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HIGH SILICA MATRIX RADIOACTIVE SOURCE AND METHOD OF PREPARATION

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This invention relates to radioactive sources and to methods of making such sources.

The term "source," as used herein, connotes a usable arrangement of radioactive material rather than the radioactive material per se. The term "radioactive material" refers to elements or isotopes, whether free or chemically combined, which spontaneously emit particles and/or rays by a process of atomic disintegration. Satisfactory sources should permit utilization of radiation from a radioactive material while preventing contamination of the surroundings through the loss of material.

Several methods have been used to prepare sources of radioactive energy. One approach has been to admix radioactive materials with binders such as clay, glass forming components, or other fusible particles and to fuse the mix by heat. Another approach has been to mix radioactive materials into a molten glass or uncured plastic and to cool or cure the mix to form a solid article. In these methods it is often difficult to obtain uniform distribution of the radioactive material and the presence of such material may adversely affect the strength of the finished article. Moreover, the amount of material which can be incorporated in a source with these methods is often limited. Such methods also result in the presence of some radioactive material at the surface of the article where it is subject to physical dislodgment, solvation, and chemical attack.

Still another approach has been to enclose the radioactive material within a container which is thin enough to permit substantial radiation penetration. If the radioactive material is soluble or is in the form of small particles, contamination can result from damage to or imperfections in the container which permits loss of the material through leakage, solvation, or particle escape. Fabrication of sources of beta radiation, by this approach, presents a particularly severe problem since the low penetrating power of beta particles requires the use of very thin containers which may be easily damaged.

Leakage hazards are especially serious in sources used for radiation therapy since introduction of radioactive materials into the body by, for example, solvation into body fluids may produce disastrous results. The advantages of and need for sources of radioactive energy which resist loss of the radioactive material are readily apparent.

Accordingly, it is an object of this invention to provide sources of radioactive energy which are substantially free of leakage hazards and to provide methods of making such sources. Another object is to provide radiation sources comprising radioactive material sealed into high-silica matrices which are highly resistant to thermal shock, physical damage, and chemical attack. The manner in which these, as well as other objects and advantages can be achieved will be readily apparent from the following detailed description.

In its broadest aspect, the process of the invention calls for introducing a radioactive material into the pores of a heat-fusible porous matrix and thereafter sealing at least the peripheral pores to provide a substantially leak-free source of radioactivity. In addition, the process results in a source which is substantially free from radioactive material on its exterior surfaces. Both of these characteristics are extremely important requirements for

sources that are to be used in radiation therapy or sources that must be directly handled by personnel.

In one embodiment of the invention, the radioactive material which is introduced into the pores of the matrix is in the form of a liquid, preferably a solution of the material. The liquid is allowed to remain in contact with the matrix until sufficient liquid has penetrated the pores. The liquid is removed leaving the material in the matrix and the pores of the matrix are thereafter sealed. Preferably, the liquid containing the radioactive material is forced deeper into the pores of the matrix by contacting the matrix with a second liquid which penetrates the pores thus forcing the radioactive material inward. After the matrix is removed from the second liquid, the liquids are removed as before leaving the radioactive material in the pores and the pores of the matrix are subsequently sealed. By forcing the radioactive material deeper into the matrix, the leakage potential of the source is further decreased.

Alternatively, or subsequent to forcing the material into the matrix with a second liquid, the radioactive material is converted to a substantially insoluble form within the pores of the matrix. Thereafter, the liquids are removed and the pores sealed as before. When the material is in an insoluble form, there is even less opportunity for the material to leak from possibly unsealed peripheral pores or fractures in the matrix as a solute in a liquid which could subsequently penetrate the matrix through the unsealed pores or fracture. Moreover, if the material is insoluble, contamination hazards associated with a fracture of the matrix can be reduced since any material which is set free from the matrix will not be spread as a solute.

In the practice of this invention, the porous matrix may be any fusible plastic or glass body having a plurality of very small interconnecting pores or channels therein. An especially preferred porous matrix is a porous high-silica glass. A method of making such a porous glass is described in United States Patent No. 2,106,744. Corning Glass No. 7930 is an example of a commercially available porous glass of this type.

Any material possessing natural or artifically induced radioactivity may be introduced into the pores of the matrix. Obviously, a non-active material may be introduced and later rendered active by well known techniques.

The choice of material is determined by consideration of such chemical, physical, and other factors as solubility, availability, cost, chemical reactivity, chemical and thermal stability, volatility, type and intensity of radiation desired, half-life, decay products, and toxicity. Generally, the radioactive material to be introduced into the pores of the matrix will be in liquid form, preferably a solution of the material or a melt. However, it is apparent that radioactive material could be introduced into the pores as vapors or very finely-divided solids.

When using a solution of the radioactive material, a solvent should be employed which does not chemically attack or dissolve the porous matrix to any great extent. For example, chlorides, nitrates, or other water soluble salts of such radioactive isotopes as strontium or cesium can be used.

The porous matrix is placed in contact with the radioactive liquid which is allowed to penetrate into the pores to the desired depth. Normally, the depth of liquid penetration into translucent or transparent porous matrix can be visually determined. Alternatively, or if the porous matrix is opaque, the depth of liquid penetration may be determined by well known methods such as X-ray techniques. Normally, the deeper the penetration the more resistant is the source to leakage.

Penetration of the liquid into the matrix can be regulated by controlling the contact time between the radioactive solution and porous matrix. The porous matrix

can then be contacted with a second liquid which will itself penetrate into the pores thereby forcing the radioactive solution inwardly. This process leaves the peripheral pores of the porous matrix substantially free of radioactive material.

Any liquid, including the liquids used as solvents for the radioactive material, can be used as the second liquid. Preferably the second liquid will not appreciably dissolve or chemically attack the porous matrix. It is generally preferable to use a second liquid which is immiscible with the first liquid and is not itself a solvent for the radioactive material in order to prevent back diffusion. For example, aqueous radioactive solutions can be forced inwardly into a porous glass by means of such liquids as carbon tetrachloride or chloroform.

As further precaution against leakage, the impregnated porous matrix can be contacted with a liquid or gas which reacts with the radioactive material to form a liquid or solid substance which will be substantially more insoluble and/or less volatile in the environment in which the source is to be used. If a solution of radioactive material is used to introduce the material into the matrix, the solvent may be evaporated prior to any subsequent reaction.

Many reactions for converting various radioactive materials into more insoluble forms will be apparent to those skilled in the chemical art. For example, if a porous glass containing strontium chloride is contacted with a sulfuric acid solution, the strontium chloride will be converted to the less water-soluble strontium sulfate. Alternatively, porous glass containing aqueous strontium chloride can be exposed to fumes of sulfur trioxide to accomplish the conversion. For even greater protection against leakage, the radioactive material can be forced inwardly into the porous body prior to being converted to a more insoluble form, as discussed above.

The impregnated heat-fusible porous matrix is subjected to a heat-sealing process which causes the pores to shrink or collapse around the radioactive material thus sealing the pores. This operation results in some reduction of volume of the originally porous matrix and in the case of a porous, high silica matrix causes vitrification. It is normally preferable to remove liquids, other than the radioactive material, if the material itself is liquid, which are present in the porous matrix prior to sealing the pores so that rapid vapor evolution will not damage the matrix. Moderate heat and/or a vacuum may be employed to remove these liquids by evaporation. It is also generally desirable to wash or wipe the exterior of the porous matrix free of radioactive material prior to heat-sealing the matrix. Washing the porous matrix also removes radioactive material from the peripheral pores. Thus, when the matrix is sealed, the periphery will be substantially free of radioactive material.

The temperature required to effect sealing depends upon the material comprising the porous matrix. The temperature should be high enough to soften the porous matrix sufficiently to permit shrinkage or collapse of the pores or channels but is preferably not so high as to cause undesired deformation of the finished source. For example, high silica matrices may be sealed at temperatures of 900° C. or higher. The preferred sealing temperature is 1000° to 1300° C. If higher temperatures are used it is desirable to support the matrix in order to prevent deformation. When plastic matrices are used, lower temperatures must be employed for the heat-sealing operation. The exact temperature range will depend on the particular plastic material being used. Generally, satisfactory heating may be obtained with a flame, or oven, or other conventional heat sources.

It is desirable to shrink the pores throughout the matrix to reduce the leakage potential. However, excellent results are achieved if only the peripheral pores are sealed.

The sealing of a thermally unstable or volatile radioactive material such as cesium chloride into a porous body sometimes presents special problems. If the porous body is, for example, a plastic sealable at temperatures which do not adversely affect the active material, the use of conventional heating means will present no difficulty. However, it may be desired to seal the active material into a porous matrix, such as high-silica glass, which requires sealing temperatures which can volatilize the active material.

One method of sealing volatile or thermally unstable materials into such a matrix is to force the active material inwardly and to limit the duration of exposure of the matrix to heat so that the heat does not penetrate to the interior of the body. It may be difficult, particularly if an irregularly shaped matrix is used, to apply heat uniformly to the periphery of the matrix and consequently incomplete peripheral sealing may result. Such difficulties may be avoided by use of high frequency inductive or dielectric heating techniques to seal the peripheral pores of the porous matrix. For example, a volatile active material can be forced to the interior of a porous matrix as previously explained. If desired, the material may be rendered insoluble. A conductive metal is then introduced into the peripheral pores and/or coated onto the exposed surfaces of the porous body. This is done by vapor deposition, electroless plating, contacting the matrix with organo-metallic compounds decomposable at a relatively low temperature to leave a metal film, or by other well known techniques of metal deposition. The deposited metal is then subjected to high frequency induction heating by conventional techniques. As high temperatures are quickly obtainable by high frequency induction, the sealing of the peripheral pores can be completed before heat penetrates to the interior of the matrix. Alternatively, peripheral sealing can be accomplished by introducing a solution of dielectrically lossy material such as a chloride of nickel, iron, or cobalt into the peripheral pores. The solvent is evaporated and the lossy material is dielectrically heated at high frequency to accomplish sealing.

The particularly preferred embodiment of our invention utilizes a porous, high-silica matrix, such as Corning Glass No. 7930. Following the heat sealing treatment, such a matrix possesses an extremely low coefficient of expansion and is resistant to thermal shock. The matrix is also physically strong, highly resistant to chemical attack and solvation, and withstands relatively high temperatures without softening. Such glass is also extremely resistant to damage by radiation.

As an additional precaution against leakage and damage, sources prepared according to this invention usually will be coated with or enclosed in a thin protective material. For example, the source may be coated with a thin layer of a non-corrodible material, preferably metals, such as nickel, steel, aluminum and the like. These coatings can be applied by vapor deposition, electroless plating, or other well known methods. Alternatively or additionally, the source may be enclosed within a housing or casing of the thin protective material. Stainless steel of about 0.4 mil thickness has been found satisfactory for this purpose. Obviously, other well known materials may be used.

The term "thin" is used in the specification and claims to indicate a thickness which does not reduce radiation below a useful level. The term "non-corrodible" is used to indicate resistance to chemical attack by the medium in which the source is to be used.

The following examples are illustrative of specific embodiments of this invention.

Example 1

A 1 inch x 1 inch x 4 mm. square of Corning 7930 porous glass was immersed for two hours in 10 ml. of a 0.25 g./ml. aqueous solution of $SrCl_2$ containing 25 microcuries Sr^{89}. The square was removed, dried in a vacuum dessicator, and gradually heated to 1200° C. to shrink and collapse the pores.

Example 2

A 1 inch x 1 inch x 4 mm. square of Corning 7930 porous glass was immersed for two hours in 10 ml. of a 0.25 g./ml. aqueous solution of $SrCl_2$ containing 25 microcuries Sr^{89}. The square was vacuum dried and placed in 10 ml. of a 1.0 normal H_2SO_4 solution to convert the chloride to a relatively insoluble sulfate. The square was vacuum dried and heated to 1200° C. to shrink and collapse the pores.

Example 3

A 1 inch x 1 inch x 4 mm. square of Corning 7930 porous glass was immersed into 10 ml. of a 0.25 g./ml. aqueous solution of $SrCl_2$ containing 25 microcuries Sr^{89}, until the solution diffused about one-third of the way into the glass. The glass was removed and placed in distilled water until diffusion of water into the glass was complete. The glass was then vacuum dried and heated to 1200° C. to shrink and collapse the pores.

Example 4

A 1 inch x 1 inch x 4 mm. square of Corning 7930 porous glass was immersed into 10 ml. of a 0.25 g./ml. aqueous solution of $SrCl_2$ containing 25 microcuries Sr^{89} until the solution diffused about one-third of the way into the glass. The glass was removed and placed in distilled water until diffusion of water into the glass was complete. The square was vacuum dried and subjected to H_2SO_4 treatment as described in Example 2. The glass was then heated to 1200° C. to shrink and collapse the pores.

The activity incorporated within sources prepared according to Examples 1, 2, and 3 was determined by measuring the radiation from the source and correcting for the adsorption of the glass. The sources were leak tested by treatment for 24 hours in a 0.01% aqueous solution of detergent maintained at 80° C. The activity in the solution was then determined. Table 1, below, summarizes the results:

Sample No.	Activity in Glass	Activity in Leak Test Solution
1	3.66 microcuries	0.604 millimicrocuries.
2	2.91 microcuries	0.100 millimicrocuries.
3	2.78 microcuries	0.076 millimicrocuries.

In Sample 1, only about 0.6 millimicrocurie of activity are dissolved from the source after 24 hours. Thus, from the standpoint of leakage, the 3.66 microcurie source exhibits a leakage potential of only 0.0006 microcurie. Therefore, if this glass source is encased in a thin metal housing, the leakage potential of the encased source is only 0.0006/3.66 or about $\frac{1}{6100}$ that of an encased source containing the radioactive material per se rather than the glass source. It is readily seen that such an encased source would be substantially free from any leakage hazard. The glass sources of Samples 2 and 3 would have even less leakage potential when encased in a suitable thin protective coating.

The above detailed description is for the purpose of illustration only and no undue limitations should be attributed to the invention as a result thereof except as reflected in the appended claims.

We claim:

1. A source of radioactive energy comprising an insoluble radioactive material enclosed substantially within the internal mass of a heat fusible, continuous matrix comprising at least 92% by weight silica, the peripheral portion of said matrix being substantially free of said radioactive material.

2. A source of radioactive energy comprising a radioactive material enclosed substantially within the internal mass of the heat fusible matrix comprising at least 92% by weight silica, the peripheral portion of said matrix being substantially free of said radioactive material, and a metal covering surrounding said matrix, said covering being sufficiently thin to permit transmission of radiation from said radioactive material.

3. A source of radioactive energy comprising an insoluble radioactive material enclosed substantially within the internal mass of a heat fusible matrix comprising at least 92% by weight silica, the peripheral portion of said matrix being substantially free of said radioactive material, and a metal covering surrounding said matrix, said covering being sufficiently thin to permit transmission of radiation from said radioactive material.

4. A process of making a radioactive source comprising introducing a liquid solution of radioactive material into the pores of a heat-fusible, porous matrix containing at least 92% by weight silica; forcing said solution inwardly into said porous matrix by contacting said matrix with a second liquid free of radioactive material; evaporating said second liquid and the solvent for the radioactive material; and sealing the radioactive material within the matrix by applying heat to said matrix to seal at least the peripheral pores.

5. The process of claim 4 further comprising chemically converting said radioactive material into an insoluble solid after forcing the radioactive solution inwardly into the porous matrix and prior to sealing at least the peripheral pores.

6. A process for making a radioactive source, said process comprising introducing a liquid solution of radioactive material into the pores of a heat fusible, porous matrix containing at least 92% by weight silica; chemically converting said radioactive material into an insoluble solid within said pores; and sealing the radioactive material within the matrix by heating said matrix sufficiently to seal at least the peripheral pores thereof.

7. A process for making a radioactive source, said process comprising introducing a liquid solution of radioactive material into the pores of a heat fusible, porous matrix containing at least 92% by weight silica; evaporating the solvent from said solution introduced into said pores; coating the matrix with an electrically conductive metal; and inductively heating said metal sufficiently to seal at least the peripheral pores of said matrix.

8. A process for making a radioactive source, said process comprising introducing a liquid solution of radioactive material into the pores of a heat fusible, porous matrix containing at least 92% by weight silica; evaporating the solvent from said solution introduced into said pores; introducing a dielectrically lossy material into the peripheral pores of said porous matrix and dielectrically heating said lossy material sufficiently to seal at least the peripheral pores of the matrix.

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