May 3, 1966 H. D. BIXBY 3,249,551

METHOD AND PRODUCT FOR THE DISPOSAL OF RADIOACTIVE WASTES

Filed June 3, 1963 2 Sheets-Sheet 1

Fig. 1.

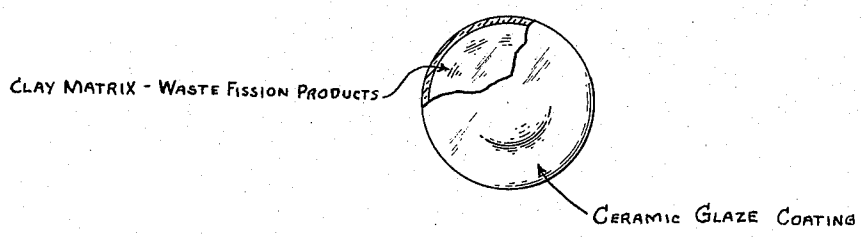
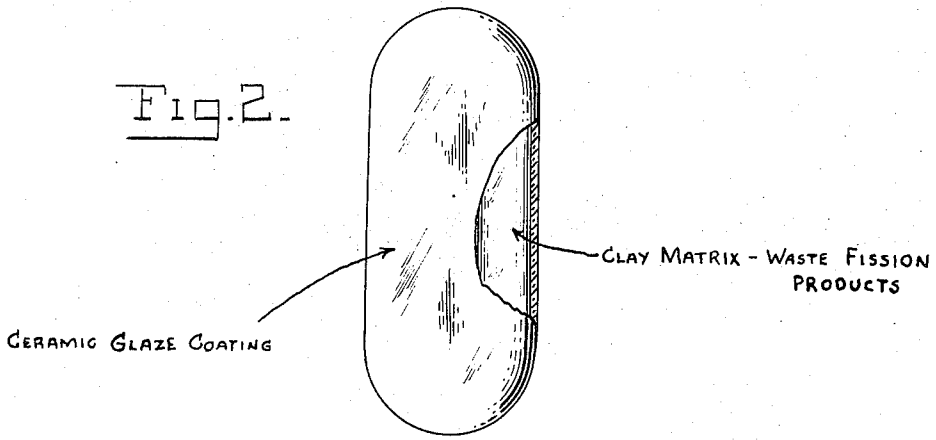


Fig. 2.



INVENTOR.
HENRY D. BIXBY
BY
James A. Koehl.

May 3, 1966 H. D. BIXBY 3,249,551

METHOD AND PRODUCT FOR THE DISPOSAL OF RADIOACTIVE WASTES

Filed June 3, 1963 2 Sheets-Sheet 2

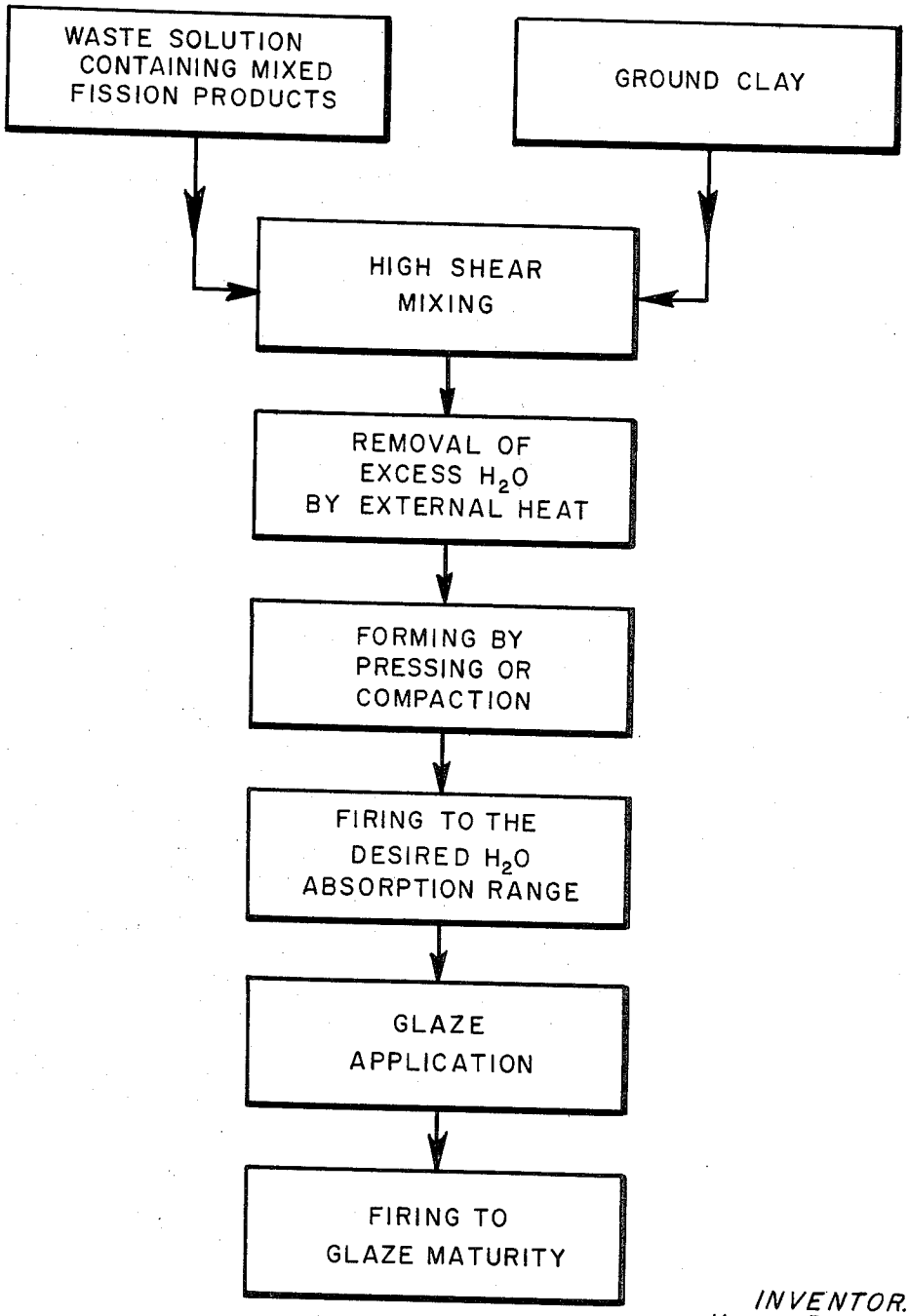


Fig. 3

INVENTOR.
Henry D. Bixby

BY
Webb, Burden, Robinson & Webb
HIS ATTORNEYS

United States Patent Office 3,249,551 Patented May 3, 1966

3,249,551

METHOD AND PRODUCT FOR THE DISPOSAL OF RADIOACTIVE WASTES

Henry D. Bixby, Beaver Falls, Pa., assignor of one-half to David L. Neil, Greenwich, Conn.

Filed June 3, 1963, Ser. No. 285,850
23 Claims. (Cl. 252—301.1)

This application is a continuation-in-part of my application Serial No. 145,605, filed October 17, 1961, relating to "Method and Product for the Disposal of Radioactive Wastes" and now abandoned.

This invention relates to a method and product for the ultimate disposal of high-level radioactive waste materials without endangering human, plant, or animal life.

The ultimate disposal of high-level radioactive wastes from chemical processing of spent nuclear reactor materials without endangering human, plant, or animal life presents a problem of significance in the development and growth of nuclear-power production. This is made more acute by international tensions, resulting in increased use of nuclear fuels in the propulsion of naval vessels, aircraft, and mobile power generation equipment. Disposal of high-level nuclear wastes, largely from Government installations is presently met by storage of unconcentrated liquids in underground steel-lined concrete vaults at locations such as Hanford, Washington and Savannah River, Georgia. Storage of wastes by this technique is both expensive and troublesome. Any leakage of these radioactive materials, especially Strontium^{90} with its bone-destroying powers, could endanger all human, plant, and animal life over a considerable area.

According to the teaching of Ginnell (Patent No. 2,616,847), advantage is taken of the property of montmorillonite to exchange cations with a waste fission product solution and to some extent to absorb cations. Upon removal of the excess liquid content, the montmorillonite is dried and fired to fix the radioactive cations. According to the teaching of Hatch (Patent No. 2,918,700) improved contact and ion exchange is provided between the waste fission product solution and montmorillonite to increase the surface area for the cation exchange.

The disclosures of the above reference patents are dependent solely on a base-exchange chemical reaction whereby radioactive cations exchange with nonradioactive ions present in the montmorillonite structure and, for this exchange to take place, the radioactive cations must have specific ion-exchange potentials, thus restricting the type as well as the amount of radioactive ions that can be immobilized. Radioactive ruthenium, Ru^{106}, which is always present in fission wastes, does not enter into these base-exchange reactions, hence cannot be immobilized by teachings of the prior art. Subsequent studies of the degree of take-up of the radioactive cations, and their retention when the fired montmorillonite was subjected to leaching tests, shows that only relatively small quantities of radioactive isotopes were taken up. Also, the tests showed substantial amounts of the radioactivity that had been taken up were released in leach tests.

Other investigators have attempted to incorporate such radioactive wastes in various glass compositions by adding the waste solutions to dry powdered glassforming materials, evaporating the mixture to dryness, and firing the mass until a glass has formed. Again, the quantity of radioactive isotope take-up and the retention of the radioactive isotopes during leaching tests has been unsatisfactory. In these attempts, the release of the radioactivity at the surface of the glass is facilitated by the proximity of the radioactive cations to the leach solution by their uniform distribution throughout the glass.

Evans (Patent No. 3,000,072) proposes forming a synthetic mica structure with the fission-product ions occupying sites in the mica crystal lattice. Such a lattice is limited as to types and amounts of ions than can be placed therein, and the process is therefore restricted in the amount and types of fission products that can be immobilized by the solid state reaction. In the structure of the synthetic mica, the patentee informs us that it appears that the fission products cesium and strontium take the place of the potassium and/or magnesium as it appears in natural fluorphlogopite. Further, Evans' process can have only a limited value in large scale usage, by reason of the "hot-pressing" technique requiring complex equipment, making the process suited for use only on small individual batch operations with the likelihood of radioactive contamination of dies which have short service life.

To the best of my knowledge, no one has ever before proposed or suggested contacting any of a wide choice of clays with a solution of high-level radioactive wastes and preparing and conditioning same enabling the take-up of radioactive isotopes in amounts appreciably in excess of that heretofore possible with processes of the prior art depending upon (1) base-exchange alone, or (2) by solid state lattice replacement alone, and encapsulating the mixture in a ceramic glaze composition highly resistant to aqueous leaching. My invention relates to use of clay or equivalent materials for production of an end product which effects, by acceptable and convincing tests, an appreciable increase in the take-up of the radioactive isotopes, including ruthenium, Ru^{106}, heretofore not immobilized by processes of the prior art. This take-up results from mechanical and/or chemical entrapment of the radioactive isotopes by the clay and/or ionic bonding to the clay. These radioactive isotopes are sensibly completely immobilized within the structure of the product to prevent migration of the isotopes to the exterior surface of the product. By finalizing procedures in the process of the clay, the core or matrix of the product is contained in a continuous encapsulating coating of a selected ceramic glaze composition which is compatible with the physical characteristics of the fired clay and insures improved resistance to solution, leaching and erosion.

One important feature of my invention is firing the treated clay-waste fission product mixture in reducing atmospheres, thereby maintaining the radioactive ruthenium isotope Ru^{106} in the form of RuO_2 rather than in the volatile form RuO_4, thus achieving the successful immobilization of this isotope, and at the same time avoiding a bloated clay matrix due to incomplete oxidation of the accessory minerals, which bloating is definitely injurious to the integrity of the end product.

Specifically, my method for disposal of high-level radioactive waste materials comprises mixing a clay and high-level radioactive waste materials to disperse the waste materials in the clay, to form a mixture of the clay and the waste materials and to effect mechanical and chemical entrapment of and ionic bonding of radioactive isotopes of the waste materials by and to the clay. Next, the mixture is treated, for example by heating, to reduce its moisture content to less than 4% by weight and then is subjected to pressure sufficient to remove substantially all entrapped air. Thereafter, the mixture is formed into a radioactive waste-containing fired ceramic body by heating it to a temperature less than the maturity temperature of the clay but sufficiently high to obtain in the clay a water absorption value which is less than that at which moisture is not withdrawn by the fired clay from a ceramic glaze which is later applied to the mixture in an amount where cracks form in the glaze upon drying substantially at room temperature, and which is greater than that at which the glaze cracks during firing of the glaze and the body to maturing temperature of the glaze. This heating is carried out at a rate below that at which the

mixture bloats or experiences uneven and erratic shrinkage.

To the fired ceramic body is applied a ceramic glaze coating to completely surround and encapsulate the body. Then the glaze-coated body is fired to the maturing temperature of the glaze for fusing the glaze upon the ceramic body and for making the glaze coating impervious. This ceramic glaze has a thermal coefficient of expansion compatible with that of the body and such that during cooling from the maturing temperature the glaze is not under tensile stress greater than the tensile strength of the glaze itself and is not under compressive stress greater than the compression strength of the glaze itself. Also, the glaze has a maturity temperature range compatible with that of the clay and such that the temperature range to mature the glaze is substantially that required to mature the body. Additionally, the glaze has a chemical composition resistant to aqueous leaching.

In the accompanying drawings, I have shown two embodiments of the product of my invention, in which:

FIGURE 1 is a view partly in elevation and partly in section of one geometrical form of the resultant product of the method; and

FIGURE 2 is a similar view showing another geometrical form of the resultant product;

FIGURE 3 represents a detailed flow diagram of the process.

In practicing my invention, a wide variety of clays may be used regardless of their base-exchange capacities and mineralogical compositions. Among such clays are kaolinite, illite, bentonite, attapulgite, halloysite, shales, fireclays, ball clays, etc., or mixtures of these clays with other mineral species. Satisfactory clays are preferably fine grained, having a particle size distribution which offers in a body of the same maximum surface area of the particles interiorly of the body, maximum interstitial volume, and optimum pore structure for the retention of radioactive isotopes when compacted and fired, together with minimum volume of the fired body. I have found that the base-exchange capacity of the clay used in the practice of my invention is not greatly significant, for example: a fireclay having a much lower base-exchange capacity than montmorillonite can be made to take-up more radioactive fission products than by base-exchange alone; and that the ability of the clay to take-up and retain radioactive waste isotopes does not depend solely on base-exchange and is a function of mechanical and chemical entrapment, as well as adsorption and absorption.

The liquid containing the high-level radioactive wastes may be either solution or a suspension. Presently known types of waste solutions generally resulting from fuel reprocessing have been classified as Purex, TBP–25, Darex, FAN, Fluoride-volatility, Thorex, Redox, and Hexone–25, indicative of the various chemical processes involved. In the practice of my invention, I have employed Purex-type waste solutions The wastes specified above are typical of the types of high-level wastes which can be produced by a large multi-purpose plant capable of preprocessing a variety of nuclear fuels. High-level wastes may be described and characterized generally as being either acid or alkaline concentrated aqueous salt solutions. Acid solutions, generally, are based on nitric acid. Alkaline solutions, generally, are nitric acid solutions which have been neutralized with sodium hydroxide. In addition to constituents other than fission products acid and alkali, the solutions may contain minor amounts of such ions as iron, aluminum, sulfate, chromium, nickel, and others, as well as residual fuel and breeder materials. These latter two are only present as trace elements. Present in the Purex waste solutions are fission product isotopes formed in the fission reaction. Some of the sufficiently long-lived activity isotopes and those produced in sufficient yield are of major importance from the standpoint of long-term waste disposal. These are principally: $Cesium^{137}$, $Strontium^{90}$, $Ruthenium^{106}$, $Zirconium^{95}$, and $Cerium^{144}$. Total fission product concentrations generally are 0.10% of less of the mole weight of the waste solution, Typical activity levels of Purex waste solution, neutralized and delivered to storage, are in the range of 250 to 1000 curies per liter. This may be further concentrated as desired for further processing and for the practice of my invention.

This liquid is introduced into the clay in my method in such a manner that airborne radioactive contamination is minimized. This is accomplised by pouring the liquid into the clay, either directly or in increments, or, conversely, by adding the clay to the liquid directly or in increments. Introduction of the radioactive waste liquid by spraying or atomizing is undesirable because of the danger of airborne radioactive contamination.

In order to obtain satisfactory mixing and dispersion of the radioactive isotopes within the clay material, a variety of mixing equipment and techniques may be employed. Included in such equipment are mullers, ribbon mixers, Sigma mixers, planetary mixers, or others suitable for high-shear mixing. The equipment and procedures should be such that dusting of the mix is minimized to prevent radioactive contamination. Preferred practice of my invention includes continuing the mixing operation until the mixture is sufficiently dry for the subsequent forming operations, i.e., until the moisture content of the mixture is less than 4% by weight. Such heat as is required may be applied to hasten the adjustment of the water content of the mixture prior to forming, but not in such quantities or at such rates as to induce pyrochemical alteration of any of the batch constituents, and effecting only the removal of physical water.

Forming of the treated clay mixture may be performed by the application of pressure preferably, but not to the exclusion of other forming processes well known in the art. In the practice of my invention, I prefer to dry press or compact the treated mixture in a steel mold using pressures which are sufficient to remove substantially all entrapped air from the mixture and which produce the desired shape of body for the product. Preferably, the desired shape is one which is substantially curvilinear throughout. These pressures impart to the radioactive waste-clay mixture a green modulus of rupture of at least about 150 p.s.i., and sufficient strength to the body to withstand normal subsequent handling procedures. Some specific pressures employed have included those in the range from about 1000 p.s.i. to 12,000 p.s.i.

In addition to removal of the entrapped air from the mixture, this compaction step effects mechanical entrapment of the radioactive isotopes in the clay and in the case where the wastes are in a suspension, entrapment of components of the slurry which carries the wastes. Furthermore, the mixture is reduced in volume and the compacted body experiences uniform shrinkage in volume during subsequent firing steps and achieves homogeneity along with a suitable texture for application of and adherence of a ceramic glaze coating to be described more in detail hereinafter.

Proper mold design and/or shaping operations are employed to avoid sharp corners or edges on the formed smooth exterior surface of the product, minimizing chipping and dusting, and to insure the integrity and ease of application of the glaze coating.

The next subsequent step in the practice of my invention involves a thermal treatment of the formed product which imparts adequate strength thereto for handling in subsequent processing and which makes a fired ceramic body. Such thermal treatment comprises heating the formed body to a temperature less than the maturity temperature of the clay but sufficiently high to obtain in the clay a water absorption value which is less than that at which moisture is not withdrawn by the fired clay from the ceramic glaze to be applied to the body in an amount whereat cracks form in the glaze upon drying substan-

tially at room temperature. Thus, the body must be fired to a temperature which reduces its water absorption property for a given clay to a value below that at which the porosity of the fired body removes and sucks out moisture from te glaze in amounts which cause cracks in the glaze upon drying at room temperatures and thereby destroys continuity in the glaze during firing and cooling and prevents production of an impervious coating upon the body.

On the other hand, the body must not be fired to maturity or to those temperatures at which the water absorption property of the clay is such that the glaze develops cracks therein during firing the body with the glaze applied thereto to the maturing temperature range of the glaze. Where the body is initially fired to maturity temperature or to a temperature at which its water absorption property is too low, the glaze coating applied to the body encounters stress concentrations at the interface between it and the body followed by generation of cracks or ruptures in the glaze during firing to the maturity temperature range of the glaze. Such stress concentration occurs because the body has been initially heated to such a degree that substantially all shrinkage has been taken out of same whereby the glaze contracts during firing while the body experiences very little, or residual shrinkage. Furthermore, production of too low a water absorption property in the body tends to prevent good adherence of the glaze to the body due to inability of the glaze to form a bond between it and the body. Thus, in order to obtain the required good adherence of the glaze to the body, together with imperviousness in the coating, the water absorption property of the body must not be so low as to avoid bonding the glaze to the body and not so high as to withdraw so much moisture from the glaze that cracks develop in the glaze upon drying at room temperatures.

For some clays, this heating is carried out to obtain a water absorption value in the body of between 4 and 12% measured by the ASTM C–126 test method for fired masonry or ceramic products.

The rate of heating to produce this fired ceramic body is less than that which generates bloating of the body and erratic shrinkage caused by inability of the gases formed during firing to escape from the mixture. Where the rate of heating is too high, the body expands during a part of the heating instead of shrinking. Presence of bloating in the body tends to prevent good adherence of the glaze coating to the body and to avoid production of glaze continuity and imperviousness.

Some such thermal treatments employ temperatures not less than 1000° F. depending on the maturing nature of the clays and waste solutions comprising the mixture. For example, a highly refractory clay would require temperatures as high as or even greater than 2500° F.

This thermal treatment insolubilizes certain soluble constituents of the waste liquid, which would be deleterious to the glazing operation; for example, if the soluble constituents are not insolubilized, they will migrate to the glaze interface, crystallize, and thereby rupture the glaze coating. In the thermal treatment, the atmosphere may be either reducing, neutral, or oxidizing, but preferably reducing or neutral atmospheres to prevent the oxidation of the ruthenium from RuO_2 to the volatile form RuO_4.

The next step in the practice of my invention comprises the application of a continuous ceramic glaze coating to the fired waste-containing ceramic body, to provide a homogeneous impermeable barrier highly resistant to the removal of the entrapped fission products by leaching action and erosion. The composition of the ceramic glaze coating is such that the physical characteristics of the glaze and the body are compatible in such properties as thermal coefficients of expansion and maturing temperature ranges. Also, the composition of the ceramic glaze coating is formulated to provide resistance to chemical attack through leaching by aqueous solutions. The glaze coating may be applied to the ceramic body by methods well known in the art, such as spraying, atomizing, or dipping.

Regarding the thermal coefficients of expansion of the clay and the ceramic glaze which are compatible, these coefficients of expansion are such that during cooling from the maturing temperature of the glaze, the glaze is not under a tensile stress greater than the tensile strength of the glaze itself and is not under compressive stress greater than the compression strength of the glaze. When the thermal coefficients of expansion of the clay and glaze are so related, continuity and imperviousness in the glaze coating are achieved.

As to compatibility of the maturing temperature ranges of the clay and glaze, same are such that the temperature range to mature the glaze is substantially that required to mature the clay. In this way, the body obtains desired physical properties from the standpoint of strength, porosity and fired density when the glaze is heated to maturity. Furthermore, the body is not fired to such a temperature that it encounters a melting to a viscous fluid and a loss in integrity of form or shape.

The next step in the practice of my invention comprises a thermal treatment or firing to mature the glaze and to form a continuous and impervious encapsulation of the waste-containing ceramic body. During this step, the ceramic body acquires maturity and more complete fixation of the radioactive fission products within the body.

The preferably geometry of the ultimate product in the practice of my invention is governed by at least two considerations. The first is to provide the minimum surface area per unit weight, in order to offer the leach solution minimum contact area. For example, it is well known that for a given mass, a sphere has the minimum surface area of any geometrical configuration. The second consideration is the avoidance of sharp corners and edges to provide continuity of the glaze coating, and to minimize the likelihood of the chipping of edges and corners during handling. I have found that a product which is substantially curvilinear throughout is advantageous.

The size of the ultimate product and the concentration of the radioactivity contained herein, are governed by at least two factors. The first is the ability of the clay to mature and retain fission products without loss of integrity of shape and structure due to the heat released by the decay of the fission products. The second is the ability of the ultimate product to dissipate the heat released by the decay of fission products in the residue, without damage to the product; that is, the amount of heat resulting from the fission product decay cannot exceed the amount of heat that can be dissipated by the clay (a function of its specific heat value), without causing the loss of integrity of shape, structure and integrity of the ceramic coating.

As aforestated, in carrying my invention into practice, use can be made of any one of a wide choice of clays or clay-like materials. Preferably, the clays have a range of particle sizes such that the particles are not greater than an equivalent spherical diameter which traverses or drops through an 18 mesh screen. Highly satisfactory results have been obtained using Lower Kittanning clay from the Western Pennsylvania-Eastern Ohio area, which clay has the following screen analysis:

	Percent by Weight				
	A	B	C	D	E
Retained on 20 Mesh	1.1	0.7	0.2	0.0	0.0
Retained on 40 Mesh	23.5	22.0	21.6	19.1	18.0
Retained on 70 Mesh	18.2	19.5	20.3	22.2	24.0
Retained on 100 Mesh	12.1	11.4	10.8	10.4	9.5
Retained on 200 Mesh	11.9	13.0	14.2	15.3	16.3
Retained on Pan	23.2	23.4	32.9	33.0	32.2
	100.0	100.0	100.0	100.0	100.0

The clay consists principally of kaolinite, quartzite, and minor amounts of illite, rutile, dolomite, siderite, and pyrite, being typical of the coal-measure fireclays of said area.

One non-limiting example of my invention is as follows:

To 500 grams of the clay, I add 100 ml. of a simulated waste solution of the Purex type. The solution was prepared from the following: $Fe(NO_3)_3 \cdot 9H_2O$, 80.8 grams; Na_2SO_4, 14.2 grams; conc. H_2SO_4, 1.4 ml.; $NaNO_3$, 40 grams; these materials being dissolved in boiling distilled water and diluted to one liter. To the cooled solution, salts of the following elements were added in quantities such as to approximate the quantities of the said elements normally found in a Purex-type waste solution; thus on a molar basis, the solution contained:

Ion:	Molarity
Na^{+1}	5.1
Fe^{+3}	0.2
SO_4^{-2}	0.2
OH^{-1}	0.8
NO_3^{-1}	4.5

plus tracer quantities of the radioactive isotopes, e.g., Strontium^{90}, Cerium^{144}, Cesium^{137}, Zirconium^{95}, and Ruthenium^{106}. In a Purex-type waste solution, the weight ratio of iron plus sodium to fission-product cations is approximately 130 to 1; that is, fission-product cations constitute about 0.8% of the total cations added to the clay.

The combination of the simulated waste solution and the clay was intimately mixed within the bowl of a Hobart planetary-type mixer, and the mixing action continued until substantially all the water had evaporated. To hasten the drying of the mixture and the evaporation of the water, heat was applied to the exterior of the mixing bowl by immersing it in a container of boiling water. When the mixture had a water content suitable for the forming process, the heat was removed, and the clay mass passed through a screen of 12–18 mesh to remove any lumps which had formed.

The thus prepared mixture of clay and waste fission-products was compacted and formed in a steel die at pressures of approximately 8,000 p.s.i. to form cylinders about ¾ inch in diameter by ¾ inch in length. After removal from the die, the corners of the top and bottom of the cylinder were shaped to form rounded ends, and a 1/16 inch diameter hole drilled in one end to a depth sufficient to permit the insertion of a setter pin to provide support during the subsequent firing and glazing operations. The setter pins are made of well-sintered, aluminum oxide (Al_2O_3) in the shape of a pyrometric cone. A drop of the ceramic glaze was inserted in the hole prior to the insertion of the setter pin to provide mechanical strength during the subsequent operations.

The formed samples were then fired in an electrically heated tube-type furnace at the rate of approximately 400° F. per hour to a maximum temperature of 1900° F. The atmosphere of the furnace was reducing, being maintained in this condition by the introduction of an excess flow of forming gas (90 vol. percent N_2–10 vol. percent H_2) during the entire firing process.

After cooling to room temperature in the above atmosphere, the samples were removed from the furnace, inspected and then the ceramic glaze composition applied to the entire surface of the sample by dipping to provide a coating 8–10 mils thick. The composition of the ceramic glaze is formulated to provide maximum resistance to aqueous leaching and to have physical characteristics matching those of the clay body, to insure freedom from crazing, pin-holing, and to provide compatible maturing temperatures.

In carrying out my invention, the following range of glaze compositions can be employed, Example A being the preferred, but not limiting composition:

Empirical molecular formula

Constituent	Molecular Equivalents			
	A	B	C	D
K_2O	0.082	0.059	0.080	0.069
Na_2O	0.137	0.099	0.133	0.115
CaO	0.354	0.277	0.343	0.304
BaO	0.187	0.149	0.165	0.158
ZnO	0.182	0.364	0.224	0.302
MgO	0.058	0.051	0.055	0.051
Al_2O_3	0.410	0.312	0.446	0.349
SiO_2	2.770	1.675	3.150	2.390
ZrO_2	0.302		0.317	0.259

The glazed samples were then given a second thermal treatment by firing in the electrically-heated tube-type furnace at the rate of 400° F. per hour to a maximum temperature of between 2100° F. and 2200° F. The atmosphere of the furnace was reducing, being maintained in this condition by the introduction of an excess flow of forming gas (90 vol. percent N_2–10 vol. per cent H_2) during the entire firing process.

After cooling to room temperature in the above atmosphere, the samples were removed from the furnace, inspected, the setter pins broken off, and the samples weighed. The samples were then introduced into distilled water and tested for 2 hrs. boil absorption according to the ASTM designation for this procedure. After the absorption had been determined, the samples were then subjected to the leaching tests.

In order to obtain comparative data on the efficiency of the glaze coating as to its leach resistance and barrier effect, additional samples were prepared in a manner identical to the above, but excluding the application of the ceramic glaze coating. To distinguish between these samples in subsequent comment, those prepared without the ceramic glaze are referred to as "unglazed" and those prepared in the normal manner are referred to as "glazed."

Both glazed and unglazed samples were leached at the boiling point of distilled water, under reflux for three consecutive leach periods varying in length from three to six days. The leaching medium consisted of 200 ml. of singly distilled water to which was added 0.5 mg. of inactive carrier of each of the radioactive isotopes contained in the samples, to minimize the possibilities of selective adsorption upon the walls of the glassware.

At the conclusion of each of the leach periods, the leach solutions were acidified and cautiously evaporated to a volume of 1–2 ml. and the radioactivity measured with a scintillation crystal gamma-ray well spectrometer. Activity leached out was expressed in terms of percentage of the activity initially incorporated into the samples. The half-lives of the species incorporated were considered to be sufficiently long that it was not necessary to correct for decay occurring during the fabrication and testing of the samples.

The following are the results of the leaching tests:

Leaching Period, Days	Percent of Activity Leached	
	Glazed	Unglazed
4.08 [a]	0.00055	0.00098
3.00	0.00020	0.00200
6.00	0.00028	0.00130

[a] Including activity removed by 2-hour (0.08 day) ASTM water porosity test.

Identification of the particular isotopes present in the above total quantities showed that cesium was predominant and that although the ruthenium^{106} was detected in the leach of the unglazed sample, no detectable amount

of this isotope was found in the glazed sample leach tests.

While I have shown and described preferred embodiments of my invention, it may be otherwise embodied within the scope of the following claims.

I claim:

1. In a method for disposal of high-level radioactive waste materials, the invention comprising the steps of making from a mixture of clay and high-level radioactive waste materials a waste-containing fired ceramic body by heating said mixture to a temperature less than the maturity temperature of said clay but sufficiently high to obtain in said clay a water absorption value defined by being less than that at which moisture is not withdrawn by said clay from a ceramic glaze to be applied to said mixture in an amount whereat cracks form in said glaze upon drying substantially at room temperature and being greater than that at which said glaze cracks during firing of said glaze and said body to maturing temperature of said glaze, carrying out said heating at a rate below that at which said mixture bloats, applying a ceramic glaze coating to said fired ceramic body to completely surround and encapsulate same, firing said glaze-coated body to a maturing temperature of said ceramic glaze for fusing said glaze upon said ceramic body and for making said glaze coating impervious, said ceramic glaze having a thermal coefficient of expansion compatible with that of said body and such that during cooling from said maturing temperature said glaze is not under tensile stress greater than the tensile strength of the glaze itself and is not under compressive stress greater than the compression strength of the glaze itself, said glaze having a maturity temperature range compatible with that of said clay and such that the temperature range to mature said glaze is substantially that required to mature said body, said glaze having a chemical composition resistant to aqueous leaching.

2. The invention of claim 1 characterized by carrying out said heating and firing steps in one of a reducing atmosphere and a neutral atmosphere.

3. The invention of claim 1 characterized by heating said mixture to a temperature which obtains a water absorption value between about 4–12%.

4. The invention of claim 1 characterized by said heating rate being about 400° F. per hour.

5. The invention of claim 1 characterized by carrying out said heating and firing steps in one of a reducing atmosphere and a neutral atmosphere and by said heating rate being about 400° F. per hour.

6. The invention of claim 1 characterized by carrying out said heating and firing steps in one of a reducing atmosphere and a neutral atmosphere, by heating said mixture to a temperature which obtains a water absorption value between about 4–12%, and by said heating rate being about 400° F. per hour.

7. A method for disposal of high-level radioactive waste materials comprising the steps of mixing a clay and high-level radioactive waste materials to disperse said waste materials in said clay and to form a mixture of said clay and said waste materials, subjecting said mixture to pressure sufficient to remove substantially all entrapped air from said mixture, forming a waste-containing fired ceramic body by heating said mixture to a temperature less than the maturity temperature of said clay but sufficiently high to obtain in said clay a water absorption value defined by being less than that at which moisture is not withdrawn by said clay from a ceramic glaze to be applied to said mixture in an amount whereat cracks form in said glaze upon drying substantially at room temperature and being greater than that at which said glaze cracks during firing of said glaze and said body to maturing temperature of said glaze, carrying out said heating at a rate below that at which said mixture bloats, applying a ceramic glaze coating to said fired ceramic body to completely surround and encapsulate same, firing said glaze-coated body to a maturing temperature of said ceramic glaze for fusing said glaze upon said ceramic body and for making said glaze coating impervious, said ceramic glaze having a thermal coefficient of expansion compatible with that of said body and such that during cooling from said maturing temperature said glaze is not under tensile stress greater than the tensile strength of the glaze itself and is not under compressive stress greater than the compression strength of the glaze itself, said glaze having a maturity temperature range compatible with that of said clay and such that the temperature range to mature said glaze is substantially that required to mature said body, said glaze having a chemical composition resistant to aqueous leaching.

8. The method of claim 7 characterized by carrying out said heating and firing steps in one of a reducing atmosphere and a neutral atmosphere.

9. The method of claim 7 characterized by before subjecting said mixture to pressure, processing said mixture to reduce its moisture content to less than 4% by weight.

10. The method of claim 9 characterized by carrying out said heating and firing steps in one of a reducing atmosphere and a neutral atmosphere.

11. The method of claim 9 characterized by carrying out said heating and firing steps in one of a reducing atmosphere and a neutral atmosphere, by subjecting said mixture to pressure sufficient to obtain a green modulus of rupture of at least 150 p.s.i., and by heating said mixture to a temperature which obtains a water absorption value between about 4–12%.

12. The method of claim 7 characterized by subjecting said mixture to pressure sufficient to obtain a green modulus of rupture of at least 150 p.s.i.

13. The method of claim 7 characterized by heating said mixture to a temperature which obtains a water absorption value between about 4–12%.

14. The method of claim 7 characterized by carrying out said heating and firing steps in one of a reducing atmosphere and a neutral atmosphere, by subjecting said mixture to pressure sufficient to obtain a green modulus of rupture of at least 150 p.s.i., and by heating said mixture to a temperature which obtains a water absorption value between about 4–12%.

15. The method of claim 7 characterized by subjecting said mixture to a pressure substantially about 1000 p.s.i.–12,000 p.s.i.

16. The method of claim 7 wherein said heating of said mixture to a temperature less than the maturity temperature of said clay but sufficiently high to obtain said defined water absorption value is carried out at substantially 1000° F.–2500° F.

17. The method of claim 7 characterized by before subjecting said mixture to pressure, processing said mixture to reduce its moisture content to less than 4% by weight, and by subjecting said mixture to pressure sufficient to obtain a green modulus of rupture of at least 150 p.s.i.

18. The method of claim 17 characterized by carrying out said heating and firing steps in one of a reducing atmosphere and a neutral atmosphere.

19. A product for disposal of radioactive waste materials comprising a body formed from a mixture of clay and high-level radioactive waste materials with said waste materials being dispersed in said clay and retained therein by at least one of mechanical entrapment in, chemical entrapment in, and ionic bonding to said clay, a ceramic glaze coating completely surrounding and encapsulating said body, being impervious and being fused upon and adhering to said body, said body prior to encapsulation having a water absorption value defined by being less than that at which moisture is not withdrawn from said clay by said ceramic glaze in an amount whereat cracks form in said glaze upon drying substantially at room temperature and being greater than that at which said glaze cracks during firing of said glaze and said body to mature same, said body and said glabe being matured, said ceramic glaze having a chemical composition resistant to aqueous leaching, said clay and said glaze having com-

patible coefficients of expansion such that during cooling from maturing temperature range said glaze is not under tensile stress greater than the tensile strength of the glaze itself and is not under compressive stress greater than the compression strength of the glaze itself, said clay and said glaze having compatible maturing temperature ranges.

20. The produce of claim **19** characterized by said clay having a particle size not greater than an equivalent spherical diameter which traverses an 18 mesh screen.

21. The product of claim **19** characterized by said body prior to being matured having a green modulus of rupture of at least 150 p.s.i.

22. The product of claim **19** characterized by said clay having a particle size not greater than an equivalent spherical diameter which traverses an **18** mesh screen, and by said body prior to being matured having a green molulus of rupture of at least 150 p.s.i.

23. The product of claim **19** characterized by the shape thereof being substantially curvilinear.

References Cited by the Examiner

UNITED STATES PATENTS

2,616,847	11/1952	Ginell	252—301.1
2,741,008	4/1956	Snoddy	264—62
2,864,711	12/1958	Boyce	102—39
3,000,072	8/1959	Evans.	

OTHER REFERENCES

AEC Documents: TID Mar. 18, 1958, pp. 5–6, 10–11, 13–14 and 16–17.

"Atomics and Nuclear Energy," vol. 8, 1957, publication of Leonard Hill Technical Group, pp. 117.

"Atomic Energy Waste," Glueckauf, Interscience Publishers, Inc., 1961, pp. 297.

Struxness et al.: "Second United Nations International Conference on the Peaceful Uses of Atomic Energy," vol. 18, 1958, pp. 44.

Loeding et al.: "Second United Nations International Conference on the Peaceful Uses of Atomic Energy," vol. 18, 1958, pp. 60–62.

LEON D. ROSDOL, *Primary Examiner.*

CARL D. QUARFORTH, REUBEN EPSTEIN, *Examiners.*

A. G. BOWEN, B. R. PADGETT, *Assistant Examiners.*