

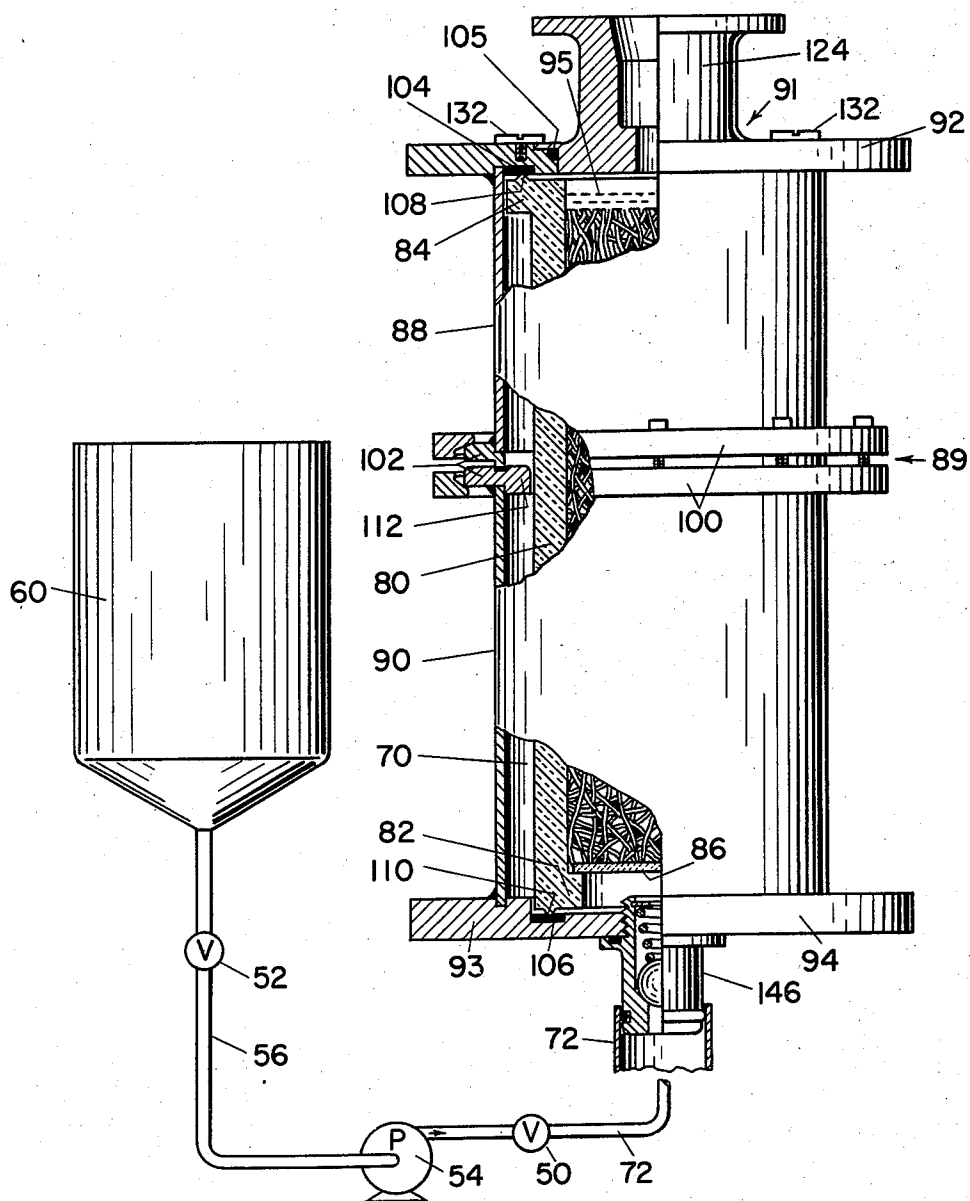
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RADIOACTIVE CONCENTRATOR AND RADIATION SOURCE

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**RADIOACTIVE CONCENTRATOR AND
RADIATION SOURCE**

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This invention relates to the absorption, adsorption and fixation of radioactive ions on Montmorillonite clay. In particular, the invention relates to a method of forming a permeable ion exchange bed to adsorb and absorb radioactive ions from liquid radioactive wastes and a product produced thereby. The invention further relates to a composition useful as a source of nuclear radiation for fluent materials and to a method of preparing the composition.

The disposition of radioactive waste solutions containing by-products resulting from nuclear fission has become an ever-increasing problem as the atomic energy industry has developed. Various methods have been developed for concentrating and ultimately disposing of these radioactive materials. One method of disposing of radioactive liquid wastes has been disclosed in U.S. Patent 2,616,847, issued November 4, 1952, to Ginnell. This method takes advantage of the well-known property of Montmorillonite clays to exchange cations with a solution, and to some extent also to adsorb cations. The sum of the two processes is generally referred to as adsorption and no distinction is made herein between these two processes.

The Ginnell process consists of bringing into contact a cation exchange mineral of the Montmorillonite group and a solution containing radioactive cations. The resulting suspension is shaken until there is no change in the radioactivity of the solution as measured by determining its specific activity. Thereafter the suspended clay is separated from the solution by centrifugation, selective filtration or other complex means, and heat treated to a temperature in the range 750 to 1000° C. to fix the adsorbed radioactive cations.

I have found the above described method has limited value in large-scale use for several reasons. First of all, the method of batch contacts is inefficient and difficult to handle, particularly for treating large volumes having high radioactivity. Secondly, for each batch contact only one equilibrium stage is possible to adsorb the radioactive ions on the clay. Frequently further contact and separation steps are necessary to effect a complete adsorption and separation of the resultant radioactive clay from the supernatant liquids. These additional steps present serious problems when processing large quantities of radioactive liquids.

It is therefore an object to eliminate the difficulties of a batch process by providing a continuous method of bringing an aqueous solution containing radioactive cations into uniform contact with a composition consisting essentially of a permeable clay aggregate to bring about efficient adsorption of said radioactive cations onto the clay, separating the solution from the clay, and subsequently heating the clay to a temperature in the range 750 to 1000° C. to fix the radioactive cations in the clay structure. Another object of the invention is to provide a method of forming a chemically stable radioactive bed suitable for flowing liquids therethrough, thereby to irradiate said liquids. A further object of the present

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invention is to provide a method of rendering a bed of Montmorillonite clay permeable to allow free flow of liquids containing radioactive cations through said bed thereby to adsorb said radioactive ions on said clay bed.

5 Another object is to provide a composition which is a source of nuclear radiation and is suitable for flowing liquids therethrough to irradiate the liquids. Still a further object is to provide a method of disposing of radioactive cations in solution by passing the solution through a bed of the kind described herein.

10 With these and other objects in mind the method of this invention, broadly speaking, comprises forming a paste consisting essentially of a mixture of Montmorillonite clay, water and a material that combines with the clay to form a stable aggregate in the presence of water, passing said paste through a small aperture into a volume of water to form a bed of permeable clay rods, displacing said volume of water with a solution containing radioactive cations to adsorb the cations from said solution, separating the rods from the solution and heating the bed of clay rods to a temperature in the range 750 to 1000° C.

15 Because of its large surface area, a packed bed of wet Montmorillonite clay is impervious to fluids, as is typical of clayey masses. Thus, methods of utilizing the cation exchange capacity of Montmorillonite have until now been limited to batch contact of finely divided clay with cation-containing liquids followed by separation of liquid and solid phases. This method is cumbersome when large quantities of solutions are involved, particularly when treating radioactive solutions. Further, when suspended in water, fine particles of clay do not settle out readily, even under quiescent conditions, and filtration is difficult. Complete separation of solid and liquid phases is imperative, because after treating radioactive solutions, the clay becomes highly radioactive.

20 My method, which produces stable aggregations of Montmorillonite clay, permit continuous processing of liquids containing radioactive ions with complete separation of solid and liquid phases. According to this method, Montmorillonite clay is mixed with a material that combines with the clay to form clay aggregates that are stable in the presence of water. Water-soluble synthetic polyelectrolytes mixed with clay particles form stable clay aggregates even in the presence of water. I have discovered that these materials, contrary to expectations, do not reduce the cation exchange capacity of the clays. Moreover, the stable, aggregated clay composition in the form of extruded clay rods is highly permeable to liquids passing through a bed prepared therefrom. While the action of these polyelectrolytes is not completely understood, it is believed that the polymer molecules are sufficiently long to form a bridge that binds the individual ultimate clay particles. This process is probably one of ion exchange. Suitable water-soluble polymers of this type are readily available under a variety of trade names. I have found that one of these that may be used with advantage is the commercially available product "Krilium." The preparation and composition of Krilium type resins suitable for use in practicing the present invention are disclosed in U.S. Patent No. 2,625,529.

25 In practicing the invention water is added to a mixture of clay and an aggregative material of the type defined above to form a paste. This paste is then extruded directly into a body of water contained for example in an ion exchange column. In order to obtain a permeable clay bed, the paste is extruded into clay rods of short length to form a loosely packed bed in the water. These extruded rods are readily broken up into short lengths upon contact of the clay with water. The short clay rods settle by gravity in the water in random fashion

to form a permeable bed. The small clay rods retain their form in water and in solutions containing radioactive ions. Even with the aggregating agent adsorbed on the clay, the cation exchange capacity of the clay is not impaired.

The clay aggregates are surprisingly stable in water moving over them. This permits continuous ion exchange with a solution containing radioactive cations flowing through the clay bed. Equilibrium is attained with complete separation between the solid clay phase and the effluent. After the process has been in operation for some time the clay rods reach their maximum capacity for adsorption of the radioactive ions. The clay rods are separated and then heated to a temperature in the range 750 to 1000° C. to fix the radioactive cations in the clay. The fired clay containing the fixed radioactive cations may then be stored for permanent disposition.

I have also found that the fired clay is extremely useful as source of gamma or beta radiation. Since the clay rods largely hold their shape after heat-treatment, the mass of material remains highly permeable to fluids. The fired clay consists essentially of closely packed ceramic rods with the radioactive cations fixed therein. The clay aggregative material is believed to be volatilized by the heat treatment.

When the clay paste is extruded into a container made of a refractory material, all the further steps of the process may be performed without handling the clay further. The container with the bed of ceramic rods containing radioactive cations contained therein, is useful as a convenient packaged source of radioactivity. When used as a gamma source, the material to be irradiated does not have to be in direct contact with the clay, although it may be. When used as a beta source, direct contact is necessary because of the relatively low penetrating power of the beta radiation. Liquids to be irradiated, such as pharmaceuticals or food products, may thus be flowed directly through the clay bed to expose the material to beta or gamma irradiation without fear of chemical contamination.

The invention will be more clearly understood by reference to the accompanying drawing which is a representation, partly in section, of an ion exchange column containing a packed bed in accordance with this invention.

The following examples illustrate the effectiveness of my invention in providing a method and composition permitting the processing of radioactive fluids. It is not intended to limit the scope of the invention by the details set forth in these examples.

Example I

An aqueous solution of .04 molar cesium chloride was prepared and to it was added a tracer quantity of the radioactive isotope cesium-134, which emits gamma particles. In this experiment, Montmorillonite clay obtained from the Filtrol Corporation was used. The mineral, as received, was heated at about 110° C. to constant weight to remove excess water and to provide a uniform basis for weighing samples of the mineral. 50 grams of the dried clay was then mixed with .5 gram of "Krilium," whose active ingredient is a water-soluble polyelectrolyte, understood to contain as its active ingredient the sodium and/or calcium salt of partially hydrolyzed polyacrylonitrile. The clay and the Krilium were mixed with 35 milliliters of water to produce a paste-like mass. This paste was then placed in the chamber of an extrusion press, and a nozzle having a diameter of $\frac{1}{32}$ " was put in place. The extrusion chamber was evacuated with a vacuum pump. With the vacuum still applied the piston was advanced until a small quantity of clay passed through the nozzle. At this point the vacuum was broken, and the clay was continuously extruded into a water-filled container. As the clay entered the water it broke into short discrete rods, which packed loosely and randomly to form a bed.

The radioactive cesium chloride was then passed continuously through the column, initially displacing the water. The activity in the column effluent was determined periodically by measuring the activity of aliquot samples of the effluent during the flow period. When the clay reached its maximum capacity for adsorption, the water was removed from the column, and the clay was heated to a temperature in the range 750 to 1000° C. A synthetic sea water solution was then flowed through the column to provide an accelerated determination of the effect of leaching from the column. The sea water had a composition approximately the same as that from the Atlantic Ocean. Over a period of 52 days it was found that less than .1% of the adsorbed cesium was leached by the sea water. The exchange capacity of the clay was calculated to be 1.1 milliequivalents per gram. In another identical experiment except that the clay was prepared without the Krilium, the exchange capacity of the clay was 1.06 milliequivalents per gram. This illustrates the fact that the clay aggregative material does not impair the cation exchange capacity of the clay rods; in fact in this case there was an increase in the ion exchange capacity even though the additional material was present.

Example II

In this experiment two columns were prepared by the procedure described in Example I. The first column was prepared with extruded clay rods containing .5% Krilium by weight of clay, while the second column was made up without Krilium. A solution containing .04 molar cesium chloride and a tracer amount of cesium-134 was flowed through each of the columns. 400 column volumes was flowed through each of the columns. A column volume is defined as the volume of solution that an empty column will hold. After 250 volumes it was noted that the second column began to disintegrate and the effluent became cloudy due to the fine particles of clay suspended therein while the effluent from the Krilium treated column was completely free of clay particles. This experiment shows graphically the enhanced stability of the clay bed prepared according to the method of the present invention.

Example III

A solution of mixed fission products from which the major part of uranium was removed was found to have a specific activity of 1.97×10^5 counts per milliliter per minute. A clay column was prepared by the extrusion of a mixture of 200 grams of dried Montmorillonite clay (Filtrol Corporation lot #R-2532), 1.75 grams of Krilium and 90 milliliters of water, by the procedure described in Example I. The solution was flowed through the column, after which the column was drained and the clay heated to a temperature in the range 750 to 1000° C. Thereafter the clay was leached by flowing a solution of a synthetic sea water through the column to provide an accelerated determination of the effect of leaching. The sea water had a composition approximately the same as that from the Atlantic Ocean. Leaching over a period of 52 days released less than .1% of the radioactivity.

In carrying out the method, it is preferable that the pH of the solution be maintained in the range 4 to 9. When the solution is more acid or basic than this, there appears to be a decrease in the amount adsorbed so the a larger volume of clay is required per volume of solution processed. The time of contact and ratio of clay to solution treated may easily be found by simple experimental procedures well known in the art.

The composition of the clay before extrusion is quite important. I have found that by preparing a composition having 40 to 45% by weight of water and from .2% to 1% of a synthetic polyelectrolyte by weight of clay an optimum mixture is obtained. The concentration of the polyelectrolyte used depends somewhat on the particular compound used. In the case of Krilium .5% by weight

of clay is preferred. At a concentration above 1% by weight of clay no substantial benefit is obtained.

While it is preferable, it is not necessary to heat the clay to constant weight before preparing the extruded clay. Where the clay is not subjected to a preliminary heat treatment, its water content should be known for optimum composition requirements.

I have found that clay rods having diameters in the range $\frac{1}{64}$ inch to $\frac{1}{8}$ of an inch may conveniently be used in the preparation of the clay beds. I prefer to use rods having a diameter of approximately $\frac{1}{32}$ inch. This dimension provides the most favorable conditions for ion exchange and mechanical strength of the aggregated clay rods.

The process may be carried out in equipment such as that shown in the drawing. With reference to the figure, the ion exchange assembly includes a cylindrical stainless steel casing 89 formed of separable upper and lower portions 88 and 90 having mating flanges 102 and a pair of bolted clamping rings 100 therefor. Casing 89 is in two parts to provide easy access to the interior, and, when held together by the clamping rings 100 bearing on the flanges 102, the casing forms a continuous cylinder.

The casing 89 encloses an inner impervious cylindrical container 80 of a refractory material such as silicon carbide. The inner container 80 has a smaller outside diameter than the inside diameter of the casing 89, and is centered therein by an outwardly directed flange 84 on the upper end of container 80 and by a guide ring 112 on the upper end of casing portion 90. Thereby an annular space 70 is formed between the inner container 80 and the casing 90.

The outer ends of casing 89 are capped with heads 91 and 93. The upper head 91 has an annular ring 92 sealed to upper casing portion 88. On its under surface the ring 92 is provided with a gasket 104 against which a boss 108 on flange 84 is caused to bear in order to seal the inner container from the annular space 70. The lower head 93, in turn, has an annular ring 94 sealed to the lower casing portion 90. On its upper surface the ring 93 has a gasket 106 against which an annular boss 110 is caused to bear to seal the lower end of the inner container from the annular space 70.

A flanged pipe fitting 124 fills the central opening in the upper head ring 92. The fitting 124 is flanged and held in fluid-tight relation by spaced screws 132 causing the fitting to bear on an O-ring gasket 105. The central opening in the lower ring 94 is threaded to receive a ball check valve 146. The check valve permits filling the container with liquid before beginning the flow of the radioactive solution to the column.

To support the packed bed and to distribute the incoming liquid through the bed, a porous disk 86 of a refractory material, such as silicon carbide, is supported on an inner shoulder 82 at the lower end of the container. When the material being treated is flowing upward, only one such disk is required. When the liquid being treated flows down, it is necessary to provide an additional disk or similar distribution means across the upper end of container 80. In the latter event, the ball check valve is replaced by a manually operated valve.

When the liquid being treated is flowed upward through the column, the ball valve 146 is connected by pipes 72 and 56 to a feed storage tank 60. Valves 50 and 52 are inserted in pipe lines 72 and 56 to control the flow of fluid. A pump 54 transfers fluid from the storage tank 60 to the column. The outlet fitting 124 may be connected to a waste receiver.

The equipment is prepared for use by inserting a silicon carbide container 80 fitted with a porous silicon carbide disk 86 into the lower portion 90 of the cylindrical casing. The upper portion 88 of the casing (with head 91) is placed on the lower portion 90 and the clamping rings 100 are placed on adjacent flanges 102 and tightened on the flanges by means of bolts to draw the two portions

of the casing together. This action forces the annular bosses 108 and 110 against the gaskets 104 and 106 respectively, to seal the interior of the container 80 from the annular space 70 surrounding it. The container 80 is then partly filled with water. Any water that passes through the porous disk 86 is retained in the space below it by the valve ball 146. The Montmorillonite clay mixture is extruded in rod form into the container 80 to fill it and keep the clay rods covered with water 95 as shown in the drawing. When the container is filled, the fitting 124 is secured in place by screws 132. The column is now ready for use.

Then, after the desired adjustments have been made to it, the solution containing radioactive cations enters the column from storage tank 60 through the feed pipe 72. As the solution passes upwards through the bed of clay rods, the radioactive cations are adsorbed on the clay. After the process has been in operation for some time the clay reaches its adsorptive limit and radioactivity will be detected in the effluent solution. When saturation has been reached, the upper casing portion 88 is removed, and the container 80 with its load of clay is removed from the lower housing 90. The container 80 with its bed of clay rods is drained and is then placed in a furnace where it is heated to a temperature in the range 750 to 1000° C. to fix the adsorbed cations in the clay.

The impervious refractory container 80 with its bed of ceramic rods is a convenient packaged source of radiation for use in irradiation of liquids. This source has several unique advantages. The labyrinthine passages between the rods in the clay bed insure that all of the liquid passing through will come in close contact with the radiation. A further advantage of this radiation source is that the clay rods are physically and chemically stable, permitting a wide variety of liquids to be irradiated without risk of radioactive or chemical contamination.

Since many embodiments can be made of the present invention and since many changes can be made in the embodiment described above, it is to be understood that the above description is to be interpreted as illustrative only and not in a limiting sense.

I claim:

1. A method of preparing a clay bed which comprises forming a paste consisting of water, Montmorillonite clay, and a synthetic water-soluble polyelectrolyte having a weight average molecular weight of at least 10,000 and having a structure derived by the polymerization of at least one mono-olefinic compound through the aliphatic unsaturated group, said structure being substantially free of cross-linking, shaping said paste into rods and passing said rods into a volume of water to form a permeable clay bed.

2. A method of preparing a clay bed which comprises forming a paste consisting of water, Montmorillonite clay and a synthetic water soluble polyelectrolyte having a weight average molecular weight of at least 10,000 and having a structure derived by the polymerization of at least one mono-olefinic compound through the aliphatic unsaturated group, said structure being substantially free of cross-linking to aggregate the clay in water and extruding said paste into a volume of water to form a permeable bed of short clay rods.

3. A method of preparing a clay bed comprising the steps of forming a paste consisting of water, Montmorillonite clay and the sodium salt of a partially hydrolyzed polyacrylonitrile and extruding said paste into a volume of water to form a permeable bed of short clay rods.

4. A method of preparing a clay bed which comprises forming a paste consisting of a mixture of water, Montmorillonite clay and the calcium salt of a partially hydrolyzed polyacrylonitrile and extruding said paste into a volume of water to form a permeable bed of short clay rods.

5. A method of preparing a clay bed which comprises forming a paste consisting of Montmorillonite clay, a

synthetic water-soluble polyelectrolyte having a weight average molecular weight of at least 10,000 and having a structure derived by the polymerization of at least one mono-olefinic compound through the aliphatic unsaturated group, said structure being substantially free of cross-linking, in the amount of .2 to 1% by weight of clay and water in the amount of 40 to 45% of the total weight of the paste mixture, and extruding said paste into a volume of water to form a permeable bed of short clay rods.

6. A method of preparing a clay bed which comprises forming a paste consisting of Montmorillonite clay, about .5% by weight of the sodium salt of a partially hydrolyzed polyacrylonitrile and water in the amount of 40 to 45% of the total weight, and extruding said paste into a volume of water to form a permeable bed of short clay rods.

7. A method of preparing a clay bed which comprises forming a paste consisting of Montmorillonite clay, about .5% by weight of the calcium salt of a partially hydrolyzed polyacrylonitrile and water, equal to 40 to 45% of the total weight of the paste mixture.

8. A method of preparing a clay bed which comprises forming a plastic mixture consisting of Montmorillonite clay, 40 to 45% by weight of water and a synthetic water-soluble polyelectrolyte having a weight average molecular weight of at least 10,000 and having a structure derived by the polymerization of at least one monoolefinic compound through the aliphatic unsaturated group, said structure being substantially free of cross-linking, and extruding said paste into a volume of water to form a permeable bed of short clay rods having diameters of $\frac{1}{64}$ inch to $\frac{1}{8}$ inch.

9. A method of preparing a clay bed which comprises forming a plastic mixture consisting of Montmorillonite clay, 40 to 45% by weight of water and a synthetic water-soluble polyelectrolyte having a weight average molecular weight of at least 10,000 and having a structure derived by the polymerization of at least one mono-olefinic compound through the aliphatic unsaturated group, said structure being substantially free of cross-linking, and extruding said paste into a volume of water to form a permeable bed of short clay rods having diameters of about $\frac{1}{32}$ inch.

10. Clay rods consisting essentially of a mixture of water, Montmorillonite clay and a water-soluble synthetic polyelectrolyte having a weight average molecular weight of at least 10,000 and having a structure derived by the polymerization of at least one mono-olefinic compound through the aliphatic unsaturated group, said structure being substantially free of cross-linking.

11. A method of preparing a chemically resistant radiation bed suitable for irradiation of liquids flowing therethrough which comprises forming a plastic mixture consisting essentially of water, Montmorillonite clay and a synthetic water-soluble polyelectrolyte having a weight average molecular weight of at least 10,000 and having a structure derived by the polymerization of at least one mono-olefinic compound through the aliphatic unsaturated group, said structure being substantially free of cross-linking, shaping said mixture into rods and forming said rods into a volume of water to form a permeable bed of randomly oriented clay rods, flowing a solution containing radioactive cations through said bed, thereby to absorb said cations on said clay rods, separating the clay rods from the solution and thereafter heating the rods to a temperature in the range 750 to 1000° C. to fix the ions chemically in the clay.

12. A method of preparing a chemically resistant radiation bed suitable for irradiation of liquids flowing therethrough which comprises forming a paste consisting of water, Montmorillonite clay and a synthetic water-soluble polyelectrolyte having a weight average molec-

ular weight of at least 10,000 and having a structure derived by the polymerization of at least one mono-olefinic compound through the aliphatic unsaturated group, said structure being substantially free of cross-linking, extruding said mixture into a volume of water to form a permeable bed of randomly oriented clay rods, flowing a solution containing radioactive cations through said bed, thereby to adsorb said ions on said clay rods, separating the rods from the solution, drying said rods and thereafter heating the dry rods to a temperature in the range 750 to 1000° C.

13. A method of preparing a chemically resistant radiation bed which comprises forming a plastic mixture consisting of Montmorillonite clay, 40 to 45% by weight water and .2 to 1% of a synthetic water-soluble polyelectrolyte having a weight average molecular weight of at least 10,000 and having a structure derived by the polymerization of at least one mono-olefinic compound through the aliphatic unsaturated group, said structure being substantially free of cross-linking, extruding said mixture into a volume of water to form a permeable bed of randomly oriented clay rods, flowing a solution containing radioactive cations through said bed thereby to adsorb said ions on said clay rods, separating the rods from the solution, drying said bed and then heating it to a temperature in the range 750 to 1000° C.

14. The method according to claim 13 in which the paste is extruded into rods having diameters in the range $\frac{1}{64}$ inch to $\frac{1}{8}$ inch.

15. The method according to claim 13 in which the paste is extruded into rods having diameters of about $\frac{1}{32}$ inch.

16. A composition suitable for irradiating liquids flowing therethrough which comprises a permeable bed of randomly oriented short ceramic rods formed from Montmorillonite clay and a synthetic water-soluble polyelectrolyte having a weight average molecular weight of at least 10,000 and having a structure derived by the polymerization of at least one mono-olefinic compound through the aliphatic unsaturated group, said structure being substantially free of cross-linking, having small diameters and having a radioactive material chemically bound with the clay.

17. A composition suitable for irradiating liquids flowing therethrough which comprises a permeable bed of randomly oriented ceramic rods formed from Montmorillonite clay and a synthetic water-soluble polyelectrolyte having a weight average molecular weight of at least 10,000 and having a structure derived by the polymerization of at least one mono-olefinic compound through the aliphatic unsaturated group, said structure being substantially free of cross-linking, having diameters of about $\frac{1}{32}$ of an inch and having a radioactive material chemically bound with the clay.

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