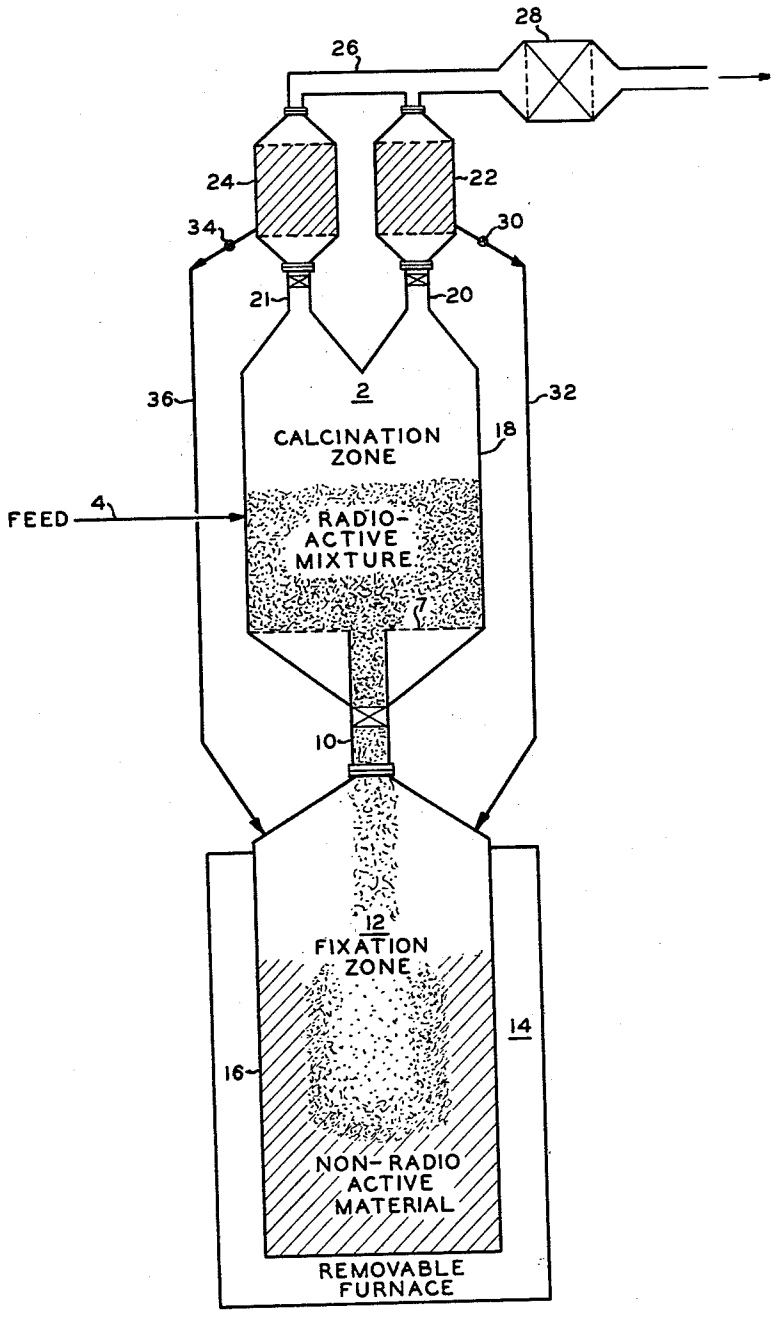
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DECONTAMINATION OF VOLATILE RADIOACTIVE EFFLUENTS

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DECONTAMINATION OF VOLATILE RADIOACTIVE EFFLUENTS

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This invention relates to the decontamination of gases and vapors containing volatile, vaporizable and/or entrained radioactive elements. In one aspect this invention relates to the decontamination of the volatile effluent in the calcination of radioactive waste materials.

This application is a continuation-in-part of my prior and copending application Serial No. 839,067, filed September 10, 1959, now U.S. Patent No. 3,110,557, issued Nov. 12, 1963.

The problem of safe disposal of waste from atomic reactors, which contains radioactive components having relatively long half-lives, is periodically increasing. Certain methods for trapping these radioactive components in insoluble matrices prior to ultimate storage or disposal have been suggested and some of these methods have proven highly satisfactory. In all of these processes, however, the major portion of radioactive material to be incorporated into the insoluble matrices must be present in the form of oxides. Since the components of the radioactive waste obtained from the full reprocessing system are in the form of nitrates and since a large amount of nitric acid and water is also present in the radioactive mixture, the waste must be pretreated before fixation to drive off water and oxides of nitrogen and to decompose the nitrates to the corresponding oxides. The pretreatment is accomplished by thermal decomposition; thus the waste mixture, which is a heat generating mixture, may be allowed to stand until the decomposition is obtained or the waste can be heated from an external source to hasten the decomposition of nitrates. This stage of the process is generally referred to as the calcination stage.

Troublesome features of the calcination is the volatilization of cesium and ruthenium which are abundant fission products in the waste mixture and entrainment of solids. Both of these elements are volatile in the upper temperature range at which calcination occurs. The volatile form of ruthenium is the tetroxide state. While normally ruthenium tetroxide is unstable at high temperatures, decomposing to insoluble ruthenium dioxide and oxygen, the oxides of nitrogen in the radioactive mixture serve to maintain the higher oxidation state of the ruthenium and thus the volatilization of this radioactive component accompanies the calcination. For this reason, prior practice in calcining radioactive wastes has been a difficult problem requiring expensive equipment operated by remote control and extensive shielding to protect the area in which the calcination is performed.

Thus, it is an object of the present invention to overcome the hazards and disadvantages of the prior art.

Another object of this invention is to provide a more commercially feasible method of calcining radioactive waste materials.

Another object is to provide a simplified process for converting radioactive nitrates to their corresponding oxides.

Another object is to provide a continuous process for calcining radioactive wastes.

Still another object of this invention is to provide a method for decontaminating the vaporous effluent in the treatment of radioactive waste materials, which method eliminates much of the protective equipment required in present operations.

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

According to this invention a radioactive mixture containing salts, such as nitrates, of ruthenium and other radioactive components is decomposed in a calcination zone to the corresponding oxides of these components at an elevated temperature, preferably between about 300° C. and about 600° C. or higher and the volatile material, for example, the oxide of ruthenium, water and oxides of nitrogen, which forms the vaporous effluent from the solid oxide mixture, is withdrawn and passed through a cartridge packed with a solid mixture of a metallic oxide selected from the group consisting of oxides of cobalt, chromium and iron, and an elemental metal selected from the group consisting of aluminum, boron, zirconium and silicon.[1] The volatile material is "trapped" or sorbed by the solid mixture in the cartridge and the solids are then fired to the ignition temperature to chemically incorporate the radioactive oxide in the fused mass. The firing and disposal of the solids in the cartridge can be accomplished by heating a sealed, disposable cartridge containing the sorbed radioactive components to a temperature of between about 200° C. and about 1500° C., preferably between about 500° C. and about 700° C., or by emptying the contents of the cartridge and firing the contents in a later stage of the process, namely the fixation stage hereinafter described. Alternatively, if desired, the entire cartridge can be removed and deposited in the fixation zone for firing.

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 0.9 and about 0.3 molar sodium nitrate, between about 0.003 and about 0.02 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.

[1] For the purposes of the present application, silicon is included in the group of elemental metals since, in many reactions, and the present reaction, it behaves similarly to boron, titanium and other metal.

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^{-6}.
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^{4}	>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^{4}	2×10^{4}	3	3.0	1.5×10^{-7}
U^{4}	7×10^{2}	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.

[4] 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 the waste mixture undergoing calcination; 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 present in a form of other than nitrates, e.g., sulfates, chlorides, fluorides, etc., depending upon the conditions employed in the atomic reactor and fuel reprocessing cycle.

In carrying out the present invention, the waste mixture is introduced into a calcination zone wherein the heat generated by the radioactive mixture with or without the assistance of external heating attains a temperature of between 300° C. and 600° C. and the salts of the radioactive waste are converted to the corresponding oxides. During this heating process, water and oxides of nitrogen derived from nitric acid are vaporized at a lower temperature, generally above 100° C.; and ruthenium in the form of ruthenium tetroxide is volatilized while the salts, e.g., the nitrates, of the waste mixture are subsequently decomposed to their corresponding oxides at higher temperatures, for example, above 300° C. Some of the cesium oxide may also be volatilized or entrained in the vaporous effluent from the solid mixture undergoing calcination. The vapors and any entrained solids are passed out of the calcination zone into a cartridge containing a fusible solid mixture on which the cesium oxide and/or ruthenium oxide are sorbed. The sorption is carried out at ambient temperature up to about 600° C.; although it is within the scope of this invention to cool or heat the vaporous effluent prior to or during sorption, if desired.

As hereinabove discussed, the sorption medium is a mixture of solids comprising a metal oxide selected from the group consisting of oxides of cobalt, chromium and iron, and an elemental metal selected from the group consisting of silicon, boron, zirconium and aluminum. Of these solid mixtures, the combination of iron oxide and silicon is preferred for the reason that both the iron oxide and silicon appear to have a great affinity for the ruthenium oxide. Other metals or metal oxides can be added to the sorption media when it is desirable to incorporate the properties of the additive in the sorption mixture. For example, alumina can be added to lower water leaching; elemental titanium can be added in order to lower the ignition temperature of the mixture.

The metal oxide and elemental metal in the sorption medium is present in a weight ratio of between about 1:1 and about 15:1, preferably between about 2:1 and about 7:1.

The cartridge which contains the solid sorption medium is employed to trap the radioactive effluent gases until sufficient quantities of the radioactive material have been collected. The use of the cartridge in the process, however, is discontinued before the entire cartridge is exhausted by deposition of ruthenium oxide, since by allowing total utilization of the sorption medium, the danger of radioactive materials passing through the cartridge into the atmosphere or subsequent decontamination equipment is increased, unless the process intends to include a plurality of similar cartridges employed in series. The extent of deposition of ruthenium oxide on the metal oxide-elemental metal solids can be physically observed by the presence of a black film which accumulates at the entrance and progresses toward the outlet of the cartridge; or the off-gases from the cartridge can be tested for radioactivity by well-known testing equipment such as a scintillation flow detector or a Geiger-Müller counter. Thus, the efficacy of the cartridge for extracting radioactive materials from the vaporous effluent of the calcination is determined. In any case, the cartridge or the contents thereof is discontinued from operation in the process before the ruthenium oxide or other radioactive species pass therethrough and a fresh cartridge, or a cartridge containing fresh solids, is introduced into use.

The solid mixture in the calcination zone which has undergone decomposition to the corresponding solid oxides can be removed and treated in various ways for ultimate disposal such as by ion exchange, fixation in a glass or ceramic matrix or fixation in a mineral rock composition. A preferred method for disposal of these solids entails the process described in copending application Serial No. 839,067, filed September 10, 1959, which comprises introducing the radioactive solids into a fixation zone containing a non-radioactive metal oxide and a non-radioactive elemental metal characterized by being polyvalent in the combined state and having a higher $-\Delta H_f^\circ/\#O$ than that of the metal oxide. The resulting mixture of solids is then fixed or fused at a temperature between about 200° C. and about 2800° C., the container in which the fixation is carried out is sealed and transported to a location for ultimate disposal or storage.

The cartridge removed from operation, which contains sorbed radioactive volatile materials can be separately sealed and fired at these temperatures, can be added to the mixture in the fixation zone before firing or as a further alternative, the contents of the cartridge can be introduced to the fixation zone along with the radioactive solids from the calcination zone for ultimate fixation therein. The fixation or firing of the cartridge or contents of the cartridge is preferably carried out at an ignition temperature between about 500° C. and about 700° C., since the reaction is exothermic and the heat generated after ignition is sufficient to carry the reaction forward to ultimate fixation. Thus, temperatures as high as 2800° C. can be generated in the fixation zone.

Some of the gaseous effluent from the calcination zone which is non-radioactive is permitted to pass through the cartridge and is treated in accordance with methods known in the art or, as a safety measure, a second cartridge or group of cartridges of the type employed in the present invention can be installed to collect the vapors passing through the first cartridge should there be any question of the presence of radioactive components in the vapors from the first cartridge. In this case, the secondary cartridge, or cartridges, is treated similarly to the first. The gaseous materials which pass through the primary cartridge comprise water and oxides of nitrogen and are non-radioactive, therefore, these gases can be vented to the atmosphere. As a safety factor, however, a plurality of cartridges may be employed to trap any infinitesimal amounts of radioactive carryover.

For a better understanding of the present invention, reference is now had to the accompanying drawing which illustrates a preferred embodiment of the operation adapted to continuous operation, but is not to be construed as limiting to the scope of the present invention since other modifications and variations of this design can be employed with equal facility and beneficial results.

The radioactive waste material comprising a mixture of nitrates of aluminum, sodium, mercury, ruthenium, cesium and nitric acid are passed into calcination zone **2** from feed line **4**. In the calcination zone, the feed is heated from 100° C. up to about 500° C. The radioactive mixture remains in the calcination zone for a period of from about 10 minutes to a period of one hour or longer depending upon the size of the charge. During the heating operation, the solid nitrates are converted to their corresponding oxides; the free water and oxides of nitrogen derived from nitric acid in the waste mixture are vaporized at lower temperatures and pass out of zone **2**. Ruthenium tetroxide and a minor portion of the cesium oxide which are volatilized at temperatures between about 300° C. and about 500° C., are then passed to the upper portion of the calcinator and out of zone **2**. The solid materials in the lower portion of zone **2** can be aerated, if desired, by an upwardly flowing gas such as steam, entering zone **2** under grid **7**. Alternatively, mixing or agitation in zone **2** can be achieved by carrying out the calcination in a ball mill or similar apparatus.

The decomposed solid mixture containing aluminum oxide, sodium oxide, cesium oxide, strontium oxide and small amounts of entrained ruthenium oxides is passed downwardly through conduit **10** into fixation zone **12** which contains a solid mixture of non-radioactive metal oxide and a non-radioactive elemental metal characterized by being polyvalent in the combined state and having a higher $-\Delta H_f°/\#O$ than that of the metal oxide. In zone **12** the solid radioactive material is mixed with the non-radioactive solids and the resulting mixture is chemically reacted by heating the mixture to its ignition temperature by means of removable furnace **14**, which encloses zone **12** when in use. For best results, it is recommended that the radioactive solids be distributed below the upper level of the bed of non-radioactive material. This can be accomplished by hollowing out an area of the bed or by providing a delivery conduit **10** slidably mounted to extend below the bed level during delivery of material. One modification which is beneficial as a means of mixing, entails alternately feeding radioactive solids and non-radioactive solids into the fixation zone; another embodiment involves continuous mixture of the feeds.

The fixation is generally conducted at a temperature between about 500° C. and about 1200° C. although, after ignition, the temperature generated by the system may rise as high as 2800° C. or higher. In certain instances, when the particle size of the solids is extremely small, for example, less than 400 mesh, the ignition temperature may be lowered.

During the reaction of the radioactive materials with the non-radioactive materials, the feed of radioactive materials through conduit **10** is discontinued, thus avoiding the deposition of radioactive materials on top of the fused fixation product. After fixation, the radioactive and non-radioactive metals are chemically bonded through oxygen atoms in a fused crystalline mass which has extremely low water leachability. At this point, removable furnace **14** is withdrawn and container **16**, containing the fused mass can be sealed and removed for ultimate deposition in a safe storage area. For ease in removal of the fixation container, it is recommended that the calcination container **18** is connected to fixation container **16** by a threaded conduit (**10**).

Any vaporous materials entering the lower portion of calcination zone **2** pass upwardly and are withdrawn from the top of the calcination zone together with vaporous and solid entrained effluent from zone **2** through valved conduits **20** and/or **21** connected to filter cartridges **22** and **24** respectively. For ease of operation it is suggested that one of the filter cartridges, or if more than two are employed, one of a series or one series of filter cartridges be used until the desired extent of saturation is reached at which point the cartridge or cartridges in use, or materials contained therein, are removed by closing the respective valve and a fresh cartridge or series of cartridges or sorbent material put on stream by opening the respective valve or valves. In the drawing, alternate operation of cartridges **22** and **24** is preferred.

The vapors from the calcination zone pass upwardly into the cartridge in operation and cesium oxide and ruthenium tetroxide are sorbed by the solid mixture contained therein. The deposition of ruthenium oxide is observed as a bluish-black film which collects in the lower portion of the cartridge. Before the black film reaches the top of the cartridge, the delivery valve is closed and the second cartridge (or cartridges) containing fresh sorbent material is put into use. The spent cartridges or spent material in the cartridge is disposed of and replaced by a fresh cartridge or fresh sorbent material for use after the second cartridge or series of cartridges become spent. In the calcination zone, as the temperature is increased from 100° C. to 500° C., the first vapors leaving zone **2** are water and oxides of nitrogen, which pass through the filter cartridges. Some entrained solid material may also pass upwardly in zone **2** and enter cartridge **22** and/or **24** wherein they are entrapped along with ruthenium oxide and cesium oxide which vaporizes at higher temperatures. The ruthenium oxide passing upwardly in calcination zone **2** is in the tetroxide state, being oxidized from ruthenium dioxide by the oxides of nitrogen. However, upon deposition the ruthenium tetroxide reverts to the dioxide state which is responsive for the black deposit which appears on the solid mixture of elemental metal and metal oxide. In the dioxide state the rutherinum is no longer volatile but is retained in the solid sorption medium.

The gases passing through cartridges **22** and/or **24** are removed by conduit **26** and are passed to cartridge **28** which may contain the same solid mixture as cartridges **22** and **24** or may be any ordinary filter. The gases leaving cartridge **28** are then vented to the atmosphere.

When the desired level of deposition of radioactive components has been observed in cartridge **22**, valve **20** is closed and valve **30** opened and the contaminated solid mixture in cartridge **22** is downwardly withdrawn through detachable line **32** and introduced into the upper portion of fixation zone **12** and valve **30** is closed. Fresh sorbent solids are then added to cartridge **22**. This same operation is repeated when, after cartridge **24** has approached the desired saturation limit, it is withdrawn from operation, except that valve **21** is closed and valve **34** open to permit withdrawal of contaminated solid through detachable line **36** for delivery to the upper portion of zone **12**.

It is to be understood, however, that in place of withdrawing the contaminating solids from cartridges **22** and **24**, the entire cartridge can be withdrawn and disposed of by the chemical fixation reaction carried out in zone **12** and a fresh cartridge substituted in its place.

The following example serves to illustrate the present invention and is not to be construed as unnecessarily limiting to the scope of this invention.

Example

A simulated waste mixture having the following composition was prepared: 1.7 molar aluminum nitrate, 1 molar nitric acid and 0.1 molar sodium nitrate. To this mixture of about 20 grams was added, 0.1 gram of ruthenium dioxide. Of this mixture, 0.63 gram was calcined at a temperature of from 100° C. to 475° C. and a yellowish vapor containing ruthenium tetroxide and oxides of nitrogen was volatilized. All of the vapors were passed from the calcination zone into a cartridge containing 4 parts by weight ferric oxide and 1 part by weight silicon. The cartridge was maintained at a temperature of about 400° C. The black deposit of RuO_2 began to collect and continued to collect on the solids in the cartridge until vapors ceased to form in the calcination zone. No trace of ruthenium oxide was found leaving the cartridge either during or after the use of the cartridge. The RuO_2-containing cartridge was then sealed and fired to red heat at which temperature the reaction between silicon, ferric oxide and ruthenium oxide is initiated (between about 500° C. and 700° C.). The solid fused mass was then removed from the cartridge and since ruthenium dioxide is not soluble in water, the leachability of the cartridge is substantially zero. No black deposit of ruthenium oxide was noted on the walls of the cartridge thus insuring complete chemical incorporation of ruthenium in the fused mass.

It is to be understood that any of the other metal oxides or elemental metals described herein can be substituted in the above example to provide suitable sealant mixtures and similar results.

Substantially the same experiment was repeated substituting 5 grams of silica in the filter cartridge for the 5 grams Fe_2O_3-Si mixture. However, it was noted that a considerable amount of ruthenium oxide (about 1 percent of that present in the original sample feed) was found in the off-gases from the cartridge during use. Alumina as the sorbent gives similar results to the silica sorbent.

While either the metal oxide or the elemental metal

when used as the sole sorbent retains some of the volatile radioactive material, it is not subject to chemical fixation. Unless the sealant mixture included both the elemental metal and the metal oxide reactants before firing, the radioactive materials are not chemically incorporated in the product.

The sorption of radioactive substances on an elemental metal or metal oxide media, which is not subject to fixation, is unsatisfactory for the reasons that these media possess a high surface area and, therefore, provide a more readily leachable product; and also that the media are composed of loose particles which can be readily dispersed to the atmosphere.

Having thus described my invention, I claim:

1. A process for the decontamination of a volatile radioactive effluent in the disposal of a mixture of radioactive salts, including a salt of radioactive ruthenium, which comprises: converting said mixture of salts to a mixture of oxides including ruthenium tetroxide, volatilizing ruthenium tetroxide, and sorbing the ruthenium tetroxide with a non-radioactive solid mixture of a metal oxide selected from the group consisting of oxides of cobalt, chromium and iron and an elemental metal selected from the group consisting of aluminum, boron, zirconium and silicon and reacting the non-radioactive components by heating the mixture to the temperature of ignition to incorporate the radioactive component in the product formed; the reacting mixture of non-radioactive components being in a weight ratio of between about 1:1 and about 15:1 metal oxide to elemental metal.

2. A process for the decontamination of a volatile radioactive effluent in the disposal of a mixture of radioactive salts, including a salt of radioactive ruthenium, which comprises: converting the salts in the mixture to oxides and the ruthenium salt to ruthenium tetroxide at an elevated temperature; volatilizing ruthenium tetroxide; sorbing ruthenium tetroxide with a non-radioactive solid mixture of a metal oxide selected from the group consisting of oxides of cobalt, chromium and iron and an elemental metal selected from the group consisting of aluminum, boron, zirconium and silicon; and reacting the non-radioactive components by heating the mixture to the temperature of ignition to incorporate the radioactive component in the product formed; the reacting mixture of non-radioactive components being in a ratio of between about 1:1 and about 15:1 metal oxide to elemental metal.

3. A process for the decontamination of a volatile radioactive effluent in the disposal of a mixture of radioactive salts, including a salt of radioactive ruthenium, which comprises: converting said mixture of salts to a mixture of oxides including ruthenium tetroxide, volatilizing ruthenium tetroxide; sorbing ruthenium tetroxide with a non-radioactive solid mixture of a metal oxide selected from the group consisting of oxides of cobalt, chromium and iron and an elemental metal selected from the group consisting of aluminum, boron, zirconium and silicon; and igniting the resulting solid mixture to produce a fused mass wherein ruthenium is chemically bonded to a metal of the mixture through an oxygen atom; the reacting non-radioactive solid mixture comprising the metal oxide and the elemental metal in a weight ratio of between about 1:1 and about 15:1.

4. The process of claim 3 wherein ferric oxide and silicon are a non-radioactive solid mixture.

5. A process for the decontamination of a volatile radioactive effluent containing radioactive ruthenium in the disposal of a mixture of radioactive salts which comprises: converting the salts to the corresponding solid oxides at a temperature of at least 300° C. in a calcination zone; volatilizing ruthenium tetroxide from the mixture; sorbing ruthenium tetroxide with a non-radioactive solid mixture of a metal oxide selected from the group consisting of oxides of cobalt, chromium and iron and an elemental metal selected from the group consisting of aluminum, boron, zirconium and silicon; igniting the resulting solid mixture containing ruthenium oxide, wherein the weight ratio of reacting metal oxide to elemental metal is between about 1:1 and about 15:1 to produce a solid fused mass wherein the ruthenium oxide is chemically combined in the mixture; and chemically incorporating the solid oxides from the calcination zone in a solid non-radioactive matix in a fixation zone.

6. The process of claim 5 wherein any vapors from the fixation zone are employed to aerate the bed of solids in the calcination zone.

7. The process of claim 5 wherein the calcination is carried out in an attrition zone.

8. A process for the decontamination of a volatile radioactive effluent containing radioactive ruthenium in the disposal of a nitrated radioactive waste from an atomic reactor which comprises: converting the nitrate mixture containing radioactive ruthenium nitrate to the corresponding oxides at a temperature of at least about 300° C.; volatilizing ruthenium tetroxide from the mixture; sorbing ruthenium tetroxide with a non-radioactive solid mixture of a metal oxide selected from the group consisting of oxides of cobalt, chromium and iron and an elemental metal selected from the group consisting of aluminum, boron, zirconium and silicon; and igniting the resulting solid mixture containing ruthenium oxide at a temperature between about 200° C. and about 1500° C. to produce a solid fused mass wherein, the weight ratio of reacting metal oxide to elemental metal is between about 1:1 and about 15:1, so that the ruthenium oxide is chemically combined in the mixture.

9. The process of claim 8 wherein ferric oxide and silicon are a non-radioactive solid mixture.

10. The process of claim 8 wherein ferric oxide and aluminum comprise the non-radioactive solid mixture.

11. A process for the disposal of a nitrated radioactive waste mixture containing nitrates of aluminum and ruthenium which comprises: calcining the nitrate mixture at a temperature between about 300° C. and about 600° C. to produce solid oxides of the nitrates; vaporizing ruthenium tetroxide during calcination; passing the vapor into a sorption zone containing a non-radioactive solid mixture of a metal oxide selected from the group consisting of oxides of cobalt, chromium and iron and an elemental metal selected from the group consisting of silicon, boron, zirconium and aluminum; sorbing the ruthenium oxide with the non-radioactive solid mixture; firing the resulting solid mixture at a temperature above about 200° C. to ignite the mixture wherein the weight ratio of reacting metal oxide to elemental metal is between about 1:1 and about 15:1 and to chemically combine the components of the mixture and the sorbed materials in a fused mass; and subjecting the radioactive solid oxides to chemical fixation in a solid matrix by admixing with a non-radioactive solids mixture of a metal oxide and an elemental metal which is polyvalent in the combined state and which possesses a higher $-\Delta H_f°/\#O$ than that of the metal oxide and heating to the ignition temperature of the mixture.

12. A process for the disposal of a nitrated radioactive waste mixture containing nitrates of aluminum, ruthenium and cesium which comprises: calcining the nitrate mixture at a temperature between about 300° C. and about 600° C. to produce the corresponding solid oxides of the nitrates; vaporizing ruthenium tetroxide and cesium oxide during calcination; passing the vapor into a sorption zone comprising a cartridge containing a non-radioactive solid mixture of a metal oxide selected from the group consisting of oxides of cobalt, chromium and iron and an elemental metal selected from the group consisting of silicon, boron, zirconium and aluminum in a weight ratio of between about 1:1 and 15:1 metal oxide to elemental metal; sorbing the ruthenium oxide and cesium oxide with the non-radioactive solid mixture; withdrawing and heating the cartridge to a temperature

above about 200° C. to ignite the contents and to chemically combine each of the components of the mixture and the sorbed material in a fused mass; passing the radioactive solids from the calcination zone to a fixation zone containing a non-radioactive solid fixation mixture of a metal oxide and an elemental metal which is polyvalent in the combined state and possesses a higher $-\Delta H_f°/\#O$ than that of the metal oxide; and igniting the contents of the fixation zone at a temperature in excess of 200° C. to chemically combine each of the components of the fixation zone mixture in a fused solid mass.

13. The process of claim 12 wherein the sorption cartridge and contents are introduced into the fixation zone for ignition and fixation therein.

14. A continuous process for the disposal of a nitrated radioactive waste mixture containing nitrates selected from the group consisting of aluminum, sodium, ruthenium, cesium, strontium and mixtures thereof which comprises: calcining the nitrate mixture under aerated conditions at a temperature between about 300° C. and about 600° C. to produce the corresponding solid oxides selected from the group consisting of the ruthenium, aluminum, sodium, cesium, strontium nitrates and mixtures thereof; vaporizing ruthenium tetroxide and cesium oxide during calcination; passing said vapor into a sorption zone containing a non-radioactive solid mixture of iron oxide and silicon in a weight ratio of between about 2:1 and about 7:1 iron oxide to silicon; sorbing the ruthenium oxide and cesium oxide with the solid mixture; passing the radioactive solid oxides from the calcination zone into a fixation zone containing a non-radioactive solid fixation mixture of a metal oxide and an elemental metal which is polyvalent in the combined state and possesses a higher $-\Delta H_f°/\#O$ than that of the metal oxide; introducing the sorbent mixture from the sorption zone into the fixation zone; and igniting the sorbent mixture, the radioactive solids and the non-radioactive fixation mixture at a temperature between about 500° C. and about 1200° C. to chemically combine the components in the fixation zone mixture in a fused solid mass.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,153,566 October 20, 1964

Marshall L. Spector

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.

In the grant, lines 2 and 3, and in the heading to the printed specification, lines 4 to 6, for "assignor, by mesne assignments, to Pullman Incorporated, a corporation of Delaware", each occurrence, read -- assignors to Pullman Incorporated, a corporation of Delaware --.

Signed and sealed this 7th day of June 1966.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents

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Patent No. 3,153,566 October 20, 1964

Marshall L. Spector

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.

In the grant, lines 2 and 3, and in the heading to the printed specification, lines 4 to 6, for "assignor, by mesne assignments, to Pullman Incorporated, a corporation of Delaware", each occurrence, read -- assignors to Pullman Incorporated, a corporation of Delaware --.

Signed and sealed this 7th day of June 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents