

1

3,716,490

## TREATMENT OF RADIOACTIVE LIQUIDS

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No Drawing. Continuation-in-part of application Ser. No.  
782,728, Dec. 10, 1968. This application June 3, 1969,  
Ser. No. 830,130

Claims priority, application Great Britain, Dec. 11, 1967,  
56,172/67

Int. Cl. G21g 19/42

U.S. Cl. 252—301.1 W

15 Claims

### ABSTRACT OF THE DISCLOSURE

A method for decontamination of radioactive liquids and the products thereof, including contacting the radioactive liquid with an ion exchange material formed from a bituminous substance, such as asphalt, and thereafter compacting the ion exchange material, as by fusion and/or compression.

### CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of my prior copending application Ser. No. 782,728, filed Dec. 10, 1968, now abandoned.

### BACKGROUND OF THE INVENTION

Heretofore it has been proposed to encapsulate radioactive wastes in bituminous matrices which immobilize the waste and prevent inadvertent release of the radioactive material following disposal.

If the radioactive material to be disposed of is dissolved or dispersed in a liquid, the liquid is separated from the waste prior to encapsulation. Such separation has heretofore been accomplished by contacting the contaminated liquid with a synthetic polymeric ion exchange resin, such as a sulfonated polystyrene or the like. Many different ion exchange resins are well known to persons skilled in the art for this purpose. Such a treatment unites the ions of the radioactive material from the waste with the ion exchange resin particles by ion exchange and the liquids may then be separated by any desired technique, such as filtering, etc. The radioactive ions freed of the liquid portion of the waste can then be separated from the used ion exchange material by regenerating or burning away the latter. However, this has proven to be both complicated and expensive. If the used resin and the radioactive material are not separated from one another, then the used resin with the accompanying waste must be encapsulated with a bituminous or the like. This has proven to be a very difficult operation since most synthetic polymeric ion exchange resins decompose at temperatures starting at about 130° C. This decomposition will be accompanied by release of gas and thus by release of the radioactive material.

Another known process for the treatment of radioactive materials in liquids involves chemical coprecipitation of the radioactive ions. The precipitate is then filtered and homogeneously mixed in hot bituminous materials, during which step the water evaporates, or the precipitate can also be mixed with bituminous emulsions. The mass thus obtained is stored in steel drums. However, chemical coprecipitation gives rise to precipitates which are difficult to filter and large filtering installations are needed. Filterability can be improved by dehydrating the precipitate by the freeze-thaw method. However, this again adds an additional undesirable step.

Accordingly, a need remains for an improved technique for the decontamination of radioactive liquids and the ultimate disposal of the radioactive waste.

2

### OBJECTS OF THE INVENTION

A principal object of this invention is to provide such improvements. Another object of the present invention is to shorten the process of decontamination and encapsulation of radioactive wastes by using the same material as an adsorbent and encapsulator for the radioactive material. Yet another object is to provide an improved method for decontaminating and immobilizing radioactive waste materials at a reduced cost. Still another object of the present invention is to provide a compacted body of radioactive waste material and an ion exchange material derived from bituminous substances, which is characterized by a high content of radioactive material for a given volume of encapsulating or immobilizing medium. Other objects of the present invention will become apparent in light of the disclosure of the invention which follows.

### BRIEF DESCRIPTION OF THE INVENTION

In accordance with one aspect of the present invention, a method is provided for decontaminating radioactive liquids in which the liquid is contacted with an ion exchange material, comprising a partially sulfonated bituminous substance to thereby transfer radioactive ions from the liquid to the ion exchange material by ion exchange. The bituminous substance has a relatively high surface area and by subsequently compacting the bituminous substance under the influence of heat to form a relatively low specific surface area, the radioactive ions may be encapsulated in the compacted bituminous substance.

In another of its aspects, the present invention provides a method of decontaminating a radioactive liquid in which the liquid is contacted with an ion exchange material, comprising a partly sulfonated, fusible, bituminous substance to thereby transfer radioactive ions from the liquid to the ion exchange material by ion exchange. The bituminous substance initially has a relatively high specific surface area and by subsequently melting the bituminous substance to form a material of relatively low specific surface area, the radioactive ions may be encapsulated in the material of low specific surface area.

In still another of its aspects, the present invention provides compacted bodies of an ion exchange material, derived from bituminous substances, having at least a portion of its exchangeable ions replaced with radioactive ions. The bituminous substance forming the ion exchange material is partially sulfonated prior to its use. The compaction of such material may be attained by fusion or by a combination of fusion and compression.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the preferred embodiment of the present invention, a bituminous substance is partially sulfonated in a manner such that it will act as an ion exchange material and can be melted without decomposition or loss. Radioactive liquids are then contacted with the sulfonated bituminous substance and, after partial saturation with radioactive ions, the bituminous substance may thereafter be melted to bring about compaction. The radioactive ions are thus fixed in an unleachable fashion. The melting of the partially sulfonated bituminous substance does not give rise to decomposition of this material or to a loss of radioactive compounds. Its effect is to reduce the bituminous substance to a compact form of low bulk having a low specific surface area.

The term "specific surface area," when used herein, means the ratio of total surface area to mass; that is to say, the proportion of the bituminous substance that is

exposed for interaction with its environment. The specific area, of course, depends upon the size of the particles utilized. The size, in turn, may be selected by one skilled in the art and is a function of the type of ion exchange material used, the required rate of passage of liquid there-through, etc. For example, particles with a diameter of 0.25 mm. have a surface area of 0.186 mm.<sup>2</sup>. It would be possible to melt these particles, after saturation, to particles with a volume of 1 cm.<sup>3</sup> having a surface area of 484 mm.<sup>2</sup>. A particle with a volume of 1 cm.<sup>3</sup> will contain 122,000 of the 0.25 mm. diameter particles and the complete surface of these 122,000 particles will be 22,800 mm.<sup>2</sup>. Therefore, the ratio between the two surface areas will be

$$2,800/484$$

or nearly 47. However, it is also clear that particles smaller than 0.25 mm. will give rise to a larger surface area and that the ratio of uncompacted to compacted material will be larger. It is thus obvious that, based on these factors, one skilled in the art can select a proper particle size and the proper surface area to accomplish the desired result.

The term "bituminous substance," when utilized herein, is meant to include a class of native and pyrogenous substances containing bitumens or pyrobitumens or resembling them in physical properties and of normally solid or liquid consistency. Hence, the term is meant to include bitumin, pyrobitumin, petroleum hydrocarbons, asphalt, asphaltite, asphaltic pyrobitumin, non-asphaltic pyrobitumin, tar, pitch, etc. For an expansion of this definition, see *Asphalts and Allied Substances* by Abraham, 3rd edition, 1932, D. Van Nostrand & Co., pp. 28 through 32, which is adopted herein.

It is to be noted at this point that the use of sulfonated bituminous substances as ion exchange materials is known. These sulfonated bituminous substances have heretofore been prepared by treating the bituminous substance with concentrated sulfuric acid at high temperatures, the resulting bituminous ion exchange material being carbonized and infusible.

On the other hand, partly sulfonated, fusible bituminous substances can be prepared in one of several alternate ways.

In one mode of operation, the bituminous substance may be treated with SO<sub>3</sub> compounds in a preselected concentration, for a preselected time and at a predetermined temperature, such that the sulfonation reaction is incomplete. Such a sulfonation reaction may comprise treatment of the bituminous substance for a period of not more than 10 minutes with SO<sub>3</sub> compounds in a ratio of about 5 to 20 equivalents of SO<sub>3</sub> per kilogram of bituminous substance and at a temperature between about 50° C. and 120° C. The temperature selected is, of course, dependent upon the softening point of the bituminous substance. For example, if the bituminous substance is very hard, the sulfonation temperature must be high. On the other hand, if the bituminous substance has a low softening point, the sulfonation temperature should be lower since the utilization of a high sulfonation temperature on a material of low softening point will cause the bituminous substance to oxidize. In order to increase the efficiency of the reaction, a metal salt (e.g., sulfates and chlorides) can be used as a catalyst. Suitable SO<sub>3</sub> compounds include sulfuric acid, sulfuric acid anhydride, chloresulfonic acid, etc.

The temperature to which the bitumin is heated for the sulfonation depends upon the reactivity, the softening point, and other characteristics of the bituminous substance. Accordingly, in another mode of operation, the ratio of sulfuric acid to bituminous substance can be anywhere between 30 to 240 equivalents of sulfuric acid per kilogram of bitumin. The sulfonation period is a function of the temperature. For example, at room temperature, the sulfonation reaction would be complete after about

12 hours while at 50° C., the sulfonation period could be reduced to about 5 minutes. As a specific example, with an acid-to-bituminous substance ratio of 150 equivalents per kilogram and a reaction time of 8 minutes at 140° C., the resulting bitumin would have an ion exchange capacity of about 2.3 equivalents per kilogram.

As a practical matter, the sulfonation reaction is preferably carried out in two steps. The first step comprises a low sulfonation, giving a material of more crystalline structure which allows increased contact between the sulfuric acid and the bituminous substance, and the second step then comprises a second sulfonation to the desired product.

The sulfonated bituminous substance is then dried and can be used as an ion exchange material for the decontamination of radioactive liquids. After the bituminous substance has been contacted with the radioactive liquid, the bituminous substance is melted to reduce its overall volume and specific surface area and the radioactive products are thereby fixed in the bituminous substance in an unleachable manner.

A partially sulfonated, fusible, bituminous substance can also be prepared by mixing a partially sulfonated, infusible, bituminous substance with fresh bituminous substance (not sulfonated). By choice of suitable proportions of these two components, it is possible to obtain a good structure and excellent fusibility of the ion exchange material.

It is further possible to fix the sulfonated, bituminous substance on particles of fresh bituminous substance or other similar products or even to enclose particles of fresh bituminous substance completely with sulfonated bituminous substance before its use as an ion exchange material.

The partially sulfonated bituminous substance can be used as an ion exchange material in its hydrogen form, as it is obtained from the sulfonation reaction, or the hydrogen form may be treated with sodium ions (for example, sodium chloride) and then used in the sodium form or even in another appropriate ionic form.

According to a further aspect of the present invention, the partially sulfonated, bituminous substance may be substantially infusible but sticky and able to be compressed into a clump when heated.

In practice, the bituminous substance will not ordinarily be melted until complete saturation with radioactive ions. However, melting of the partially saturated bituminous substance is also to be considered within the scope of the present invention.

The bituminous substance can be used in granular or powder form, or as a sponge, thin sheets or strips, in a conventional installation for ion exchange materials.

The invention will be further illustrated with the help of the following, non-limiting examples.

When used herein, the term "Penetration" refers to a measure of the consistency of a bituminous substance, expressed as the distance in tenths of a mm. that a standard needle vertically penetrates a sample of the substance under known conditions of loading, time and temperature. Where the test conditions are not specifically mentioned, the load, time and temperature are 100 g., 5 sec., and 25° C., respectively, and the units of penetration or hundredths of a cm. The load is defined as the total moving weight of the needle and attachments. See *Asphalts and Allied Substances*, Abraham, D. Van Nostrand Co., Third edition, 1929, pp. 664 to 668.

#### EXAMPLE 1

##### Preparation of partially sulfonated, fusible bituminous substance

One kilogram of bituminous substance, obtained by distillation of a crude petroleum oil and having a penetration of 280-320, was heated to a temperature of 90° C. and maintained at this temperature. A mixture of 15 equivalents of sulfuric acid and 1 p.p.m. silver sulfate

5

was added to the hot bituminous substance while stirring the mixture. The reaction time was 4 minutes and the product was thereafter poured into cold water. The cooled substance thus obtained was ground under water, removed from the water and dried. The product comprised a partially sulfonated bituminous substance that was readily fusible at a temperature of about 80° C.

#### EXAMPLE 2

##### Preparation of partially sulfonated, fusible bituminous substance

One kilogram of the bituminous substance of Example 1 was heated to 140° C. 30 equivalents of sulfuric acid were added while stirring and the reaction was continued for 4 minutes. The product then was poured into cold water. The substance obtained was filtered and dried at 80° C. This substance was then re-heated to 140° C. and again sulfonated with 120 equivalents of sulfuric acid. The mixture was stirred during a reaction time of 4 minutes and then poured into cold water, filtered and dried at 80° C. 50% of this sulfonated bituminous substance was then mixed with 50% fresh bituminous substance having a penetration of 280-320. The resultant mixture was washed, dried and ground to particles of about 35 to 65 mesh.

Where the sulfonated bituminous substance is not fusible, it can be mixed with fresh (not sulfonated) bituminous substance, as illustrated by the preceding example, in a ratio varying from 80 to 20 parts fresh bituminous substance to 20 to 80 parts sulfonated bituminous substance. Such mixtures are readily fusible and have an excellent ion exchange capacity. For the mixture described above, the ion exchange capacity is in a region of 1.5 equivalents per kilogram. It is to be noted that the mixing of sulfonated bituminous substance and fresh bituminous substance gives rise to a very strong sulfonation reaction with the fresh bituminous substance which is accompanied by gas release. Consequently, the fresh and fusible sulfonated bituminous substance must be mixed before ion exchange. If the infusible bituminous substance were mixed with fresh bituminous substance after the ion exchange (which mixing would give a fusible bitumin), the gas release would cause release of the radioactive material.

#### EXAMPLE 3

##### Preparation of partially sulfonated bitumin which is not fusible but may be made so

One kilogram of bituminous substance having a penetration of 155-7 was ground to particle size of 35 mesh. These particles were added to 90 equivalents per kilogram of sulfuric acid at a temperature of about 20° C. Stirring was continued for a reaction time of about 3 hours. The substance obtained was then poured into water and dried at 100° C. The product of this reaction was a partially sulfonated bituminous substance having a good ion exchange capacity but it was infusible. The bituminous substance, however, was sticky and could be compressed after ion exchange to form a clump when heated. For the preparation of the bituminous substance in this instance, a hard species of bituminous material must be used. The ratio of sulfuric acid to bituminous substance should be between about 30 to 180 equivalents of sulfuric acid per kilogram of bituminous substance. The reaction temperature should be in the region of room temperature, i.e., plus or minus 20° C., and the sulfonation time should be about 1 to 12 hours.

#### EXAMPLE 4

##### Treatment of radioactive liquids

To water containing 32 p.p.m. calcium and 4.8 p.p.m. magnesium, a tracer of Sr<sup>85</sup> was added in amount sufficient to cause a counting rate of 20 counts/sec./ml. This water was passed through a column containing a bed of par-

6

ticles of partially sulfonated bituminous substance, having a mesh size of 30 to 65 mesh and prepared according to the method of Example 2, at a rate of 30 bed volumes per hour. After 300 bed volumes of water had passed through the column, a breakthrough of 10% Sr<sup>85</sup> was detected.

The particles of partially sulfonated bitumin were then dried and melted and the ion exchanged radioactive ions were fixed in an unleachable manner in the bituminous substance. The melting reduced the volume of the bituminous substance by a factor of 5. The total volume reduction factor is thus 1500, i.e., the bituminous substance decontaminated 300 bed volumes of water before saturation and the bituminous particles when melted were reduced to a compact mass of bitumin occupying 1/5 of the volume occupied by the particles and having a many times lower surface area. The volume reduction may be increased by initially complexing some non-radioactive cations in the liquid in such a manner that only the free radioactive cations will take the free places on the ion exchange material.

#### EXAMPLE 5

The procedure of Example 4 was repeated with EDTA (ethylenediaminetetracetic acid) added to the radioactive water so that 0.2 meq. calcium/liter of water remained free, i.e., the Mg and Ca ions were complexed with the exception of 0.2 meq. Ca/liter. This water was passed through the column, the 10% breakthrough occurred only after 1600 bed volumes had passed through the column, the total volume reduction being a factor of about 8000.

I claim:

1. A method of decontaminating radioactive liquids containing radioactive ions comprising; providing a solid, fusible, partly sulfonated bituminous substance; thereafter contacting said fusible, partially sulfonated bituminous substance with a liquid waste containing radioactive ions to ion exchange said radioactive ions with the sulfonated portion of said bituminous substance; and finally, melting said bituminous substance to reduce the volume thereof and encapsulate said radioactive ions.

2. A method as claimed in claim 1 wherein the partially sulfonated bituminous substance is a bituminous substance prepared by treating a bituminous substance for less than 10 minutes with SO<sub>3</sub> compounds in a ratio of 5 to 20 equivalents SO<sub>3</sub>/kilogram of bituminous substance and at a temperature between 50° C. and 120° C.

3. A method as claimed in claim 1 in which the partially sulfonated bituminous substance comprises a mixture of a substantially infusible, partially sulfonated bituminous substance and a non-sulfonated fusible bituminous substance.

4. A method as claimed in claim 3 in which the sulfonation of the bituminous substance is conducted in two stages.

5. A method of decontaminating radioactive liquids containing radioactive ions, comprising; providing a solid, partially sulfonated bituminous substance which is substantially infusible but will cohere when heated; thereafter contacting said bitumin with a liquid waste containing radioactive ions to ion exchange said radioactive ions with the sulfonated portion of said bituminous substance; and finally, compacting said bituminous substance under the influence of heat to reduce the volume thereof and encapsulate said radioactive ions.

6. A method as claimed in claim 1 in which the ion exchange material is in granular form.

7. A method as claimed in claim 5 in which the ion exchange material is in granular form.

8. A method as claimed in claim 1 in which the partially sulfonated bituminous substance is in the hydrogen form.

9. A method as claimed in claim 5 in which the partially sulfonated bituminous substance is in the hydrogen form.

7

10. A method as claimed in claim 1 in which the partially sulfonated bituminous substance is in the sodium form.

11. A method as claimed in claim 5 in which the partially sulfonated bituminous substance is in the sodium form. 5

12. A compacted mass of ion exchange material prepared from a bituminous substance having at least a portion of its exchangeable ions replaced with radioactive ions, said mass of compacted bituminous substance forming a matrix surrounding, encapsulating and immobilizing said radioactive ions whereby the leaching of said radioactive ions from said mass is effectively prevented. 10

13. A mass as claimed in claim 12 in which the partially sulfonated bituminous substance comprises a mixture of a substantially infusible, partially sulfonated bituminous substance and a non-sulfonated fusible bituminous substance. 15

14. A mass as claimed in claim 12 in which the partially sulfonated bituminous substance is in the hydrogen form. 20 23—337

8

15. A mass as claimed in claim 12 in which the said partially sulfonated bituminous substance is in the sodium form.

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U.S. Cl. X.R.