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METHOD OF SEALING REFRACTORY VESSEL CONTAINING RADIOACTIVE WASTES

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This invention relates to the fixation of radioactive materials in a solid matrix of low water leachability. In one aspect this invention relates to lowering the water leachability of a mass comprising radioactive waste solids fixed in a non-radioactive rock-like matrix of low water leachability. Another aspect of this invention concerns reducing degradation of containers wherein radioactive components are deposited. Another aspect relates to retarding loss of volatile or entrained radioactive components from a fixation matrix during the fixation process.

With the increasing use of nuclear reactors for power and production, it is becoming increasingly urgent to devise safer and more economical methods for the disposal of fission by-products or waste materials. The storage of intensely radioactive solutions in underground tanks, etc., has many disadvantages including bulk and the possible failure of the container. 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, for example, as solids, and in a condition in which the radioactive elements will not escape to ground water, atmosphere or the surrounding area. The criteria of the latter condition is determined by the water leachability rate of the disposable mass.

Many methods are currently being offered for the fixation of radioactive materials in non-radioactive solids of low water leachability, such as the incorporation of fission by-products in glass, ceramic glaze, or rock-like minerals. However, since all of these methods require high temperature for the fixation reaction of the solid reaction mixture, the lower boiling metal oxides, some of which possess a high level of radioactivity, escape from the system. These and other radioactive components may diffuse to the surface of the fixation charge, are subject to water leaching after fixation of the solid mixture is complete. Particularly troublesome in fixation mixtures are the oxides of ruthenium and cesium which volatilize readily.

Heretofore extensive scrubbing and filtering apparatus has been employed to trap the more volatile radioactive oxides leaving the fixation zone but these methods fail to remedy the problem of radioactive elements in the surface of the fixation matrix. Moreover, the solid products of all of the methods now in operation report a low, but varying degree of water leachability which, in some instances, is initially tolerable but which, over an extended period of time, may exceed safety limits due to overheating or transmutation and consequent degradation of the matrix and/or container in which the solid mass is deposited.

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

Another object of this invention is to provide a method for the disposal of radioactive materials in a less soluble package which is also resistant to erosion and degradation.

Another object of this invention is to provide a commercially feasible method for the disposal of concentrated radioactive waste mixtures in a rock-like matrix treated to provide a water leachability rate lower than any heretofore obtained.

Another object is to provide a simplified process for the ultimate disposal of a mixture of solid radioactive

oxides in a container resistant to degradation, water leaching, corrosion, and warping.

Another object is to retard volatility of radioactive components during the fixation process.

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

According to the process of this invention, a mixture in a fixation zone comprising radioactive components and a non-radioactive solid for effecting the fixation of the radioactive component is sealed with a sealant comprising a solid, non-radioactive mixture of a metal oxide and an elemental metal and the sealant is fired to its ignition temperature to provide a fused, rock-like covering over the fixation mass. The fixation mass can be deposited in a crucible or container and the sealant affixed over the outer surface of the container, or the fixation mass can be directly coated with the sealant. When directly coating the fixation or impregnated mass, at least the mouth of the container through which the impregnated mass is fed, is completely covered over with non-radioactive sealant. Alternatively, the entire outer surface of the fixation mass can be directly coated, if desired.

The selection of the metal oxide and elemental metal components of the sealant is such that the product of ignition is highly insoluble in water, preferably having a water leachability at 100° C. less than 1×10^{-4} g./sq. cm./yr.; and is not detrimentally affected by the temperature generated by the radioactive material in the fixation mass. A preferred sealant mixture having the above properties is a mixture of ferric oxide and silicon,* although other metal oxides such as the oxides of chromium and cobalt, in combination with zirconium, boron, silicon or aluminum are also suitable as sealant mixtures. The sealant composition is preferably at a weight ratio between about 2:1 and about 7:1, although mixtures between about 1:1 and about 15:1 metal oxide:elemental metal can also be satisfactorily applied. If desired, additional metal oxides, e.g., boria or alumina, can be added in order to produce a more insoluble product and titanium can be added to lower the ignition temperature.

The sealant should be applied in such thickness that the coating after fixation remains substantially unimpregnated with radioactive components at least at its outer surface. For example, a fired 10 inch coating on the fixation mass and over the mouth of a crucible containing a fixed five pound sample containing 1 millicurie/gram of cesium 137 and 1 millicurie/gram of strontium 90 mixture lowers the water leachability at 100° C. to approximately zero while an identical uncoated sample exhibits a leach rate of 1×10^{-5} g. of the fixed mass/sq. cm./yr.

The sealant material may be introduced over the fixation mixture of radioactive and non-radioactive solids either before or after reaction of the fixation mixture and thus is subjected to firing and ignition either simultaneously or after the fixation of the radioactive impregnated mixture. In cases where the sealant and fixation mixtures are reacted concurrently, the sealant mixture serves to retard volatilization and entrainment losses during fixation. When the non-radioactive sealant is applied only over the top of the fixation mass at the open end of the container in which the radioactive fixation mixture is deposited, the technique is referred to as "capping" the radioactive mix. Preferably the sealant is applied over the entire outer surface of a sealed container in which the radioactive mix is deposited, to provide not only the lowering of the water leachability rate of the sample, but also to provide a barrier against erosion and decomposition of

* 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 metals.

the container. This technique is referred to as "potting" and preferably involves embedding or submerging the entire container in the sealant. However, the sealant material can be applied to the surface of the container in the form of a paste or the container can be submerged in an outer container containing sealant to present a unit package for disposal, if so desired.

The sealant mixture after application is heated to ignition temperature to react and chemically combine the metal oxide and elemental metal and to provide a fused, impervious coating for the surface on which it is deposited. Preferred ignition temperatures vary between about 500° C. and about 700° C. depending upon the particle size of the solids in the mixture. Generally, the solid particles are between about 200 mesh and about 400 mesh in size, although larger or smaller particles may be used. At a particle size of less than 400 mesh, the ignition temperature required to react the solid components is greatly reduced.

The radioactive mix or fixation mixture can be any one of a number of mixtures prescribed for fixation of radioactive solids. For example, a common fixation medium presently being employed comprises a glass-like composition of silica, alumina, and oxides of sodium, potassium, calcium, iron, magnesium and titanium. A preferred glass matrix commonly used is nepheline syenite and calcium oxide, although, it is to be understood that simulated mixtures which contain additive metal oxides and which may or may not contain all of the oxides in the above-mentioned glass can also be employed. Another fixation medium, which has been found useful, is a porcelain glaze comprising alumina, silica and calcium oxide fluxed with boria to provide a product incorporating the radioactive compound in a Al_2O_3-CaO-SiO_2-B_2O_3 ceramic glaze product. Impregnation of radioactive components in micas such as sodium and potassium fluorophlogopite are also used as fixation media as well as ion exchange mixtures which involve reaction between the radioactive oxides and metal oxides in a clay such as montmorillonite or fuller's earth, etc.

A preferred fixation medium comprises a non-radioactive mixture of a metal oxide and an elemental metal characterized as being polyvalent in the combined state and having a higher $-\Delta H_f°/\#0$ than that of the metal oxide. One of the reasons this system is preferred is that the reaction is exothermic thus greatly reducing the external heat requirements, compared with the other systems mentioned above, to carry the reaction to completion. Another advantage is that the higher temperature generated in this particular mix permits metal oxides added to enhance certain properties in the product, to undergo chemical reaction even though they are not initially reactive in the system. Hence, tailor-made matrices for the radioactive components are provided by this method.

The ignition temperature employed for the preferred metal oxide-elemental metal fixation media can be as low as 200° C. or lower, but is preferably between about 500° C. and about 1200° C., although after ignition the heat generated in the system may rise as high as about 2800° C. In the other systems mentioned above, sufficient external heat must be supplied to raise the temperature to between 1300° C. and about 1500° C. or higher and, to maintain the temperature at this level during the course of the endothermic reaction. For a better understanding of the preferred fixation media and the components present in the radioactive mixtures presented for disposal, reference should be made to the copending application Serial No. 839,067, now Patent 3,110,557, filed September 10, 1959.

Heretofore, in carrying out the fixation process, radioactive materials were introduced into a container or crucible wherein they are contacted or mixed with a fixation medium such as those discussed above. The resulting mixture was heated to react the components and the container or crucible removed for ultimate disposal or storage. In carrying out the present invention, the radioactive waste materials are introduced into the fixation medium in a container. In one embodiment, the fixation charge is reacted as explained above to produce a solid, preferably uniform, chemically combined mass of solids and a sealant mixture of the type discussed above is then used to "cap" or in addition to "capping," coating the entire fixation container as in "potting." The sealant then can be separately fired to ignition in order to react the metal oxide with the elemental metal of the coating and provide a fused, rock-like, substantially water-unleachable covering over the mouth and/or entire outer surface of the fixation container. Thus the container is prepared as a unit for ultimate disposal having a remarkedly reduced water leachability rate and increased resistance to erosion and decomposition.

Another embodiment of the present process involves introducing the radioactive components into the fixation medium and, after the desired fixation charge has been added to a container, capping and/or potting the container and then firing the fixation mixture and the sealant simultaneously with the aid of an ignitor, removable furnace, or any other convenient heating means at the temperature necessary to ignite the sealant. This technique is particularly beneficial with an endothermic fixation media which normally require temperatures above 1300° C. to induce chemical reaction. By the process of this embodiment, the sealant can be ignited at a relatively low temperature (e.g., 500° C.) and the heating discontinued after ignition for the heat generated in the sealant mixture, e.g., up to about 2500° C. or higher, is sufficient to react any of the proposed endothermic fixation media. Thus the sealant mixture around the crucible or bomb containing the fixation charge serves as an automatic furnace to react the solid components contained therein endothermically with a smaller input of external heat.

In the potting technique, the container can be immersed in a solid sealant mixture or the sealant mixture can be moistened to paste-like consistency with water or a volatile material such as alcohol, acetone, chloroform, etc., and the paste applied to the outer surface of the container in which the radioactive materials are deposited. This latter method is also suitable for capping the fixation mixture and sealing the container. An alternative method for capping involves merely adding the sealant mixture through the entrance port of the container over the fixation mixture deposited therein and allowing the sealant mixture to reach the level of the entrance port.

It is found that the sealant material forms a strong bond with the surface on which it is deposited and that, after ignition, the coating is resistant to stress cracking due to pressures up to 1000 p.s.i.g. The coating is also resistant to corrosion by acids such as hydrochloric acid. In the case of capping, the concentration, and thus the water leachability, of the radioactive species on the surface of the disposable mass has been reduced to essentially zero as compared with uncapped samples, which have radioactive species on the surface and which dissolve along with the matrix at a rate 1×10^{-4} grams of matrix per square centimeter per year.

The following example is presented for a better understanding of the invention and is not to be construed as unnecesarily limiting to the scope thereof.

Example illustrating the effect of sealing

The following experiments were carried out for comparison between a fixed, unsealed radioactive product and a fixed, sealed radioactive product of the same composition.

A 116 gram mixture having the following composition: 1 part silicon, 4 parts ferric oxide and 0.4 part alumina was prepared and introduced into two porcelain crucibles. The first crucible contained 5 grams of the mixture impregnated with 1 millicurie of Cs^{137}. This impregnated mixture was sealed and capped with 50 grams of the un-

impregnated mixture having the above composition. The second crucible contained 58 grams of the above mixture (1 part silicon, 4 parts ferric oxide and 0.4 part alumina) and 1 millicurie of Cs^{137} was mixed uniformly with the 58 gram sample.

Both of the crucibles were covered with a fine wire gauze and ignited at a temperature of about 600° C. for fixation of the samples. After the fixation was complete, the crucibles were allowed to cool to ambient temperature and the gauze from each of the crucibles was removed and examined for radioactivity. In the case of the first sealed crucible, no radioactivity was detected on the gauze with a Geiger-Muller counter; however, 37 percent of the total Cs^{137} was found on the gauze from the second unsealed crucible.

The contents of both crucibles were also separately examined for water leachability by boiling in water for one hour. The leach water from the first sealed crucible contained 4×10^{-3} microcuries of Cs^{137}; whereas the leach water from the second unsealed crucible contained 1.3 microcuries of Cs^{137}.

It is to be understood that the leachabilities reported are initial leachabilities which are considerably higher than steady state leachability rates due to surface contamination and traces of the total radioactive material that were not incorporated into the reaction.

The steady state leach rates for both samples is less than 1×10^{-4} grams/cm.^{2}/year.

Example illustrating the effect of potting

Two empty refractory lined stainless steel containers of about 100 ml. capacity, suitable for containing radioactive fixation mixtures are covered with a tight fitting lid and placed in a larger container of refractory lined stainless steel containing a 4:1:0.4 weight mixture of iron oxide:silicon:alumina. The free space between the two containers is completely packed with the sealant mixture and a portable furnace is lowered over the outer container to supply heat to the sealant. The sealant was uniformly heated to a temperature of about 600° C. to react the the iron oxide with silicon. The furnace is then removed and, after the reaction was complete, the outer container was allowed to cool to ambient temperature. Thus, the inner containers adaptable to contain the fixation mixture, are doubly protected by the outside stainless steel container and by the fused sealant mass.

The above procedure is repeated except that the inner container adapted for containing the fixation charge is glass and contains a fixation charge comprising nepheline syenite and calcium oxide, non-radioactive cesium, in an amount of about 1 percent and non-radioactive strontium in an amount of about 1 percent. After ignition of the sealant at about 500° C. and completion of the sealant fixation reaction, the outer steel container is allowed to cool to ambient temperature. The fused inner glass container is completely surrounded by a protective coating and at the temperature generated by the sealant during fixation, the solid cesium and strontium oxides are chemically reacted with the nepheline syenite in a fused mass. The concentration of cesium and strontium at the surface of the outer coating is zero, thus providing a low leachability rate of cesium and strontium. The sealant provides an outer wall which was resistant to pressure as high as 1000 p.s.i.g., showing no signs of rupture or cracking, and is resistant to corrosion by acids such as hydrochloric acid.

Having thus described our invention, we claim:

1. A method for sealing a refractory vessel containing a solid fixation mixture of a radioactive component and non-radioactive fixation components which mixture has been fed through an entrance port of the vessel which comprises: sealing the entrance port of the vessel, submerging the sealed vessel in a sealant mixture contained in a second larger container, said sealant mixture containing a metal oxide selected from the group consisting of oxides of chromium, cobalt and iron and an elemental metal selected from the group consisting of aluminum, boron, zirconium and silicon, applying heat to the outer surface or the second container to raise the sealant mixture to its ignition temperature and allowing the heat generated by the sealant mixture to chemically react said solid fixation mixture, to chemically react the sealant mixture and to provide a protective barrier around said vessel which is resistant to corrosion, erosion and degradation.

2. A method for sealing a refractory vessel containing a solid fixation mixture comprising a radioactive component and a non-radioactive fixant which comprises: applying a non-radioactive sealant mixture of a metal oxide selected from the group consisting of oxides of chromium, cobalt and iron and an element selected from the group consisting of aluminum, boron, zirconium and silicon in a weight ratio of between about 1:1 and about 15:1 over the entire outer surface of the vessel and heating the sealant mixture to its ignition temperature to provide a seal around said vessel which is resistant to erosion and thermal degradation.

3. The process of claim **2** wherein the solid fixation mixture is heated and reacted simultaneously with the sealant mixture.

4. The process of claim **2** wherein the solid fixation mixture is thermally reacted before the sealant mixture is heated to its ignition temperature.

5. A method for sealing a refractory vessel containing a radioactive component and non-radioactive components as a fixation medium which has been fed through an entrance port of the vessel which comprises: coating the inner walls of said vessel with a sealant mixture containing a metal oxide selected from the group consisting of oxides of chromium, cobalt and iron and an elemental metal selected from the group consisting of aluminum, boron, zirconium and silicon prior to the introduction of the solid fixation mixture; introducing the fixation mixture into the vessel; introducing an additional quantity of sealant mixture after the introduction of solid fixation mixture to the vessel over the surface of the fixation mixture which is immediately adjacent the entrance port to form a seal over said entrance port and igniting the contents of the sealed vessel at a temperature between about 500° C. and about 700° C. to form a protective shell around the radioactive charge within the vessel.

6. The process of claim **5** wherein the sealant mixture contains iron oxide and silicon in about a 4:1 weight ratio.

References Cited by the Examiner

UNITED STATES PATENTS

1,531,839	3/25	Booraem	117—133
2,713,787	7/55	Rose	117—123
2,918,717	12/59	Struxness et al.	252—301.1
2,961,399	11/60	Alberte	252—301.1
3,000,072	9/61	Evans	252—301.1
3,050,409	8/62	Bayer	117—123

OTHER REFERENCES

AEC Document TID 7613, Book I, pp. 27, 34–39, 127, 243, 270, 271; book II, pp. 462, 514–534, 586. "Fixation of Radioactivity in Stable Solid Media"; meeting held at Idaho Falls, Idaho, Sept. 27–29, 1960.

First International Conference on Peaceful Uses of Atomic Energy, vol 9, page 689, August, 1955.

Second International Conference on Peaceful Uses of Atomic Energy, vol. 18, pages 19, 22, 24, 27–36, September 1958.

Reactor Fuel Processing, vol. 4, No. 3, July 1961, pages 53, 56 which reports bibliographic reference 17, Canadian Report CRDC–855 (AECL–1071) July 1960.

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