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(54) **Immobilisation of hazardous waste**

(57) Hazardous waste, e.g. radioactive waste, particularly that containing caesium-137, is immobilised by mixing with cement and solidifiable organic polymeric material. When first

mixed, the organic material is preferably liquid and at this time can be polymerisable or already polymerised. The hardening can result from cooling or further polymerisation e.g. cross linking. The organic material may be wax, or a polyester which may be unsaturated and cross-linkable by reaction with styrene.

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SPECIFICATION

Immobilisation of hazardous waste

5 This invention relates to the immobilisation of hazardous waste, more particularly radioactive waste, in order to reduce the likelihood of contamination of the environment by leakage of hazardous materials from such waste during prolonged storage.

10 Disposal of hazardous waste is commonly by way of land burial, deep geologic burial, disposal on the sea bed or burial under the sea bed. It is particularly important that hazardous water-soluble components of waste be sufficiently immobilised to prevent these components being leached out into the environment upon accidental contact of the waste with water.

15 A number of techniques for immobilising hazardous waste have been proposed hitherto. One method has been to encapsulate the waste. Cement has been widely used for encapsulation because of its ready availability and low price, and its ability to react with aqueous materials to form solids. These solids are thermally very stable and resistant to radiation. However, highly soluble hazardous materials are only very poorly immobilised in conventional cement products. One such material is caesium-137, which is a natural fission product generated during the decay of radioactive fuel elements. The half-life of caesium-137 is long, and its concentration in waste from nuclear power stations is high. Consequently, immobilisation techniques which fail to inhibit caesium leaching are highly unsatisfactory.

20 Polymers have also been proposed to provide this encapsulation, but these have the drawback of being expensive and, more importantly, being susceptible to break-down by irradiation.

25 Workers in this field have therefore been searching for alternative encapsulating materials which will avoid these disadvantages incurred with cement and polymers. The present invention is based upon the surprising discovery that, by using a combination of cement and polymeric material, the disadvantages of using cement and polymer singly can be substantially reduced.

30 According to the present invention, there is provided hazardous waste immobilised in a mixture of cement and a polymeric organic material. This mixture would normally be an intimate mixture.

A preferred process for producing such a mixture comprises the steps of

- 35 i) forming a mixture of waste with an intimate blend of cement and a liquid organic material,
 40 ii) hydrating said cement, and
 45 iii) simultaneously with, or subsequent to step ii), allowing or causing the organic material to solidify. The organic material, which as aforesaid must be polymeric when the waste is immobilised,

50 can be polymeric when performing step i) or can become polymerised in step iii). If the organic material is polymeric when performing step i), it

55 can be solidified in step iii) by cooling or by further polymerisation, for example cross-linking.

60 The organic material may, for example, be a wax which is blended with the cement at a temperature above its melting point, and which is later solidified by cooling. Preferably, however, the organic material is a compound or mixture of compounds which is polymerisable in the presence of hydrating cement and which becomes solid upon polymerisation. The polymerisable organic material may contain, for example,
 70 hydroxy, ether, ester or epoxy groups (including polyhydroxy, polyether, polyester and polyepoxy groups), and is preferably unsaturated.

75 It is particularly preferred that the final polymeric material is a cross-linked polymer. Cross-linked polymers are preferably formed by reaction of an unsaturated polymer with an unsaturated cross-linking agent, such as styrene. Cross-linking of such materials may be affected by exposure to ionising radiations (for example, λ -radiation), or addition of free-radical initiators such as organic peroxides and ammonium persulphate.

80 Examples of cements which are suitable for use in the present invention are those materials which conform to British Standards 12 (1958), 4027 (1966), 4246 (1968), 4248 (1968), 1370 (1958), 146 (1968) or 915 (1947). Pozzolan cements may also be used, such cements being made by combining any suitable cement (such as those described above) with a pozzolan, i.e. any material which forms a solid monolith in the presence of water and calcium oxide or hydroxide. Pozzolans occur naturally as volcanic deposits and are also produced in coal-fired power stations in the form of pulverised fly ash.

85 The process of the present invention is applicable to the disposal of waste in either liquid or solid form, or in the form of a semi-solid, for example a sludge. The waste may be radioactive waste, as mentioned above, particularly low and intermediate level wastes which have gross radioactivity up to 10,000 curies per cubic metre. Alternatively the waste may be chemical and include highly poisonous materials.

90 The waste is preferably mixed with cement shortly before the cement is mixed with the solidifiable material. If the waste is in an aqueous medium (for example, as an aqueous solution or an aqueous dispersion), hydration of the cement will, of course, automatically be effected by mixing the waste with the cement.

95 The waste/cement mixture is preferably blended with the solidifiable material by relatively low shear mixing, since high shear mixing may cause the cement and the solidifiable material to form two visibly discernable phases.

100 If the waste material comprises radioactive caesium in soluble form, it is particularly preferred to cause precipitation of such caesium by adding nickel ferrocyanide. This step is preferably performed before mixing the waste with cement.

105 Particular embodiments of the present invention are now described by way of example.

Example 1

2 moles of phthalic anhydride, 1 mole of maleic anhydride, 2.15 moles of propylene glycol and 1.15 moles of diethylene glycol were heated under reflux in a stirred flask and in an atmosphere of nitrogen until the condensation product had an acid number of 28-30 KOH/g. The water produced in the condensation reaction was removed by azeotropic distillation with xylene. The product, a viscous, amber-coloured liquid, was then diluted with half its weight of styrene. The resulting resin mixture was easily pourable, and could be safely stored and transported. Premature polymerisation and cross-linking of the resin mixture was prevented by the addition of 100 ppm of hydroquinone.

When required for use, ammonium persulphate (1.7g) was added to resin mixture (85.7g) in an electrically driven mixer and stirred at high speed for two minutes.

71.4g of simulated waste, herein defined as consisting of a molar solution of caesium chloride in water, was added to 142.8g of ordinary Portland Cement (OPC) in a second vessel and mixed. This cementitious mixture was then slowly added to the resin mixture prepared as described above, with very low speed mixing. The product obtained (Composite 1) was a pourable, apparently single phase mixture, which was cast into paraffin wax moulds and stored prior to testing.

After storage for 28 days under standard conditions in a vessel containing air saturated with water vapour, the leaching characteristics were determined.

The test employed was based on a draft proposal issued by the International Standards Organisation (Ref: 150/TC85/5C5/WGSN), and was chosen to permit comparative leaching information to be obtained in a short period of time. The test conditions expose a sample to continuously redistilled water at 100°C, under which condition the rate of leaching is enormously accelerated compared with the rate at which leaching might take place under typical waste storage conditions.

It was found that under the test conditions, leaching of caesium from Composite 1 was very markedly slower than from control samples using cement without organic polymer.

Composite 1 was also tested for compressive strength in a Mohr and Federhoff Compression Testing Machine under constant load. The fracture of the specimen was not entirely brittle, and some evidence of plastic deformation before failure was observed. A compressive strength of approximately 1.3 MN m⁻² was measured, this figure being sufficiently high to suggest the suitability of Composite 1 as a waste immobilisation medium.

Example 2

1 mole of phthalic anhydride, 4 moles of maleic anhydride and 5 moles of propylene glycol were used in the preparation of this polymer. The synthesis was carried out as described in Example

65 1. The resulting resin was then diluted with half its weight of styrene.

When the resin mixture was required for use, 0.3g of cobalt octoate (a solution in white spirit containing 10% cobalt) and 6.0g of a highly oxylated castor oil was added to the resin (60g) and stirred at high speed for two minutes. The mixture produced was amber in colour and quite stable. Methyl ethyl ketone peroxide 1.2g (a free-radical initiator) was then added to this mixture and high speed stirring was continued for another two minutes.

50 g of the same simulated waste was added to 100 g of Portland cement in a second vessel and mixed. This cementitious mixture was then slowly added to the resin mixture, with very low speed mixing.

The castor oil acted as a non ionic emulsifying agent and was found to assist in stabilising the mixture during the cross-linking process.

The product obtained (Composite 2) was stored for 28 days and then tested as described in Example 1. Leaching of caesium from Composite 2 was likewise found to be very markedly slower than with control samples using cement without organic polymer.

The incorporation of Intermediate Level Waste with a specific activity of 10,000 Ci per cubic metre within a composite would be expected to give an internal integrated dose of approximately 500 Mrads over the first 100 years of its life. Specimens of Composite 2 were subjected to 500 Mrad doses of λ -radiation in order to test the radiation stability. No significant changes in leaching characteristics were detected. However, such a radiation dose was found to increase the compressive strength of Composite 2 from approximately 10 MN m⁻² to approximately 14 MN m⁻². Similar figures were obtained when pozzolanic cement was used in place of Portland cement.

Example 3

The same simulated waste was pre-treated before mixing with cement, by adding 78.9g nickel sulphate heptahydrate per litre of 1 molar caesium chloride, followed by adding 59.3g potassium ferrocyanide trihydrate. This caused the caesium waste to precipitate out as a caesium/nickel ferrocyanide complex. The remainder of the procedure was as described in Example 2. The resulting composite (Composite 3) was found to have leaching characteristics which were improved over those of Composite 2.

Example 4

1 mole of Bisphenol A was refluxed at 125°C with 4 moles of epichlorohydrin in an atmosphere of nitrogen. The mixture was continuously stirred for 16 hours, during which period 2 moles of sodium hydroxide (as 30% NaOH) was added dropwise in order to maintain the mixture alkaline to phenolphthalein. The resulting organic layer was separated and dried with sodium under vacuum. The product (diglycidyl-ether of

Bisphenol A, M. W. approx. 340) was then diluted with half its weight of styrene, and acrylic acid added in an amount of 144g per mole of diglycidyl ether of Bisphenol A.

5 Polymerisation of the resulting resin mixture was initiated by the addition of 0.2g of N,N'-dimethylaniline and 2.4g of benzoyl peroxide (a 50% paste in paraffin) to the resin mixture (60g).
10 6g of highly oxylated castor oil was also added, with high speed stirring for 2 minutes.

50g of the same simulated waste was mixed with 100g of pozzolanic cement in a second vessel, and the cementitious mixture was then added to the resin mixture with low speed mixing.
15 The resulting Composite 4 was cured and tested for leaching characteristics by the procedures described in Example 1 and it was found to be even more resistant to leaching.

Example 5

20 The pre-treatment of Example 3 was followed, and the procedure of Example 4 then adopted.

The resulting Composite 5 was found to have even better leaching characteristics compared with Composite 4.

25 It will be appreciated that many different polymers, cements, cross-linking agents and polymerisation initiators may be used in accordance with the present invention.

For example the cross-linking agent in
30 Examples 4 and 5 could be any of a number of different monomers e.g. unsaturated amines or acids. Furthermore, the proportions of such components may also be varied, as may the ratio of aqueous medium to cement. In the Examples, a
35 cement/waste ratio of 0.5 was chosen, but this ratio may be varied widely, for example between 0.95 and 0.33. Generally, the lower this ratio is, the more efficient is the immobilisation of caesium within the resulting composite.

40 If, for any reason, it is desired to increase the compressive strength and/or the tensile strength of any of the composites described above, this can be achieved by incorporating reinforcing agents
45 into the composite. Examples of such reinforcing agents are steel rods and turnings, and fibrous materials such as wood shavings, glass fibre and carbon fibre.

CLAIMS

50 1. Hazardous waste immobilised in a mixture of cement and a polymeric organic material.

2. Immobilised waste according to claim 1 wherein the polymeric organic material is a polyester.

55 3. Immobilised waste according to claim 1 or claim 2 wherein the polymeric organic material is cross-linked.

4. Immobilised waste according to claim 3 wherein the cross-linked polymer is the product of

60 a cross-linking reaction between an unsaturated polymer and an unsaturated cross-linking agent.

5. Immobilised waste according to claim 4 wherein the unsaturated cross-linking agent is styrene.

65 6. Immobilised waste according to any preceding claim wherein the waste is radioactive waste.

7. A process for immobilising hazardous waste in a mixture of cement and a synthetic polymeric organic material, comprising the steps of

70 i) forming a mixture of waste, cement and a polymerisable liquid organic material,

ii) hydrating said cement, and

75 iii) simultaneously with, or subsequent to step ii), allowing or causing the organic material to polymerise and thereby to solidify.

8. A process according to claim 7, wherein the polymerisable liquid organic material contains hydroxy, ether, ester or epoxy groups.

9. A process according to claim 7 or claim 8
80 wherein the polymerisable liquid organic material is a polyester.

10. A process according to claim 7, 8 or 9 wherein the polymerisable liquid organic material is unsaturated.

85 11. A process according to any of claims 7 to 10 wherein the polymerisable liquid organic material is solidified by a cross-linking reaction.

90 12. A process according to claim 11 wherein the cross-linking reaction is between an unsaturated polymer and an unsaturated cross-linking agent.

13. A process according to claim 12 wherein the cross-linking agent is styrene.

95 14. A process according to any of claims 7 to 13 wherein the waste is radioactive waste.

15. A process according to claim 14 wherein the waste comprises radioactive caesium, and said caesium is caused to precipitate by the addition of nickel ferrocyanide prior to said mixing step.

100 16. A process for immobilising hazardous waste in a mixture of cement and a polymeric organic material, comprising the steps of

i) forming a mixture of waste, cement and a liquid organic polymer,

105 ii) hydrating said cement, and iii) simultaneously with, or subsequent to step ii), allowing or causing the liquid organic polymer to solidify.

110 17. A process according to claim 16 wherein said organic polymer is a wax which is mixed with the cement at a temperature above its melting point and which is subsequently solidified by cooling.

115 18. A process for immobilising waste substantially as hereinbefore described with reference to the Examples.

19. Hazardous waste when immobilised by a process according to any of claims 7 to 18.