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RADIOACTIVE GAS DISPOSAL

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This invention relates to a process for the preparation of unleachable complex compounds. In another aspect this invention relates to radioactive gas disposal and more specifically to a process for the incorporation of radioactive gases in a water-unleachable crystalline solid.

The production and processing of radioactive materials has presented many problems, one of which is the ultimate disposal or storage of radioactive wastes produced as a by-product from a nuclear reactor. One of the waste disposal problems associated with reactor fuel processing is concerned with the handling of gaseous waste which has been processed for the removal of fertile and fissionable uranium.

Because of the potential hazard of these gaseous radioactive waste products, they cannot be treated in the same manner as the waste products of other industries. Because of the nature of these stable gases (the noble gases) they do not react with compounds to produce solids in which form they can be readily disposed of. Consequently, much of the gaseous waste from fuel processing plants is diluted and admixed with non-radioactive gases before being passed to the atmosphere, and in some instances, the gas is absorbed on a charcoal absorbent to prepare it for disposal.

As the demand for processing materials which produce these radioactive gases increases, more of these gaseous wastes are introduced into the atmosphere. This increasing concentration of gaseous radioactive materials in the atmosphere is not desirable and another method for storing and disposing of these gases is urgently needed.

Therefore, it is an object of this invention to provide an improved method for disposing of radioactive gases.

Another object of this invention is to provide a process for the preparation of water-unleachable attrition resistant radioactive materials.

Another object of this invention is to provide a method for the permanent and safe disposal of radioactive gases.

Another object of this invention is to eliminate the introduction of radioactive gases into the atmosphere.

Still another object of this invention is to provide a commercially feasible and simple method for the production of a water-unleachable rock containing gaseous radioactive components.

Other objects and advantages of the present invention will become apparent to those skilled in the art from the following description and disclosure.

According to the process of the present invention, a metal oxide is reacted in a sealed container with a base metal in the elemental state in the presence of a gaseous radioactive component. The elemental metal is characterized as being polyvalent in a combined state and as having a higher exothermic heat of oxide formation per oxygen atom ($-\Delta H_f^\circ/\#O$), than the monoxide of the metal oxide reactant. The reaction is initiated at a temperature usually above 200°C . and the exothermic reac-

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tion is allowed to proceed to completion after which the reactor and the contents of the reactor is allowed to cool gradually and a crystalline, water-unleachable rock-like product, containing the gaseous radioactive component in the interstices of the crystalline lattice, is formed within the container.

The metal oxides which react with the elemental metals of the present invention to produce the water-unleachable crystalline products of the reaction include the oxides of chromium, vanadium, cadmium, iron, copper, titanium, manganese, lead, tungsten, indium, gallium, bismuth, nickel, tin, cobalt, molybdenum, etc.

The preferred metal oxide reactants of the present process are those having a $-\Delta H_f^\circ/\#O$ at or below about 100 kcal./mole. These oxides include iron oxide, lead oxide, stannic oxide, titanium oxide, manganese oxide, nickel oxide, cobalt oxide, chromium oxide, copper oxide, molybdenum oxide, silver oxide and zinc oxide. Most preferred of this group are the higher oxides of iron, lead, titanium, manganese, copper and nickel.

The metal oxides of the reaction discussed above can be employed alone or in admixtures of any combination of the above-mentioned oxides such as mixtures found in haematite, magnetite, ilmenite, etc. Metal oxide compounds may be employed in the reaction which produce the reactant oxides in situ when heating the reaction mixture to the initiation temperature. Such compounds are the organic oxygen-containing salts of the above metals, for example, the oxalates and the acetates and inorganic oxygen-containing salts of these metals such as the carbonates and the nitrates.

Metal oxides which have a higher heat of monoxide formation than the monoxide of the elemental metal, may also be present in the reaction mixture with the reactant metal oxide and the elemental metal. These stable oxides, however, are incorporated in the final product since the temperatures generated by the reactants after the initiation temperature is reached, is sufficient to cause the stable oxides to react. Thus, aluminum oxide, which is inert with respect to silicon at ordinary temperatures, is incorporated into the product of the reaction between ferric oxide and silicon after initiation, since the temperatures chemically generated in this reaction, for example, up to 2500°C ., are sufficient to cause incorporation of the alumina.

Any of the metal oxides of the aforementioned preferred group can be added to a reactive system to lower the initiation temperature and to hasten the initiation, if desired. For example, when silicon is reacted with ferric oxide, the initiation temperature can be considerably lowered by adding a minor amount of CuO , although, the reaction would occur without the addition of CuO under more severe conditions.

The radioactive gases, referred to in the above description, which form a radioactive component in the mixture of the present process include the halogens and the noble gases or those gases which appear in Group 0 of the Periodic Table. Iodine, krypton and xenon are of particular importance since these gases are liberated in quantity when a fuel element in an atomic reactor is dissolved.

Some of the nuclides within the scope of this invention and which have relatively long half-lives are shown in Table I.

TABLE OF NUCLIDES I

Element	Symbol	Half-Life	Radiation Mode of Decay	Decay Subsequent Radiations
Halogens:				
Fluorine	F ¹⁸	1.87 hours	β^+	γ
Chlorine	Cl ³⁶	4×10^5 years	β^-	
Bromine	Br ⁷⁷	57 hours	K, β^+	γ
	Br ⁸²	36 hours	β^-	γ , e ⁻
	I ¹²³	13 hours	K	γ
	I ¹²⁴	4 days	K, β^+	γ
	I ¹²⁵	60 days	K, L	γ
Iodine	I ¹²⁶	13 days	K, β^- , β^+	γ
	I ¹²⁹	1.7×10^7 years	β^-	γ , e ⁻
	I ¹³¹	8.14 days	β^-	γ
	I ¹³³	22 hours	β^-	γ
Noble Gases:				
Argon	Ar ³⁷	34 days	K, L	
	Ar ³⁹	>15 years	β^-	
	Ar ⁴²	>200 days	β^-	
Krypton	Kr ⁷⁹	34 hours	K, β^+	γ
	Kr ⁸¹	2×10^5 years	K	
	Kr ⁸⁵	9.4 years	β^-	
	Xe ¹²⁷	32 days	K	γ
	Xe ^{129m}	8.0 days	IT	e ⁻
Xenon	Xe ^{131m}	12 days	IT	e ⁻
	Xe ¹³³	5.27 days	β^-	
Radon	Rn ²²²	3.83 days	α	

 α =Alpha particle. β =Beta particle.

K=K-electron capture.

L=L-electron capture.

IT=Isomeric transition.

 γ =Gamma ray.

e=Prominent internal conversion electron.

Any of the radioactive halogens or noble metal gases can be employed individually as the radioactive component in the present process. However, generally combinations of two or more of these gases are thus employed since the radioactive gaseous waste obtained from a reactor is usually a mixture of gases. This gaseous mixture may or may not contain some entrained solids which need not be removed for the successful operation of the present process.

When water is present in the gaseous radioactive mixture, the mixture is preferably heated to drive off the water before initiating the reaction between the metal oxide and the elemental metal. After drying, the elemental metal is contacted with the metal oxide in the presence of dried radioactive gas and the temperature is generally raised to initiate the reaction, whereupon heating is discontinued and the reaction proceeds to completion exothermically with the formation of a liquid product. This liquid product is allowed to undergo gradual cooling in order to produce the crystalline product of the reaction. The product of the reaction is the corresponding complex oxide in which the metal oxide reactant and the elemental metal are chemically bonded through oxygen atoms and the radioactive gas is "trapped" in the interstices of the crystalline lattice of the solid water-unleachable product. After initiation of the reaction, all of the oxides in the reaction mixture, when mixtures of metal oxides are employed, are incorporated into the crystalline, water-unleachable rock which is produced by the process of this invention.

The elemental metal hereinabove described, is preferably a metal having a $-\Delta H_f^\circ/\#O$ of a crystalline monoxide greater than 100 k cal./mole and capable of having a valence greater than two in the combined state. Examples of metals included in this preferred group are aluminum, magnesium, phosphorus, plutonium, silicon, tantalum, thorium, zirconium and vanadium; and preferred for the process of the present invention are zirconium, aluminum and silicon. Although, it is to be understood that any polyvalent base metal in the elemental state having a higher monoxide $-\Delta H_f^\circ/\#O$ k cal./mole than the monoxide of the metal oxide reactant and capable of producing a water-insoluble product, is a suitable elemental metal reactant in the present process and also that mixtures of these metals may be

employed in the present process. It is also to be understood that other metals, which are desirable to incorporate into the product of the reaction, can be added to the reaction mixture as an elemental metal to produce the corresponding complex metal product.

In certain instances, it is desirable to incorporate silica or alumina into the product produced by the process of this invention to improve its unleachable characteristics. When such is the case, silica, alumina and/or other stable metal oxides can be incorporated into the product by the exothermic reaction of an alkali or alkaline earth elemental metal, such as, for example, magnesium with a reactive metal oxide, such as, for example, Fe_3O_4 , TiO_2 , etc., to provide the thermal energy necessary for the endothermic incorporation of these generally inert metal oxides into the product.

The elemental metal which initially reacts with the metal oxide and the metal oxide reactant in the process, have a particle size not in excess of 10 mm. diameter. Preferably, the elemental metal and the metal oxide reactants, are ground to pass at least about 70 percent through a 100 mesh Tyler screen, and most preferably at least about 90 percent through a 170 mesh Tyler screen. In the present invention, it has been found that the initiation temperature varies directly with the particle size of the elemental metal and the metal oxide reactants, so that with a sufficiently clean fine powder of these reactants, e.g. below 0.005 mm. in diameter, the reaction may be initiated at room temperature ($30^\circ C. \pm 5^\circ C.$) or even below.

The particle size of the metal can be reduced by any one of a number of methods. For example, the metal can be ground to the desired size or a metal, such as silicon or aluminum, can be treated with a hydrogen halide such as hydrogen fluoride to reduce the size of the particles. It is to be understood, of course, that a combination of these procedures may also be employed, if desired.

More often, the reactions of the present invention are initiated at a temperature in excess of about $200^\circ C.$, preferably between about $700^\circ C.$ and about $1200^\circ C.$ Once the reaction is initiated, it is not necessary to continue supplying heat to the system since it goes to completion exothermically. Temperatures up to $2800^\circ C.$ or higher are generated chemically by the reaction after the reaction is initiated.

According to the process of the present invention, the reactant metal oxide and the elemental metal are mixed in a mole ratio of between about .01:1 and about 20:1, preferably between about 0.1:1 and about 5:1. When inactive metal oxides are also present in the reaction mixture, the active ingredients should not be diluted to the point where the exothermic reaction of the elemental metal and reactive metal oxide is prevented from occurring. The degree of dilution varies with the specific metal and reactive metal oxide employed. The pressure selected for a given reaction is in accordance with the particular requirements of the reaction. The reaction is preferably conducted at atmospheric pressure, reduced pressure or in vacuo and in a closed reactor.

Obviously, equipment must be used which will withstand the extreme temperature generated by the reaction. Therefore, metal, ceramic or ceramic-lined and insulated reactors, are preferred since they are readily available and relatively inexpensive. When reactors composed of steel or other materials having temperature resistance below the temperature generated by the reaction are employed, a coolant or diluent must be present in the reaction mixture to carry off excess heat. Such coolants are materials which generally do not react exothermically; for example, silicon oxide or aluminum oxide or any of the other materials known to be useful for this purpose. Thick-walled vessels are not necessary unless employing pressures substantially above atmospheric.

As previously stated, the reaction of the present invention is initiated in a sealed reactor, heating is discontinued after initiation and the exothermic reaction is allowed to run to completion. Completion of the reaction is indicated by the failure of the reactance to generate additional quantities of heat. After the reaction is complete, the reaction product in the sealed container is allowed to cool slowly. For example, the cooling operation may require several days, but more often is accomplished within a period of from about 2 hours to about 15 hours. In order to provide gradual cooling and prevent a sharp drop in temperature at the point where the transition of the product from a liquid to a solid takes place, an adjustable heating source may be employed, if desired, to further slow the cooling process. Heat may be supplied to the reactor undergoing cooling by an oven equipped with a temperature control, or the reactor can be insulated to prevent rapid cooling, if large crystals are desired. Preferably, the temperature of the reaction product is allowed to drop between about 100° C. and about 280° C. in an hour at the transition stage for better orientation and crystalline formation in the product.

In the process of the present reaction, the product produced is a crystalline water-unleachable solid which is suitable for permanent and safe disposal in the ceramic or other container in which the reactants are sealed prior to the reaction. The container and contents are then deposited for storage.

One of the advantages of the present process is that after the reaction is initiated in the sealed reactor, at a comparatively low temperature, an instantaneous release of heat, up to 2000° C. or 2800° C. is obtained, thus eliminating the escape of gaseous materials; reducing expense by avoiding the necessity of treating large gas volumes before the release into the atmosphere and employing extensive shielding equipment. All of these advantages of the present process are obtained while providing a greatly simplified procedure of improved safety.

For a better understanding of the present invention, reference is now had to the accompanying examples, which are not to be construed as unnecessarily limiting to the invention hereinabove described.

Of the following examples, Examples 1 through 3 were carried out to illustrate some of the various reaction systems which can be employed with elemental aluminum or silicon in the presence of a gaseous radioactive mixture to produce a crystalline water-unleachable solid product wherein the elemental metal and the metal oxide are chemically bonded together by oxygen atoms and the radioactive gases are confined in the interstices of the crystalline lattice of the product. In the presence of a dried radioactive gas, the procedure set forth in these examples for obtaining the crystalline product would be unchanged. The drying of the gaseous mixture can be accomplished at a temperature of about 100° C.

EXAMPLE 1

Reaction of red ferric oxide-silicon mixture

Into an open crucible was admixed 60 grams of Fe_2O_3 and 15 grams of silicon. The mixture, having an average particle size below 200 mesh (Tyler Standard Sieves), was heated to 900° C. to initiate the reaction. After about two minutes heating time, ignition occurred and a tremendous quantity of heat was generated, which was visually observed by emission of bright light. The material in the crucible was converted to a crystalline mass. The crystalline mass was analyzed for silica and iron content and was found to contain 29.3 weight percent silicon exposed as SiO_2 , and 70.5 weight percent iron expressed as FeO . The X-ray diffraction pattern of the powdered product was similar to the naturally occurring mineral fayalite, Fe_2SiO_4 . The powdered product was placed in boiling water at about 100° C. for one hour and was found to be substantially insoluble.

EXAMPLE 2

Reaction of red ferric oxide, magnesium oxide and silicon

Into an open porcelain 90 cc. crucible was admixed 45 grams of ferric oxide, 3.8 grams of magnesium oxide and 15 grams of silicon. The admixture, having an average particle size of below about 200 mesh (Tyler Standard Sieves) was heated to 900° C. to initiate the reaction between the metal oxides and the elemental metal. After about two minutes heating time, ignition occurred and the mixture generated a tremendous quantity of heat, which was visually observed by a flash of white light. The material in the porcelain crucible was converted to a rock-like mass containing a complex mixture of oxides of magnesium, iron and silicon. The powdered product after cooling was placed in boiling water for one hour and the product found to be insoluble. The X-ray diffraction pattern of the powdered reaction product was isomorphic to the mineral fayalite.

EXAMPLE 3

Reaction of aluminum-red ferric oxide mixture

One part by weight of aluminum powder was admixed with 4.45 parts by weight of Fe_2O_3 . Both reactants were finely divided powders which passed through a 200 mesh sieve. The reactants were transferred to an open porcelain crucible and after heating to 500° C. for one minute, an extremely exothermic reaction was observed to occur. The major portion of the product was a grey crystalline material. Chemical analysis of the crystalline portion of the product indicated that the aluminum content was 31.89 weight percent expressed as Al_2O_3 and the iron content was 67.8 weight percent expressed as FeO . The analysis indicated a compound having the formula $\text{Fe}_3\text{Al}_2\text{O}_6$. The powdered product was immersed in boiling water for one hour and was found to be substantially insoluble.

It is to be understood that other elemental metals may be substituted for silicon or aluminum in Examples 1 to 3, for example, zirconium or magnesium metal and these elemental metals are reacted with the metal oxides according to the procedure set forth in these examples. It is also to be understood that other metal oxides may be substituted in the above examples for ferric oxide, for example, a cobalt oxide, a chromium oxide, a copper oxide or bismuth oxide and these metal oxides reacted with the elemental metal according to the procedure set forth in Examples 1 to 3 to produce the crystalline water-unleachable products of this reaction.

EXAMPLE 4

Disposal of gaseous radioactive components

Into a porcelain lined reactor is introduced, at room temperature, ferro-ferric oxide, Fe_3O_4 , and metallic silicon in a weight ratio of 4:1. The particle size of the solid mixture is about 0.089 mm. diameter. The reactor is then closed except for a gas entry port. The following procedure is carried out by remote control behind a lead shielded wall.

The closed reactor containing the ferro-ferric oxide and metallic silicon is brought into a radioactive area wherein radioactive gases from a nuclear reactor, for example, krypton, xenon and iodine are introduced into the reactor which has been evacuated of gas, through the aforementioned entry port. The radioactive gas mixture is pressured into the lower portion of the reactor up to a pressure of about 14 p.s.i.a.

The introduction of gaseous materials is then discontinued and the entry port sealed. The temperature of the mixture is then raised to about 900° C. by means of a furnace, which is lowered to enclose the reactor. After the contents of the reactor have reached 900° C., the spontaneous chemical generation of heat causes the reaction between the iron oxide and silicon and the radioac-

tive gases are admixed with the liquid product. The reactor is allowed to cool gradually (160° C. an hour cooling) until room temperature is reached, whereupon a solid water-unleachable highly crystalline product is formed containing the radioactive gases within the interstices of the crystalline lattice.

The reactor and the contents sealed therein is then placed in a vehicle and transported to a site of ultimate storage or disposal.

It is to be understood that many modifications and alterations of the above technique may be employed without departing from the scope of this invention for example, in place of metallic silicon, any of the previously mentioned elemental metals, for example, aluminum, zirconium, magnesium, etc., may be employed as the reactant elemental metal. In like manner, an oxide of cobalt, bismuth, chromium, copper or any of the other previously described metal oxides having a lower monoxide $-\Delta H_f^\circ/\#O$ than the monoxide of the elemental metal, may be substituted for the ferro-ferric oxide employed in Example 4 to produce the highly crystalline water-insoluble product containing radioactive gases described in Example 4. It is also to be understood that any of the other radioactive gases either singly or in combination may be employed in Example 4 in place of the mixture used therein without departing from the scope of this invention.

Having thus described my invention I claim:

1. The process which comprises: reacting in the presence of a gaseous radioactive component selected from the group consisting of a radioactive halogen and a radioactive noble gas, a non-radioactive mixture of normally solid inorganic oxide of a metal, which metal is polyvalent in the oxide composition and a solid elemental metal, said elemental metal being polyvalent in the combined state and having a higher oxide $-\Delta H_f^\circ/\#O$ than that of the metal oxide by heating the reaction mixture to at least the temperature at which the exothermic reaction between the metal oxide and the elemental metal is initiated in a reaction zone and allowing the resulting complex oxide product of the reaction to cool to produce a solid chemically combined mass containing the radioactive gas.

2. The process which comprises: reacting, in the presence of a gaseous radioactive component selected from the group consisting of a radioactive halogen and a radioactive noble gas, a non-radioactive mixture of a normally solid inorganic oxide of a metal, which metal is polyvalent in the oxide composition and a solid elemental metal, said elemental metal being polyvalent in the combined state and having a higher oxide $-\Delta H_f^\circ/\#O$ than that of the metal oxide by heating the reaction mixture to at least the temperature at which the exothermic reaction between the metal oxide and the elemental metal is initiated and a liquid product is formed in a sealed reaction zone and converting the liquid product to a solid gas-impregnated product by allowing the resulting liquid product of the reaction to cool at least until the transition of the liquid product to the solid product takes place to produce a solid chemically combined mass containing the radioactive gas.

3. The process of claim 2 wherein the gaseous radioactive component comprises a noble gas.

4. The process of claim 2 wherein the gaseous radioactive component comprises a gaseous mixture of halogen and noble gases.

5. The process of claim 2 wherein the gaseous radioactive component comprises a halogen.

6. The process of claim 2 wherein the gaseous radioactive component comprises a gaseous mixture of xenon, krypton and iodine.

7. The process of claim 2 wherein the gaseous radioactive component comprises iodine.

8. The process which comprises: reacting, in the presence of a gaseous radioactive component selected from

the group consisting of a radioactive halogen and a radioactive noble gas, a non-radioactive mixture of a normally solid inorganic oxide of a metal, which metal is polyvalent in the oxide composition and a solid elemental metal, said elemental metal being polyvalent in the combined state and having a higher oxide $-\Delta H_f^\circ/\#O$ than 100 kg. cal./mole and higher than that of the metal oxide, by heating the solid reactants to a temperature in excess of about 200° C. at which the exothermic reaction between the metal oxide and the elemental metal is initiated and a liquid product is formed in a sealed reaction zone and forming a crystalline gas-impregnated product by cooling the liquid product at a rate of between 100° and 280° per hour until the transition of the liquid product to the solid crystalline product takes place to produce a crystalline chemically combined mass containing the radioactive gas.

9. The process of claim 8 wherein the elemental metal is aluminum.

10. The process of claim 8 wherein the elemental metal is silicon.

11. The process of claim 8 wherein the elemental metal is zirconium.

12. The process of claim 8 wherein the elemental metal is magnesium.

13. The process of claim 8 wherein the metal oxide is an oxide of iron containing more than one oxygen atom.

14. The process of claim 8 wherein the metal oxide is bismuth trioxide.

15. The process of claim 8 wherein the metal oxide is an oxide of cobalt.

16. The process of claim 8 wherein the metal oxide is an oxide of chromium.

17. The process of claim 8 wherein the metal oxide is an oxide of copper.

18. A process for the disposal of a radioactive gas which comprises: reacting, in the presence of a radioactive gas selected from the group consisting of a radioactive halogen and a radioactive noble gas, a non-radioactive mixture of a normally solid inorganic oxide of a metal, which metal is polyvalent in the oxide composition and a solid elemental base metal, said elemental base metal being polyvalent in a combined state and having a higher oxide $-\Delta H_f^\circ/\#O$ than 100 kg. cal./mole and higher than that of the metal oxide by heating the solid reactants having an average particle size not in excess of 10 mm. in diameter in a sealed reactor at a temperature between about 700° C. and about 1200° C. at which temperature reaction is effected and a liquid product is formed, and converting the liquid product to a crystalline gas-impregnated product by cooling the liquid at a rate of between 100° and 280° per hour until the transition of the liquid product to the solid product takes place to produce a crystalline product containing the radioactive gas.

19. The process of claim 18 wherein the mole ratio of metal oxide:elemental metal is between about 0.01:1 and about 20:1.

20. The process which comprises: reacting, in the presence of a gaseous radioactive component selected from the group consisting of a radioactive halogen and a radioactive noble gas, a non-radioactive mixture of a normally solid inorganic oxide of a metal, which metal is polyvalent in the oxide composition and a solid elemental metal, said elemental metal being polyvalent in the combined state and having a higher oxide $-\Delta H_f^\circ/\#O$ than that of the metal oxide by heating the reaction mixture to at least the temperature at which the exothermic reaction between the metal oxide and the elemental metal is initiated in a reaction zone and allowing the resulting complex oxide product of the reaction to cool to ambient temperature to produce a solid chemically combined mass containing the radioactive gas.

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