(12) UK Patent Application (19) GB (11) 2 096 390 A

(21) Application No 8205165
(22) Date of filing 22 Feb 1982
(30) Priority data
(31) 250439
(32) 2 Apr 1981
(33) United States of America (US)
(43) Application published 13 Oct 1982
(51) INT CL[3] G21F 9/08 9/16
(52) Domestic classification G6R 1A10
(56) Documents cited
GB 1580611
GB 1547952
GB 1378229
GB 0959751
(58) Field of search G6R

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(54) Volume reduction and encapsulation process for water containing low level radioactive waste

(57) In encapsulating solutions or slurries of radio-active waste within polymeric material for disposal, the water is removed therefrom by adding a water insoluble liquid forming a low boiling azeotrope and evaporating the azeotrope, and then a polymerisable composition is dispersed throughout the dewatered waste and allowed to set.

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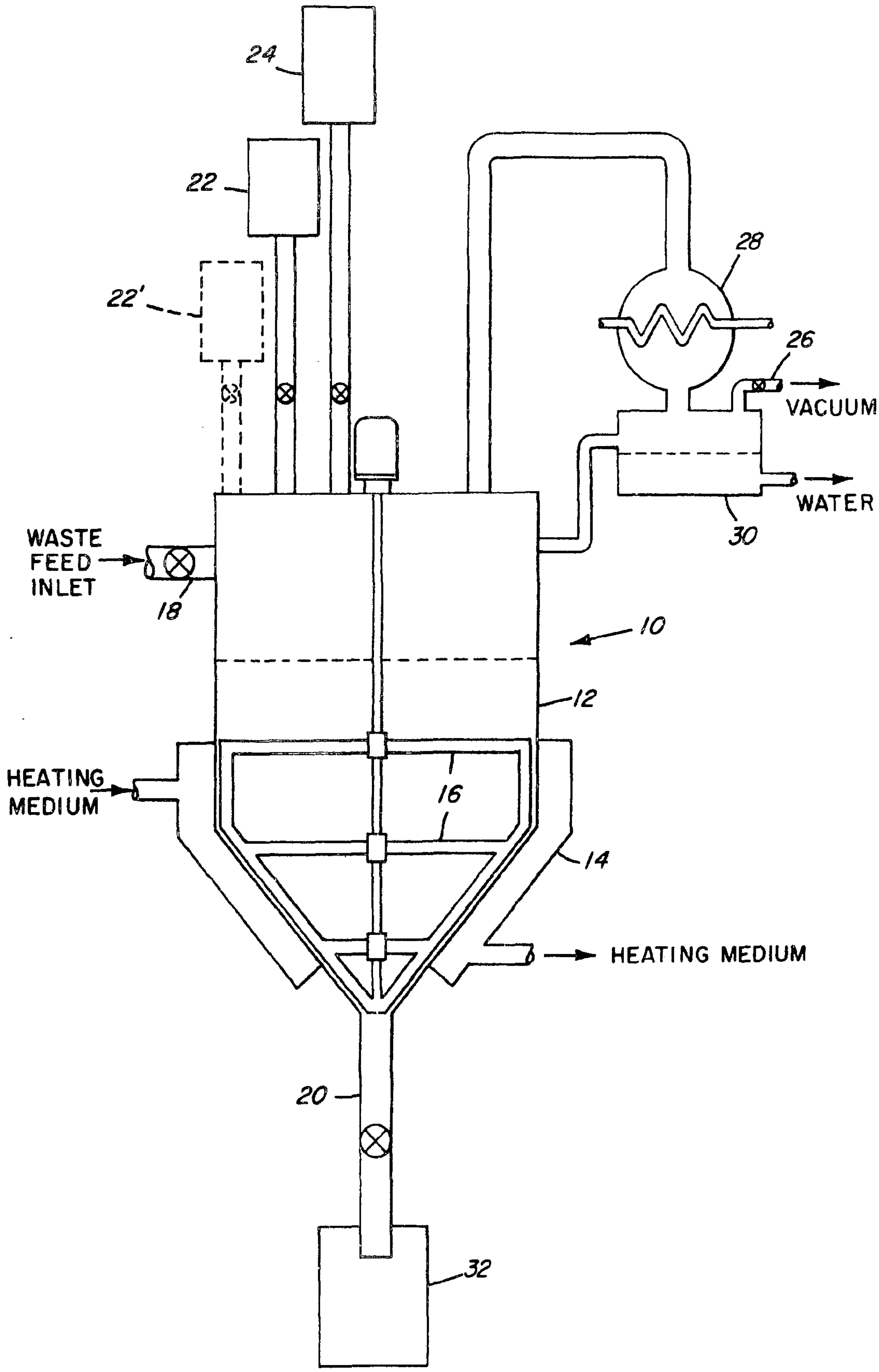
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HEATING MEDIUM
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SPECIFICATION

Volume reduction and encapsulation process for water containing low level radioactive waste

This invention generally relates to the prepartion of waste materials containing water as solutions or slurries for effective disposal thereof. The invention particularly relates to the disposal of water-containing radioactive waste materials from nuclear power plants, and provides for their volume reduction and safe storage or burial.

Light water moderated and cooled nuclear power plants require extensive water treatment facilities to maintain the water within prescribed radioactivity and purity levels. Corrosion products entrained within the water become activated during their passage through the reactor core and some fission products leak out of the fuel bundles into the water. The treatment processes for purifying such water produce effluents of ion exchange regeneration solutions which commonly comprise solutions of sodium sulfate, filter sludges combined with either ion exchange or other filter-aid materials, and waste ion exchange resins that are all somewhat radioactive. These wastes require encapsulation to minimize ground-water leaching and burial for the final disposal.

Heretofore, these wastes have been mixed with concrete, asphalt, or urea-formaldehyde as encapsulation media. However, these processes do not provide a significant volume reduction, and in the case of concrete encapsulation, the volume increases. Burial and transportation cost have escalated appreciably in recent years which make burial volume and hence waste volume reduction of paramount economic importance. Leachability of radioactive materials from the buried waste into the ground water has also become a very sensitive issue. None of the above encapsulating materials provide a low enough leach rate, over a long term period, to avoid problems in this area.

Other disposal techniques are discussed in U.S. Patent No. 4,077,901 where the radioactive waste solutions, or slurries, are dispersed within a polymerization agent which forms a solid polymer about the waste for disposal. Also, U.S. Patent No. 4,119,560 discusses dehydrating the wastes with a heated inert carrier with ultimate encapsulation of the dried waste in a polymerized epoxy for disposal.

This invention comprises a method and system for dewatering a waste stream by azeotropic distillation utilizing a non-water soluble hydrocarbon, and encapsulating the residue of the dewatered waste with an organic polymer. In the preferred embodiments of the invention, a polymerizable monomer may function as a component of the azeotropic mixture to facilitate water removal and then become part of the encapsulating polymer.

The present invention will be further described, by way of example only, with reference to the accompanying drawing, in which:

The invention utilizes a principle of azeotropic drying to remove water from contaminated solutions or slurries. The distillation temperatures are always lower than the lowest boiling component of the mixture. The dewatered waste reduced in volume and preferentially wet with a polymerizable monomer is thereupon encapsulated by combining with a coreactive polymer encasing the waste therein.

In the preferred embodiments of this invention, a polymerizing monomer such as styrene is utilized for producing the azeotropic mixture and as a co-reactant for producing the encapsulating polymer. Thus, the same liquid providing a component of the azeotropic mixture for the dewatering operation can be retained with and/or returned to the waste to produce the encapsulating polymer. Referring to the drawing, the exemplary dewatering and encapsulating waste disposal system 10 shown therein also serves to aptly illustrate the process operations and sequence of this invention as well as a suitable means for the performance thereof.

Water-containing waste material is conducted to a vessel 12 of the system 10 for removal of water and encapsulation according to this invention. Vessel 12 is provided with a suitable heating means such as a jacket 14 for a heating medium, e.g. steam or hot water, and mixing means to combine ingredients therein such as a mixer blade 16 with a drive such as a motor. The vessel 12 includes a feed inlet 18 for receiving water-containing waste, and an outlet 20, preferably located in a lower portion thereof, for the discharge of its contents therefrom.

A water insoluble organic liquid is fed into the vessel 12 from a supply thereof such as container 22 for mixing with the water-containing waste and thereby form a low boiling temperature mixture of the organic liquid with the water.

The system can be operated with a number of organic material feeds. For example, styrene can be fed from tank 22 and this material used to form the azeotrope with water for the water removal, or materials containing styrene such as commercially available unsaturated polyesters or curable vinyl terminated esters can be added from tank 22 with the styrene component of the mixture being used to form the azeotrope with water.

The system 10 can be provided with a plurality of supply containers 22, 22', etc., for providing the vessel 12 with a supply of any one or several of azeotropic mixture and/or polymer producing agents.

The vessel 12 can also be provided as needed or appropriate with a supply, such as container 24, of any applicable polymerization governing agent comprising a polymerization inhibitor such as mono-t-butyl hydroquinone, or a polymerization catalyst or curing agent such as benzyl peroxide.

When the vessel 12 holding water containing waste is supplied with a water insoluble organic liquid, such as for example, the polymerizable monomer styrene or vinyl toluene, the organic liquid is dispersed through the water to form an azeotropic mixture of a relatively low boiling temperature. Upon heating the azeotropic mixture, such as with steam in jacket 14, the low boiling temperature mixture of water and organic liquid is evaporated and the vapor mixture directed into a condenser 28 connected with the evaporating vessel 12. Evaporation of the azeotropic mixture can be encouraged and the temperature thereof lowered by reducing the atmospheric pressure within the vessel. Vessel pressure reduction means constitutes a connection to a vacuum source 26 such as a vacuum pump.

The water-organic vapor of the evaporated azeotropic mixture is cooled to a liquid within the condenser 28 and the condensate passed to a liquid phase separator 30. The two liquid phases are parted within the separator and the water phase discharged therefrom.

The water insoluble organic liquid phase is decanted from above the water phase within the separator 30 and can be cycled back into the evaporating vessel 12 for reuse, or otherwise disposed of. The separated and recycled organic liquid can be used to further the formation of an azeotropic mixture with water for an ongoing low temperature evaporation in a continuing operation, or simply returned for subsequent batch operation.

Accordingly, the dewatering of the water-containing waste can proceed to any degree of elimination of the water content by either renewing or recycling the organic liquid for maintaining the azeotropic mixture and its evaporation.

Upon achieving a suitable degree of volume reduction through dewatering of the water-containing waste, encapsulation of the residual waste material with an organic polymer can take place.

Polymerizing agents, catalyst, additional monomers or unsaturated prepolymers can be supplied to vessel 12 by any one or combination of sources thereof and forms. Organic compositions which will polymerize through conventional reactions can be newly introduced into the vessel 12 through supply containers 22, 22′, etc., for combination with the waste and its encapsulation. However, in accordance with a preferred embodiment of this invention, at least one of the ingredients of the polymerization for the encapsulation is preferably utilized whenever feasible or possible in the dewatering operation as a component of the low boiling temperature azeotropic mixture. When the organic liquid suitably fulfils the dual role of forming the azeotropic mixture with the water and an ingredient of the encapsulating polymer, it need only be cycled back into the evaporating vessel 12 from the condensor 28 and separator 30 and therein participates in the encapsulating polymer formation. Of course, a portion of the polymer producing ingredient(s) can be provided by recycling from the azeotropic mixture evaporation and a portion thereof can be newly introduced. Or one component for producing the polymer can be used to produce the azeotropic mixture and cycled back to the vessel 12 while one or more other components for the polymer can be newly introduced directly into the vessel for the encapsulation.

In any case, the polymer compositions, polymerizing reactions and polymerizing agents and the like employed in their formation, comprising monomers, catalysts and curing agents, all comprise conventional compositions, reactions and ingredients well known in the art. Note for example the polymers described in U.S. Patent Nos. 4,077,901 and 4,119,560.

Polymers of the unsaturated polyester, curable vinyl terminated esters and epoxy classes are generally suitable for waste encapsulation and comprise preferred embodiments of this invention.

Polyesters and di-vinyl ester comprise examples of suitable polymers that may include styrene or vinyl toluene as a monomer. A typical unsaturated polyester polymer comprises a reaction product of phthalic acid, maleic acid and polyhydric alcohol. And a typical curable vinyl terminated ester comprises a bis-(acrylate ester) of a diol.

The following procedure illustrates an embodiment of the invention employing a polymer such as an unsaturated polyester or di-vinyl ester and a monomer of the type of styrene or vinyl toluene which functions as a component of the azeotropic mixture and the encapsulating polymer. Styrene is combined with a water-containing waste containing 20 weight percent of sodium sulfate to simulate an ion exchange regeneration solution effluent, in a suitable vessel heated with steam such as that shown in the drawing as 12. Styrene is added in an amount of about 17 pounds per a 100 pounds of sodium sulfate salt in the waste water. The mixture is heated and maintained at its boiling point of 94°C at atmospheric pressure and the azeotrope of water-styrene forms and evaporates in a ratio of about 59.1% styrene and about 40.9% water. The vapor is collected and condensed, and water and styrene being insoluble in one another, the two phases are separated, the water disposed of in any apt manner, and the styrene is cycled back to the waste solution or slurry within the vessel. Recycling of the styrene is continued until substantially all water is removed from the 100 pounds of sodium sulfate. At this stage the temperature will rise with the expiration of any remaining azeotropic styrene-water mixture, and the temperature increase signals the substantial elimination of the water.

Aproximately 26 pounds of polyester or di-vinyl ester ingredients are added to the dewatered waste and dispersed therethrough by mixing. The ingredients of the particular polymer formulation can be introduced individually such as from the illustrated supply containers 22, 22′, etc., or as a commercially available composite of the ingredients. Approximately 0.3 lbs. of catalyst, such as benzyl peroxide, is added to the other components within the vessel 12, and the combination of polymerizing agents and dewatered waste discharged into a container 32. Alternatively, the polymerization activating agent such as catalyst or curing agent can be applied after the polymer ingredients and dewatered waste have been removed from the evaporating vessel. With either procedure, the polymerization is effected with the waste within the polymerizing ingredient(s), providing a solid mass encasing the dewatered waste material within a low leaching polymer. Volume reduction from a 20% sodium sulfate solution to a solidified product ranges from four to ten fold.

Polymerization catalyst are available that become effective at a given temperature level. Thus, the catalyst can be introduced along with the other polymerizing agents in an azeotropic mixture and the dewatering by azeotropic mixture evaporation carried out below the catalyst activation temperature to forestall polymerization until after an adequate volume of water has been removed. After discharging the waste-polymer mixture into the product drum 32, the drum is heated to initiate polymerization. Any residual catalyst in vessel 12 will not polymerize the subsequent batch since the catalyst trigger temperatures will not be reached.

Commercially available composites of polymer ingredients containing styrene frequently include polymerization inhibitors to preclude the premature polymerization of the styrene. Reduced pressures can be used to carry out the dewatering evaporation at lower or more moderate temperatures compatable with the inhibited styrene containing formula, and polymerization carried out at subsequently applied higher temperature levels.

Typical epoxy-type polymer compositions, or the ingredients therefor, do not include styrene or a comparable ingredient producing an azeotropic mixture with water. Thus when using an opoxy-type polymer encapsulation, a suitable water insoluble organic liquid such as benzene, toluene, petroleum ethers, a ketone or an aldehyde is included or added to the water-containing waste at a rate or quantity suitable to produce the azeotropic mixture with the water. For example, the azeotropic boiling temperatures and composition ratios for two of said organic liquids at atmospheric pressure are as follows:

Azeotrope	*Boiling Temp.*	*Vapor Composition Wt. % H_2O*
Benzene-H_2O	69.3°C	8.9
Toluene-H_2O	84.1°C	19.6

In addition to being insoluble in water to enable easy separation from water, the organic liquid for azeotropic formation must have boiling temperature substantially below the ingredients of the polymer formulation if all such components are to be included at the same time. Also, the liquid should be selected to provide a minimum boiling temperature azeotrope, and the higher the proportion of water in the azeotropic ratio the more efficient the dewatering operation.

An illustration of another embodiment of the invention utilizing an epoxy-type encapsulating polymer is as follows. A water-borne waste containing about 20 weight percent of sodium sulfate is fed into the vessel 12 containing toluene and an epoxy resin formulation of diglycidyl ether of bisphenol A (Epon 828, Shell Chemical Co.). The waste is applied until about 100 pounds of NA_2SO_4 has been accumulated. The temperature in the vessel is held at about 85°C while the water-toluene azeotrope evaporates, and the toluene is returned while the water is discarded. A temperature rise indicates substantially all water removed, for a volume reduction of about 7 fold. The toluene is then evaporated at about 111°C to remove it from the epoxy and waste, and the evaporated toluene is condensed and saved for reuse.

The residue of waste and epoxy resin is mixed to distribute the resin through the waste, a hardening agent consisting of 5 to 6 parts by weight of diethylamino propyl amine, per 100 parts by weight of the epoxy resin, is added and blended with the residue, and a cure thereof effected to encase the waste within the solidified epoxy polymer.

Claims

1. A method of removing water from water-containing waste material and encapsulating the resultant dewatered waste material, comprising the combination of steps of:

a) combining with water and non-volatile waste material a water insoluble organic liquid forming a low boiling azeotropic mixture with water, and heating said azeotropic mixture to evaporate the water and organic liquid and thereby dewater the waste material; and

b) dispersing a polymerizable composition through the dewatered waste material, and forming a polymer encapsulation about the dewatered waste material.

2. A method as claimed in claim 1, wherein the water insoluble organic liquid comprises a polymerizable monomer.

3. A method as claimed in claim 2, wherein the polymerizable monomer comprises styrene or vinyl toluene.

4. A method as claimed in claim 2 or claim 3, wherein the water insoluble organic liquid is polymerizing component forming the polymer encapsulation about the dewatered waste material.

5. A method as claimed in any one of claims 2 to 4, wherein copolymerizing agent is combined with the monomer to form the polymer encapsulation about the dewatered waste material.

6. A method as claimed in claim 4, wherein a polymerizing catalyst is added to the monomer to form the polymer encapsulation about the dewatered waste material.

7. A method as claimed in any one of the preceding claims, wherein the polymer encapsulating the dewatered waste material comprises a polymer selected from polyesters, di-vinyl esters and epoxies.

8. A method as claimed in any one of the preceding claims, wherein the water insoluble organic liquid is a polymerizable monomer, and said monomer is separated from the water of the evaporated azeotropic mixture and combined with dewatered waste material to form a polymer encapsulation about the dewatered waste material.

9. A method as claimed in any one of the preceding claims, wherein the waste material comprises radioactive ingredients.

10. A method of reducing the volume of water in water-containing waste material and encapsulating the resultant dewatered waste material, comprising the combination of steps of:

a) combining with water containing therein waste material a water insoluble organic liquid forming a low boiling temperature azeotropic mixture with water, and heating said azeotropic mixture to evaporate the water and organic liquid and thereby dewater the waste material;

b) separating the organic liquid from the water of the evaporated azeotropic mixture; and

c) dispersing a polymerizing agent through the dewatered waste material, and forming a polymer encapsulation about the dewatered waste material.

11. A method as claimed in claim 10, wherein the organic liquid separated from the water of the evaporated azeotropic mixture is recovered and combined with the waste material.

12. A method as claimed in claim 10 or claim 11, wherein the water insoluble organic liquid comprises a polymerizable monomer.

13. A method as claimed in claim 12, wherein the polymerizable monomer is styrene.

14. A method as claimed in any one of claims 10 to 13, wherein the water insoluble organic liquid comprises a polymerizable monomer and when separated from the water of the evaporated azeotropic mixture said monomer is recovered and combined with the waste material for encapsulation thereof.

15. A method as claimed in claim 14, wherein a copolymerizing agent is combined with the monomer to form the encapsulating polymer about the waste material.

16. A method as claimed in claim 14, wherein a polymerizing catalyst is added to the monomer to form the encapsulating polymer about the waste material.

17. A method as claimed in any one of claims 10 to 16, wherein the polymer encapsulating the waste material comprises a copolymer selected from the group consisting of unsaturated polyester, curable vinyl terminated esters and epoxies.

18. A method as claimed in any one of claims 10 to 17, wherein the heating of the azeotropic mixture to evaporate the water and organic liquid thereof is at a low temperature below the boiling temperature of water with soluble waste material therein.

19. A method as claimed in any one of claims 10 to 18, wherein the waste material comprises radioactive ingredients.

20. A method of reducing the volume of water in water-containing radioactive waste material and encapsulating the resultant dewatered radioactive waste material in a polymeric material, comprising the combination of steps of:

a) combining with water containing therein radioactive waste material a water insoluble organic liquid forming a low boiling temperature azeotropic mixture with water, and heating said azeotropic mixture to a low temperature of less than 100°C to evaporate the water and organic liquid and thereby dewater the waste material;

b) separating the organic liquid from the water of the evaporated azeotropic mixture and combining the separated organic liquid with the waste material; and

c) dispersing a polymerizing agent through the dewatered radioactive waste material, and forming a polymer encapsulation about the dewatered radioactive waste material.

21. A method as claimed in claim 20, wherein the water insoluble liquid is a polymerizable monomer and comprises the polymerizing agent.

22. A method as claimed in claim 21, wherein the polymerizable monomer is styrene.

23. A method as claimed in claims 21 or 22, wherein a polymerizing catalyst is added to the monomer to form the encapsulating polymer about the radioactive waste material.

24. A method as claimed in any one of claims 20 to 23, wherein the polymer encapsulating the radioactive waste material comprises a copolymer selected from unsaturated polyesters, curable vinyl terminated esters and epoxies.

25. A method as claimed in any one of claims 20 to 24, wherein the polymer encapsulating the radioactive waste material comprises an epoxy polymer, and the water insoluble organic liquid of the azeotropic mixture comprises at least water insoluble organic liquid selected from the group consisting of benzene, toluene, petroleum ether, a ketone and an aldehyde.

26. A method as claimed in claim 1, 10 or 20, substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

27. Waste material when removed by a method as claimed in any one of the preceding claims.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1982. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.