United States Patent Office 3,161,601
Patented Dec. 15, 1964

3,161,601

RADIOACTIVE CESIUM CONTAINMENT

Gerald B. Barton, Kennewick, Wash., assignor to the United States of America as represented by the United States Atomic Energy Commission

No Drawing. Filed Dec. 18, 1962, Ser. No. 245,950
5 Claims. (Cl. 252—301.1)

The invention relates to a novel composition and method of containing radioactive cesium, more particularly to its containment within a nonflammable, highly insoluble material from which it may later be readily extracted, thereby making it suitable for ordinary shipping operations.

Cesium-137 has many useful applications in industrial, medical, and food-processing irradiations; in leak testing, and thickness; and as a heat source for thermoelectric devices. However, it is highly dangerous and care must be taken to prevent even trace amounts from escaping since these can create a public health hazard. Mechanical containers have inherent risks of failure no matter how carefully made, and for this reason it is known to encapsulate radioactive cesium in organic plastics, or inorganic materials such as metals, cement or glass. Inorganic materials have the advantages of being nonflammable and resistant to the solvent action of water and organic liquids, so that accidental wetting by either of these constitutes no great hazard. These materials are disadvantageous in that once the radioactive material is placed within them it is difficult to extract it. Any such extraction requires that the cement or glass be finely ground or otherwise comminuted, and this creates a problem of radioactive dust which militates against the use of inorganic materials for encapsulating cesium-137 in ordinary shipping operations where the consignee normally needs to have the radioactive material in a soluble form before he can process it further.

It is the general object of the invention to provide a method of containing cesium in a nonflammable, highly insoluble material.

It is, accordingly, a more particular object of the invention to provide a method of containing radioactive cesium within a nonflammable, highly insoluble material from which it may be readily extracted.

It is a more particular object to provide a method of handling cesium-137 in ordinary shipping operations, so as to avoid the hazards due to accidental wetting by water or organic liquids and those of radioactive dust resulting from comminution.

The above objects are attained by my discovery that the addition of a member of the class consisting of lanthanum in the plus 3 oxidation state and zirconium in the plus 4 oxidation state to an alumina-phosphate glass incorporating about forty-five percent cesium, causes the glass to be only very slightly soluble in water. I have further discovered that, unlike other additives that suppress water solubility such as Zr^{+4}, La^{+3} still permits the glass to be dissolved in acids. Theoretical explanations have been advanced to explain this unique effect of La^{+3} when used as an additive in the way referred to, but since these have not been proved it would serve no purpose to set them forth, and my invention is offered on an empirical basis as established by experiments, some of which will now be described.

A number of Cs_2O alumina-phosphate glasses were made up from appropriate precursor materials in varying proportions. To some of these were added precursors to the oxides of silicon, zirconium, and lanthanum. The glasses were cast, without annealing, into small buttons of approximately 6.9 grams and their solubility in boiling water was determined by weighing them and immersing them separately in 200 ml. of boiling water four hours,

and observing their behavior meanwhile visually. Some of the buttons without any of the silicon, zirconium, or lanthanum oxide additives dissolved completely during the four hour period; the others, including those containing the additives, were withdrawn at the ends of the period, dried and weighed. From the weight loss so recorded for the individual buttons their solubilities in percentages were determined.

The buttons having a solubility in boiling water of less than one percent were then placed separately in 200 ml. of boiling 7.9 aqueous nitric acid for four hours, and their behavior meanwhile was observed visually. The results of these experiments are set forth below in Table I in which the first six horizontal lines contain the weight percentages of the constituents of the glasses tested, and the bottom two lines their respective solubilities, all data as to the individual glasses being in the same vertical column.

TABLE I

[Weight Percent (w/o)]

Cs_2O	62.5	61.4	54.3	53.7	45.2	42.5
Al_2O_3	11.3	11.1	15.3	15.0	12.7	12.0
P_2O_5	26.3	27.6	30.4	30.1	30.4	30.2
SiO_2				1.2		
La_2O_3					11.6	
ZrO_2						15.4
Solubility in boiling water, percent	(disintegrated completely)		21	22	0.65	0.60
Solubility in 7.9 N HNO_3					Almost complete	Slight

From the foregoing it is apparent that lanthanum in the plus three state and zirconium in the plus four state both have the property of supressing water solubility in glasses of the cesium oxide-alumina-phosphate type. Both these would therefore make such glass satisfactory containers for radioactive cesium in such application as for heat sources in thermoelectric generators, beta sources for thickness testers and the like.

It is also apparent from the above table that lanthanum in the plus three state as La_2O_3 has the unique property of suppressing water solubility in glasses of the cesium oxide-alumina-phosphate type, and at the same time of permitting dissolution in aqueous nitric acid. This is in contrast to zirconium dioxide which lacks this selective type of suppression, and suppresses solubility of the glass to which it is added in both cases.

It is further apparent that the selective action of La^{+3} in suppressing water solubility while permitting acid dissolution provides an efficient method of containing radioactive cesium, and of handling it in ordinary shipping operations. The glass composition permits the incorporation of a large amount of cesium, the equivalent of about 45 w/o Cs_2O. While so incorporated, the cesium is held with a greater degree of physical dependability than any mechanical container can attain, and it is at the same time highly resistant to leaching, should it accidentally come into contact with water. Should it accidentally come into contact with organic liquids such as gasoline, chlorinated solvents and the like, it would, of course, be entirely unaffected since the composition is a true glass. Yet when the glass reaches the consignee in a shipping operation, the consignee may easily extract the cesium from the glass simply by dissolving it in strong acid such as nitric acid, without any grinding or other dangerous comminuting operation. This permits the consignee to proceed to process the cesium in any manner he wishes, in contrast to ordinary glass compositions in which the cesium is extractible only with great difficulty.

In carrying out our invention it would, of course, be possible simply to mix the ingredients in the oxide form of the final composition and melt them together. However, this is less convenient than to blend stoichiometric

amounts of materials which are precursors to the oxides such as chlorides, nitrates, hydroxides and the like. Some of these are water-soluble and hence permit a thorough blending, and others, such as colloidal silica sol, which is predominately silicic acid, may be suspended more completely than can pure silica. Our preferred precursors are CsCl for Cs_2O, $Al(NO_3)_3 \cdot 9H_2O$ for Al_2O_3, H_3PO_4 for P_2O_5, Ludox colloidal silica sol for SiO_2, $La(NO_3)_3$ for La_2O_3, and $ZrO(NO_3)_2.XH_2O$ for ZrO_2, X being an indefinite number. These are oxidized to the corresponding oxides in the glass melt if access of air is permitted. All are water-soluble with the exception of the colloidal silica sol; the latter may therefore be suspended in a solution of the water-soluble precursors, solubility of the latter preferably being increased by acidifying the solution. The resulting suspension is evaporated to dryness. Since some segregation may occur during the evaporation the resulting solids are preferably finely ground and blended and then put into a melting vessel such as a platinum crucible. The pouring temperature of the glasses in question is from 1200° to 1375° C.

While my experiments were carried out with ordinary cesium, my invention contemplates a glass containing radioactive cesium, or $Cs_2^{137}O$. Ordinarily it is not necessary that the glass be annealed but, of course, if it were to be cast into extremely large shapes, annealing might become advisable in order to reduce internal stresses.

Example I

10 grams of CsCl, 17.32 grams of $Al_2(NO_3)_3 \cdot 9H_2O$, 11.88 ml. of 6.67 M H_3PO_4, and 5.72 grams of $La(NO_3)_3$ were dissolved in 200 ml. of water. The resulting solution was then evaporated to dryness on a hot plate under a heat lamp. The resulting solids were ground to a powder with a mortar and pestle and the powder was placed in a platinum crucible. The crucible was placed in a cold muffle furnace with an atmosphere of air and heated to a pouring temperature of about 1200° C.

The crucible was removed from the furnace and the melt was cast into buttons.

Example II

10 grams of CsCl, 17.3 grams of $Al_2(NO_3)_3 \cdot 9H_2O$, 12.5 ml. of 6.67 M H_3PO_4, and 5.67 grams of $Zr(NO_3)_4$ were in 200 ml. of water. The resulting solution was then evaporated to dryness on a hot plate and under a heat lamp. The resulting solids were ground to a powder in a mortar and pestle and the powder was placed in a platinum crucible. The crucible was placed in a cold muffle furnace with an atmosphere of air and heated to a pouring temperature of about 1375° C.

The crucible was removed from the furnace and the melt was cast into buttons.

It will be understood that the invention is not to be limited to the details given herein but that it may be modified within the scope of the appended claims.

What is claimed is:

1. A method of containing radioactive cesium, comprising incorporating it in a glass containing cesium oxide, alumina and phosphate and having an additive selected from the class consisting of lanthanum in the plus three oxidation state and zirconium in the plus four oxidation state.

2. A method of containing radioactive cesium, comprising incorporating it in a glass containing cesium oxide, alumina and phosphate and having an additive of lanthanum in the plus three oxidation state.

3. A glass consisting essentially of about 45 weight percent Cs_2O, about 13 weight percent Al_2O_3, about 30 weight percent P_2O_5, and about 12 weight percent La_2O_3.

4. A glass consisting essentially of about 45 weight percent $Cs_2^{137}O$, about 13 weight percent Al_2O_3, about 30 weight percent P_2O_5 and about 12 weight percent La_2O_3.

5. A glass consisting essentially of about 42 weight percent Cs_2O, 12 weight percent Al_2O_3, 30 weight percent P_2O_5 and 15 weight percent ZrO_2.

References Cited by the Examiner

C & E News, Dec. 11, 1961, pages 62–64. TP 1 I418.

CARL D. QUARFORTH, *Primary Examiner.*
REUBEN EPSTEIN, *Examiner.*