources of energy for example, as a heat source in converting saline water to potable water, or as a source for producing other forms of energy. As developments in the field of utilities expand, these radioactive by-products which are incorporated in a solid matrix will find ever increasing application since the matrices containing the radioactive element can be "tailor-made" to meet certain requirements of composition, concentration, size and shape to suit the application of the radioactive unit.

Upon mixing and igniting the matrix and radioactive material, the exothermic reaction between the iron oxide and element is initiated. While non-reactive metal oxides do not initially react, the heat generated in the ensuing reaction causes coalescence of all of the metal oxdies into the mass at the higher temperature, and thus induces the reaction of these otherwise non-reactive oxides so that they are chemically incorporated in the product.

The maintenance of temperature above the melting point of the components to allow for coalescence of the normally solid mixture can be aided by employing insulation around the reactor to retain the heat in the system. This insulation can be employed outside of the reactor shell or can be used as a liner inside of the reactor container. Suitable materials include bentonite, asbestos, fire brick and any castable refractory material which is thermally stable up to about 1400° C. However, the insulation of the reaction, while extremely beneficial, is not essential to the success of the present process since the temperature is easily controlled at a high level by the energy content and heat capacity of the mixture.

A beneficial step in the present process which, in addition to the ratio of oxide: elemental component, is largely responsible for the improved low surface area product, involves preheating the solid matrix mixture. This preheating of the mixture supplies heat energy to the system so that the exothermic heat of reaction, generated during ignition, results in the attainment of higher temperatures in the mixture, which allows for better coalescence of the components of the ignition charge. Accordingly, non-radioactive components of the matrix are mixed in the proper proportion and heated to a temperature below ignition, preferably at a temperature between about 400° C. and about 750° C., depending on the particle size of the mixture. Generally, the smaller the particles, the lower the ignition temperature.

Prior to the preheating, the components of the matrix are mixed either in their final form or as compounds, which upon heating, will generate the components of the

desired matrix. Thus, for example, a mixture of ferric oxide-silicon and aluminum nitrate can be mixed, and subjected to preheating to yield a matrix mixture of ferric oxide-silicon-aluminum oxide. The components of the matrix can be mixed in a dry or a wet state. Moistening a dry mixture with water results in more uniform distribution of the components and a more compact cake which, after firing with radioactive component, leads to a product having lower surface area.

Some radioactive wastes are obtained as a precalcined, dry powder while others are obtained in the form of nitrates, in a liquid state. The dry radioactive components can be mixed with the matrix prior to the preheating step; but the process of this invention is particularly beneficial in cases where radioactive waste solutions are involved. In this way the drying and denitrification of a radioactive solution can be accomplished simultaneously with the matrix preheating step. It has been observed that volatilization of ruthenium tetroxide and cesium is effectively inhibited by the silicon and iron oxide present in the matrix.

A particular embodiment of the present invention comprises impregnating a fixation mixture with a nitrated radioactive waste containing aluminum nitrate and radioactive elements and subjecting the resulting mixture to preheating to convert nitrates to the corresponding oxides, to vaporize inerts and to put heat energy into the system. The preheated mass, devoid of water and oxides of nitrogen, is then sealed and ignited causing initiation of the exothermic reaction and the melted components of the reaction are allowed to coalesce and gradually solidify to form a radioactive impregnated product having low surface area and greatly reduced water leachability. Another embodiment of the present invention comprises introducing dried, calcined radioactive components to a dried matrix mixture. The reactor containing the mixture is then sealed over with non-impregnated matrix and the resulting mass is heated to its ignition temperature for reaction. This method greatly reduces the loss of volatile components such as ruthenium and cesium which are usually present in the radioactive waste mixture. The elemental components and the oxides are allowed to coalesce before gradually cooling to the solid state.

The basic heat of the fixation reaction, disregarding loss of heat by convection, can be determined by the equation

$$\Delta H = \Delta C\,(T_2 - T_1)$$

where ΔH is the heat of reaction; ΔC is the heat capacity of products minus the heat capacity of the reactants; T_2 is the maximum temperature achieved; and T_1 is the ignition temperature. The apparatus employed for carrying out the reaction is selected on the basis of the heat generated by the system.

The process of the present invention, in commercial operation, can be carried out in a metal container such as stainless steel, cast iron, carbon steel, etc., which is lined with a suitable insulating material such as asbestos, a castable refractory, magnesia brick, fire brick or any of those enumerated above as insulators; or the reactor container can be fabricated out of the castable refractory itself. In any case, the composition of the container will depend largely on the components of the mixture undergoing ignition and its ability to withstand the temperatures generated in the system.

The ignition temperatures of the present process vary between about 700° C. and about 1300° C. and can be higher or lower than temperatures in this range depending upon the heat sources available and the particle size of the solids mixture. Also small amounts of a metal oxide or zirconium metal additive, less than about 1 percent of the total mixture, can be employed to lower the ignition temperature. For example, a metal oxide having this effect is lead oxide; others include CuO, BaO_2 and AgO. An advantageous method of achieving a lower ignition temperature comprises inserting an ignitor such as a 1:3 part by weight mixture of aluminum and magnetite, or a magnesium ribbon around a wire of iron oxide, into the core or placing the ignitor on the surface of the mass to be reacted. In such instances, it is only necessary to heat the ignitor to a temperature sufficient to initiate the reaction, while the bulk of the matrix can be at temperatures as low as ambient temperature.

For economic reasons, pressures are allowed to develop in the system during fixation, although it is to be understood that the fixation can be conducted in vacuo which, aside from the economic disadvantages, has certain beneficial effects such as descreasing flow of the metal oxides.

As hereinabove stated, the products of this process are characterized as crystalline materials which have a surface area less than 100 cm.^{2} per gram and an intrinsic leach rate less than 1×10^{-5} grams per cm.^{2} per year in boiling water. When the preferred matrix mixture is employed, namely Fe_2O_3-Si in a weight ratio of at least 2.5:1 and is admixed with a waste containing aluminum oxide or an aluminum salt, the product of the reaction after firing is similar to the mineral almandite and displays a melting point between 1100° C. and 1300° C. The radioactive components which have been added to the matrix prior to ignition are chemically combined in the form of oxides in the product mass; although some of the more volatile materials, such as rare gases, may be interstitially entrained therein. Heretofore other solid fixation media have been used for incorporating radioactive components such as ceramic glazes. However, these products have displayed higher water deachability than the products of the present process. The leachability of some commonly employed matrices are reported below in Table II.

TABLE II

Glasses [1]	Specific Surface Area, cm.^{2}/g.	H_2O Leaching Temp., ° C.	Percent Cs^{137} Leached/yr.	Grams/cm.^{2} of Cs^{137} Leached/day	Microcuries Cs^{137} initially present in 4 g. sample
65% Nepheline syenite+35% CaO	16	25	7.2×10^{-2}	5×10^{-7}	100
60% Nepheline syenite+20% CaO+20% BaO	16	25	7.2×10^{-2}	5×10^{-7}	100
65% PbO+10% B_2O_3+25% SiO_2	16	25	5.8	1×10^{-5}	100
Glazes: MIT Ceramic [2]	125	60–80	15.6		

[1] The leachability of the Glasses is reproduced from Table 2—The Disposal of Fission Products in Glas by L. C. Watson, R. W. Durham, W. E. Erleback and H. K. Rae—article appearing on page 19 of Volume 18 of Proceedings of the Second International Conference, Geneva, September 1958, U.N. Publication.

[2] The Fixation in Vitreous Matrices of High Activity Fission Product Wastes from Aqueous Reprocessing of Spent Stainless Steel—Uranium Fuel Elements by M. L. Goldman, T. H. Y. Tebbutt, A. R. McLain, B. C. Kim, and R. Eliassen, A.E.C. Report AT (30-1)-621., February 1, 1960, page 114.

Comparing these matrices with the following examples of the present invention, it is found that the present products are capable of retaining radioactive components better than these existing materials by several orders of magnitude.

The following examples are presented in order to further illustrate the invention and are not to be regarded as unnecessarily limiting to the scope thereof.

EXAMPLE 1

Illustrating the effect of mass on surface area

Two samples, each containing silicon, ferric oxide and hydrated aluminum nitrate in a weight ratio 1:4:3 are mixed and calcined at 450° C. Sample 1 weighs 3 pounds and sample 2 weighs 0.25 pound after calcination. Both samples are then preheated to 750° C. after which they are each ignited at the same temperature by the addition of 6 grams of magnetite-aluminum ignitor wherein the weight ratio of magnetite to aluminum is 3:1.

Sample 1 and sample 2 are allowed to cool overnight whereupon the surface area of each sample is measured. The surface area of sample 1 is less than 100 cm.^{2} per gram and the surface area of sample 2 is found to be about 1,000 cm.^{2} per gram.

EXAMPLE 2

Illustrating the effect of surface area on cesium^{137} leachability

The above procedure employed in Example 1 to obtain a 3 pound matrix mass and a 0.25 pound matrix mass is repeated to provide samples 3 and 4 respectively; however, before igniting at 750° C., 1 mc. of Cs^{137} is added to each of the samples 3 and 4. The impregnated samples are each ignited according to the procedure set forth in Example 1, to react the mixtures and the product of each of the reactions is allowed to cool to room temperature. The leach rates of the resulting samples 3 and 4 are measured in water at 100° C. and at 25° C. The leachability of sample 3, which represents the 3 pound sample is found to be 0.001 percent Cs^{137} per year at 25° C. and 0.1 percent Cs^{137} per year at 100° C. The leachability of sample 4, representing the 0.25 pound sample is 0.01 percent Cs^{137} per year at 25° C. and 1 percent Cs^{137} per year at 100° C.

It is concluded on the basis of Examples 1 and 2, and on additional work, that greatly reduced surface area, i.e., surface areas less than 100 cm.^{2} per gram, result in greatly reduced leachability of radioactive materials. The following Table III correlates the intrinsic leach rate with the leachability of Cs^{137} in water at 100° C. and at 25° C.

TABLE III

[Leachability of matrix possessing leach rate of 1×10^{-3} g./cm.^{2}/yr. in water at 100° C. and 1×10^{-7} g./cm.^{2}/yr. in water at 25° C.]

Surface Area, cm.^{2} per gram	Leachability of Cs^{137} in Water	
	At 100° C., Percent Leached per Year	At 25° C., Percent Leached per Year
11	1×10^{-3}	1×10^{-5}
10	1×10^{-2}	1×10^{-4}
100	1×10^{-1}	1×10^{-3}

EXAMPLE 3

Illustrating the effect of preheating on surface area

Two 3 pound charges (samples 5 and 6) of silicon-ferric oxide and aluminum nitrate in a weight ratio of 1:4:3 are mixed. Sample 5 is preheated to a temperature of 750° C. and sample 6 is allowed to remain at room temperature. To each of the samples is added 1 mc. of Cs^{137} after which sample 5 is ignited at a temperature of 750° C. and sample 6 is ignited at room temperature with 10 grams of a 3:1 mixture of magnetite and aluminum.

The surface area of sample 5 is about 100 cm.^{2} per gram and its water leachability with respect to Cs^{137} is about 0.1 percent per year at 100° C. Sample 6 has a surface area of 1,000 cm.^{2} per gram and a water leachability with respect to Cs^{137} of 1 percent per year at 100° C. and 0.01 percent per year at 25° C.

EXAMPLE 4

Illustrating the effect of excessive coolant on the surface area and leachability of the product

A mixture of 205 grams of silicon, 821 grams of ferric oxide and 2460 grams of hydrated aluminum nitrate are mixed with 1 mc. of Cs^{137} and calcined at 425° C. The weight of the calcined mass is 1360 grams or 3 pounds. The calcined material is then preheated to 750° C. and ignited at the same temperature with 3 parts magnetite, 1 part aluminum ignitor. After completion of the reaction and cooling, the product obtained had a surface area in excess of 1 square meter per gram and a leachability of Cs^{137} in water at 100° C. of 10 percent per year and in water at 25° C. of 0.1 percent per year.

This example illustrates that excessive amounts of coolant (a metal oxide which does not enter into the initiating exothermic reaction) will not allow sufficient coalescence in the reaction mixture to take place and will result in a product of higher surface area and increased water leachability. Thus, to obtain the advantages of the present invention, metal oxides which do not enter into the initial exothermic reaction should not exceed a weight ratio of 1:1 with respect to the reactant elemental metal of the matrix mixture.

EXAMPLE 5

A 25 pound matrix mixture of ferric oxide-silicon in a weight ratio of 5:1 is admixed with a radioactive waste mixture containing 2 molar aluminum nitrate, 1 molar nitric acid, 0.5 molar sodium nitrate and about 7 mc. Cs^{137}. The resulting mixture contains a weight ratio of aluminum nitrate to silicon of about 1:1.5. This mixture is preheated to a temperature of about 700° C. over a period of 2 hours, after which the 25 pound charge is ignited at a temperature of 1,000° C. An exothermic reaction ensues and is allowed to run to completion, after which the charge is cooled to ambient temperature.

The resulting product has a surface area less than 0.001 square meter per gram and a water leachability with respect to the cesium^{137} of about 0.01 percent per year at 100° C. and about 0.0001 percent per year at 25° C.

EXAMPLE 6

Illustrating critical matrix compositions and preheating

To a 7 pound matrix mixture comprising silicon and ferric oxide in a weight ratio of about 1:6 and having an average particle size of about 0.15 mm. is added an aqueous radioactive waste solution containing aluminum nitrate, nitric acid, sodium nitrate in a mole ratio of 2:0.5:0.5:2 and traces of cesium^{137}, ruthenium and strontium^{90}, each in a concentration of 7×10^{-6} microcuries. The mixture, after being uniformly admixed is dried at a temperature of 110° C., and then preheated at 600° C. to convert the nitrates of the mixture to their corresponding oxides. The weight ratio of aluminum oxide to silicon is about 1:2. The preheated mixture is then sealed in its porcelain container and heated to its ignition temperature at about 1,000° C., whereupon a chemical reaction takes place between the oxides in the mixture and the elemental reactants. The reaction is allowed to run to completion and to cool at a slow and normal rate to ambient temperature. The resulting product is a highly fused crystalline mass wherein the radioactive components are chemically combined with the oxides of aluminum and iron. The product displays a surface area less than 100 cm.^{2} per gram and a leachability of cesium^{137} and strontium^{90} in boiling water of less than 0.001 percent per year.

COMPARATIVE EXAMPLES 7 THROUGH 9

Illustrating the effects of matrix compositions outside of the preferred range of size

Matrices having compositions reported in Table IV are prepared by mixing the hydrated aluminum nitrate, silicon or aluminum and iron oxide in a porcelain crucible. The average particle size of each of the matrix mixtures is about .15 mm. Cesium^{137} (1.0±15 percent mc.) is added as an aqueous nitrate solution to each of the matrices. Each of the matrices includes aluminum nitrate to simulate a mixture corresponding to a radioactive waste. Each of the impregnated mixtures is heated in air at from 100° C. to 150° C. to remove moisture and at 300° C. to convert the oxides of nitrogen to the corresponding oxide materials. The mixtures are then heated to 900° C. whereupon an exothermic reaction occurs and the self-sustaining reaction is initiated. Heating is then discontinued and the reactions allowed to run to completion. One of the mixtures, sample 8, is capped with a layer of unimpregnated matrix material prior to ignition at 900° C.

After the reactions are completed, each of the solid masses is allowed to cool to room temperature and the rock-like products which have a surface area of 1.6±0.5 square meters per gram are ground to a powder and transferred to a glass beaker containing 100 ml. of water. The solids in each of the products or samples are extracted with boiling water for 1 hour after which the water is decanted through a filter and a second extraction is made in which the solids are heated with 100 ml. of water for 16 hours at 75° C. and then at 100° C. for 1 hour. The results of the second extraction are reported for each sample in the following Table IV. The products of these samples (Examples 7 through 9), are crystalline and contain the cesium in a chemically combined cesium oxide complex. However, the products of Examples 7 through 9 are not highly fused and possess a higher surface area than the products of samples 1, 3 and 5 of Examples 1, 2 and 3 and the products of Examples 5 and 6 above, therefore, the leachability of Examples 7 through 9 is much greater than that shown by the improved products of the present invention.

TABLE IV

Example No.	Composition, g.				Surface Area, meter^2/gram	Percent Cesium Leached per year at 100° C.
	$Al(NO_3)_3$-$9H_2O$	Si	Fe_2O_3	Al		
7	3	1	1	0	1.6	>20
8	3	2	2	0	1.6	>20
9	3	0	1	1	1.6	>20

The above examples are presented for the purpose of illustration and, therefore, should not limit the scope of the scope of the invention, as it will be apparent to those skilled in the art that many modifications and changes can be made in the above examples which result in equally valuable products. For example, a matrix mixture having a composition within the critical proportions defined above, can be dried and preheated and then mixed with a dry pre-calcined radioactive waste mixture without additional wetting before fixation. It should also be understood that matrix mixtures consisting of iron oxide, silicon and aluminum or iron oxide and aluminum or iron oxide, silicon oxide and aluminum can be substituted for any of the matrix mixtures in the above examples in mole ratios consistent with the critical limits set forth above to provide similarly improved products having a surface area below 0.01 square meter per gram and a water leach rate of 1×10^{-5} grams per square cm. per year or less. Also the iron oxide in the matrix can be in the form of pure ferric oxide or as an iron ore such as magnetite and matrix mixtures containing a metal oxide additive such as a calcium, magnesium, titanium, barium, strontium or zirconium oxide in an amount most preferably about 1 percent of the total mixture can be substituted in any of the above examples.

Many other modifications and variations in the technique set forth above will become apparent to those skilled in the art and are considered to be well within the scope of this invention.

Having thus described our invention, we claim:

1. The process which comprises: forming a mixture of iron oxide and an element in its elemental state selected from the group consisting of silicon and aluminum and mixtures thereof wherein the iron oxide is in at least a 2.5:1 weight ratio with the elemental portion of the mixture; preheating the mixture to a temperature below ignition and reacting a radioactive element with the heated mixture by igniting the mixture in the presence of said radioactive element to produce a crystalline mass having a surface area less than 0.01 square meter per gram wherein the radioactive element is chemically combined within the mixture.

2. The product of the process of claim **1**.

3. The process which comprises: forming a mixture of iron oxide and an element in its elemental state selected from the group consisting of silicon and aluminum and mixtures thereof wherein the iron oxide is in at least a 2.5:1 weight ratio with the elemental portion of the mixture; preheating the mixture to a temperature of between about 400° C. and about 800° C., but below the ignition temperature of the mixture; and reacting a radioactive mixture with the preheated non-radioactive mixture by thermally initiating exothermic reaction in the combined mixture to produce a crystalline mass having a surface area less than 0.01 square meter per gram wherein the radioactive mixture is chemically combined with the non-radioactive mixture in a crystalline product.

4. The process of claim **3** wherein the iron oxide and elemental components are compacted by moistening with an inert liquid prior to preheating at a temperature between 400° C. and about 800° C. at which temperature the liquid is evaporated from the solid mixture.

5. The process of claim **3** wherein the radioactive mixture is a radioactive waste solution containing cesium^{137}, strontium^{90} and aluminum nitrate.

6. The process which comprises: forming a mixture of iron oxide and an element in its elemental state selected from the group consisting of silicon and aluminum and mixtures thereof, wherein iron oxide is in at least a 2.5:1 weight ratio with the elemental portion of the mixture; introducing a radioactive mixture, containing compounds selected from the group consisting of metal oxides and compounds decomposable to metal oxides, to the mixture of iron oxide and elemental material in an amount such that the metal oxide in the radioactive mixture does not exceed a 1:1 weight ratio with the elemental material; preheating the resulting mixture to a temperature of between about 400° C. and about 800° C. below ignition; igniting the resulting mixture to initiate a self-sustaining chemical reaction between the radioactive components and iron oxide and elemental material to produce a crystalline mass having a surface area less than 0.01 square meter per gram wherein the radioactive components are chemically combined.

7. The process which comprises: forming a non-radioactive mixture of iron oxide and an element in its elemental state selected from the group consisting of silicon and aluminum and mixtures thereof wherein the iron oxide is in at least a 4:1 weight ratio with the elemental portion of the mixture; introducing a radioactive mixture, containing compounds selected from the group consisting of metal oxides and compounds thermally decomposable to metal oxides, to the non-radioactive mixture in an amount such that the metal oxide of the radioactive mixture does not exceed a 1:1 weight ratio with the element of the non-radioactive mixture; preheating

the resulting mixture to a temperature of between about 400° C. and about 800° C. below ignition in a refractory container; adding a metal ignitor to the surface of the resulting mixture and sealing the container; igniting the resulting mixture to chemically react the radioactive mixture with the non-radioactive mixture to produce a highly fused crystalline mass having a surface area less than 0.01 square meter per gram, wherein the radioactive components are chemically combined.

8. The process of claim **7** wherein the ignitor comprises a dry, particulate mixture of aluminum with an excess of ferric oxide.

9. The process of claim **7** wherein the ignitor is an iron oxide wire wrapped with a magnesium ribbon.

10. The process of claim **7** wherein the container is sealed with a layer of the non-radioactive mixture.

11. The process which comprises: forming a mixture of iron oxide and silicon wherein the iron oxide portion of the mixture is in at least a 4:1 weight ratio with silicon; adding a radioactive waste solution comprising a mixture of nitrates; calcining the resulting mixture at a temperature of between about 400° C. and about 800° C. below ignition for a period of at least 0.5 hour; sealing the calcined material in a refractory container by covering the mixture with a dry, granular layer of iron oxide and silicon; and igniting the mixture in the container to initiate a self-sustaining chemical reaction between the elements and oxides therein to produce a highly fused crystalline mass having a surface area less than 0.01 square meter per gram.

12. The process of claim **11** wherein the ignition temperature is between about 700° C. and about 1300° C.

13. The process which comprises: forming a mixture of iron oxide and silicon wherein the iron oxide portion of the mixture is in at least a 4:1 weight ratio with silicon; adding a radioactive waste solution comprising a mixture of nitrates to form a slurry with the iron oxide-silicon mixture; drying the mixture and converting nitrates to the corresponding oxides; preheating the resulting dried mixture at a temperature of between 400° C. and about 800° C. below ignition for a period of at least 0.5 hour to put heat energy into the resulting compact solid mass; sealing the resulting radioactive compact mass in a refractory container with an outer layer of the iron oxide-silicon mixture; and igniting the resulting mixture to initiate a self-sustaining chemical reaction between the elements and oxides of the mixture to produce a highly fused crystalline mass having a surface area less than 0.01 square meter per gram wherein the radioactive components are chemically combined.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,303,140 February 7, 1967

Heinz Heinemann et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 40, for "in", second occurrence, read -- the --; line 66, for "leachabality" read -- leachability --; column 2, in TABLE I, third column, line 14 thereof, for "12.2x10" read -- 12.2×10^4 --; column 5, line 8, after "with" insert -- the --; column 6, line 27, for "in vacuo" read -- *in vacuo* --, in italics; line 47, for "deachability" read -- leachability --; columns 5 and 6, TABLE II, footnote 1, line 1 thereof, for "Glas" read -- Glass --; column 7, TABLE III, first column, line 1 thereof, for "11" read -- 1 --.

Signed and sealed this 18th day of June 1968.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents