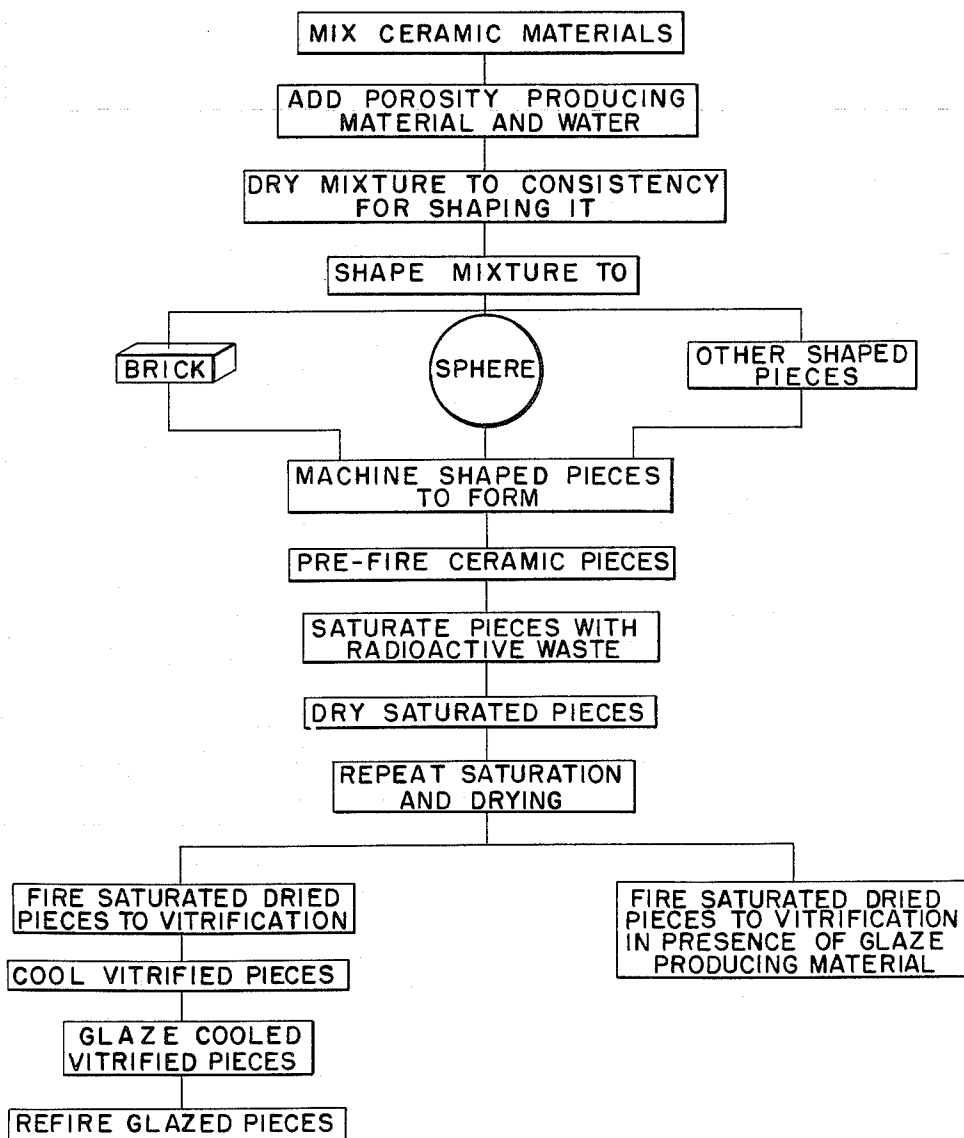


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WASTE AND RESULTANT PRODUCT  
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**METHOD FOR DISPOSING OF RADIOACTIVE WASTE AND RESULTANT PRODUCT**

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This invention relates to a method for disposing of radioactive waste and to the resultant product in which the radioactive materials have become combined with ceramic material in the form of insoluble silicates and other insoluble or slightly soluble minerals. The resultant product has two distinct uses: (1) to serve as a means of disposing safely of radioactive waste by burial of the product and (2) to serve as a source of useful radiation to provide heat for buildings, for sterilization of foods and other products, and other purposes.

The disposal of "hot" or radioactive waste presents a serious problem, particularly when it exists as a liquid. Such wastes may continue to release dangerous radiation for periods of 600 to 800 years or more. Due to the great danger of contamination of ground waters, the waste cannot be buried or safely disposed of in the earth. It cannot be disposed of at sea without resultant contamination, not to mention the cost and danger of contamination during transportation. Liquid wastes usually are highly acid in nature and corrode or destroy containing tanks, even those made of stainless steel, concrete or other resistant material.

One of the sources of radioactive waste is the de-cladding of fuel elements. Such elements often are clad with aluminum or stainless steel and when they are removed from a reactor, they are taken to processing plants and the metal case is removed by solution acids. The acid bath usually is largely nitric acid and may contain phosphoric acid. The bath is strongly acidic, with a pH of about 1. The used bath therefore is a highly acidic solution containing aluminum or iron nitrate and other salts and is highly radioactive, emitting high concentrations of dangerous radiation.

The present practice of storing radioactive wastes in underground tanks made of mild steel or stainless steel often enclosed in thick concrete is expensive and has practical and economic limitations as well as not capable of providing safe storage for the long periods of time involved. The present volume of such wastes is over 100 million gallons, increasing rapidly as the amount of work in the nuclear field expands.

The object of my invention is to produce a method whereby the radioactive waste materials are caused to combine with other materials for the purpose of forming insoluble silicates and other insoluble or slightly soluble minerals in a product which can be buried without danger of leaching out soluble radioactive material.

To achieve the desired result, I have produced a product which may have varied forms, which during an intermediate stage of production has maximum porosity and absorptive capacity, and in its final stage is completely vitrified and non-absorptive. If any pores exist, they are closed pores. The intermediate highly porous and absorptive condition of my product permits maximum saturation thereof by the waste material. In its final condition, the product contains the radioactive material combined with other materials in a composition from which the components cannot be leached out by ground waters or otherwise.

In addition to affording a means for safe disposal of radioactive waste by burial, the product produced by my method has great economic value in that the radioactive materials contained therein can be put to use to serve mankind. My product, if made in brick-like shapes

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of suitable size, can be arranged in a checker-work through which air can be warmed. In interlocking tubular shapes, food and other products may be passed for sterilization purposes through the tubes of my invention which then serve as a radioactive tunnel. In spherical form, the product provides ideal bed materials for the generation of heat. These uses are merely examples of the many to which the product resulting from practice of the following described method can be put.

The flow sheet filed herein shows diagrammatically the several steps of my method.

The first step of my method consists in manufacturing a highly porous and absorptive ceramic product. Preferably I use the following named ingredients in approximately the proportions stated:

|                                                                         | Percent |
|-------------------------------------------------------------------------|---------|
| Georgia kaolin, calcined at 1000° C., known commercially as "Ajax"----- | 40      |
| Bentonite -----                                                         | 5       |
| Feldspar -----                                                          | 40      |
| Talc -----                                                              | 10      |
| Whiting -----                                                           | 5       |

The stated formula provides 55% flux. The proportions of the stated ingredients may be varied within the following ranges:

|                                                                         | Percent |
|-------------------------------------------------------------------------|---------|
| Georgia kaolin, calcined at 1000° C., known commercially as "Ajax"----- | 20-80   |
| Bentonite -----                                                         | 1-10    |
| Feldspar -----                                                          | 20-80   |
| Talc -----                                                              | 0-20    |
| Whiting -----                                                           | 0-10    |

The reason for the wide ranges in proportions of stated ingredients will become apparent from the following explanation. Some radioactive wastes contain relatively large amounts of aluminum, which when absorbed by the ceramic pieces herein described, affect the composition of the pieces and their subsequent vitrification. Since the hereinbefore mentioned clay, "Ajax," is rich in aluminum, the proportion of that component may be substantially reduced and the feldspar content proportionally increased in the manufacture of ceramic pieces designed, in their intermediate state, for absorbing radioactive wastes which contain relatively large amounts of aluminum. Other waste materials contain relatively large amounts of other elements which affect the proportions of the materials chosen for making the ceramic pieces referred to herein as the intermediate product.

Some variation in composition as well as in proportions of ingredients of the ceramic pieces is permissible. For example, pre-melted ground glass known commercially as "Vitromix" may be substituted for talc, spar and whiting in a mixture which includes "Ajax" and bentonite in proportions which provide approximately 35% flux. When these mixtures were treated as herein-after described, highly porous and water absorptive intermediate products and completely vitrified, non-absorptive end products were produced.

One of several means may be employed to increase porosity of the ceramic pieces. To the ingredients above mentioned, materials which will decompose or burn out at low firing temperatures may be added. Examples of such materials are naphthalene, sawdust, walnut shells, cork and the like. For example, 10% ground walnut shells, —250 mesh, may be added to the formula. The ingredients are weighed and dry mixed, 5 to 10% of water is added to the mixture which is dry pressed into cylindrical forms under 1000 to 10,000 p.s.i. pressure. 3000 p.s.i. is the average pressure employed.

Instead of adding materials which will decompose or burn out at low firing temperatures for the purpose of

increasing porosity, a foaming procedure may be employed. For this purpose, 50% water is added to the dry ingredients to form a slip or slurry which is subjected to agitation or whipping to produce air pockets, or a chemical agent such as aluminum powder may be added to induce foaming and resultant cellular structure in the ceramic. The slurry mixture is dried to remove water and to permit the mixture to be formed into bricks, pellets or other shapes which can be handled. As an example, the drying step may begin at room temperature, slowly increasing for 20 hours to 200° F., holding for 4 hours at the stated temperature, and gradually cooling.

Anticipating use of the final product to serve mankind, it is advisable after the drying step to machine the ceramic to desired shape.

The described bricks, balls or other ceramic forms, whether produced by the dry pressed method or from the dried slurry mixture, are fired to a minimum temperature to harden and produce sufficient mechanical strength for handling and not have a tendency to slake on absorption of water. This firing is referred to herein as the pre-firing step. The pre-firing temperature is in the 800 to 1100° C. range, depending on the composition. In addition to hardening the ceramic pieces for handling and to prevent slaking on absorption of fluid, the described pre-firing at temperatures within the stated range automatically destroys the ion-exchange capacity of the ceramic materials and thus prevents ion exchange when the pre-fired pieces are saturated with radioactive waste as hereinafter described. Preferably the pre-firing step is carried out in 24 to 36 hours, by gradually increasing the temperature from room temperature to 800 to 1000° C. followed by gradual cooling. The resultant intermediate product has maximum porosity and absorptive properties. The pre-firing step must be controlled to achieve maximum resistance to breakage while retaining maximum porosity and absorptive properties which are preserved under low firing conditions.

Porosity and absorptiveness are not synonymous. Pores may be closed pores and if so, the product is not highly absorptive. The lower the firing temperature the greater will be the porosity and absorptiveness. Within the temperature range stated, the intermediate product described will acquire the required strength and retain the desired porosity and absorptive properties.

The degree of absorptiveness of the intermediate product (the ratio of absorbed material to ceramic bodies, by weight) varies within a wide range depending on the ingredients and proportions thereof, as well as the pre-firing temperatures used in the manufacture of the intermediate porous pieces.

Following the pre-firing procedure, the highly porous, absorptive ball, brick or other form, referred to herein as the intermediate product, is soaked in radioactive waste material. The saturation step may be carried out in various ways. The ceramic pieces may be placed in a tank and then the tank is filled with the radioactive solution which is to be absorbed. After soaking, the tank is drained and the ceramic pieces are dried without being moved. Another method is to place the ceramic pieces on a conveyor which is passed through the liquid to be absorbed. For some purposes it may be desirable to attach a handle or hook to the ceramic pieces to facilitate mechanical handling, as for example, by being suspended from a conveyor. The time required for complete saturation depends on the weight and volume of the ceramic pieces. Soaking of a standard sized brick, 9 x 4 x 2½", for an hour or less, resulted in absorption of 43 to 57% by weight of the material, but repeated additional soakings in the waste material, each followed by drying of the ceramic product, greatly enhanced the absorption. For example, after four successive soakings and dryings, absorption was approximately 170% by weight of material, and additional soaking thereafter resulted in still greater absorption of the radio-

active waste material. Repeated soakings and dryings make it possible to contain more waste material in a given piece and thus reduces the number of pieces required to carry the process out on an economical and practical basis. Due to the nature of the waste material, the saturation and subsequent steps must be carried out under controlled conditions, in a shielded area.

Drying of the saturated ceramic is done at temperature several degrees above the boiling point of water. The time required to remove water from the soaked product depends on drying conditions such as velocity, relative humidity and volume of drying air. The drying operation of course is carried out behind suitable shields by remote control.

The next step is the firing of the saturated dried ceramic pieces to produce complete vitrification and formation of a stable glassy phase. The initial composition of the ceramic pieces and the composition of the radioactive waste absorbed by the pieces in the saturation treatments determine the degree of firing required to produce complete vitrification. Firing of the saturated dried ceramic pieces at temperatures up to 1200° C. (2192° F.) in a suitable furnace or kiln has produced the desired results, but under some conditions, firing at temperatures up to 1400° C. may be required to produce complete vitrification. An example of the conditions referred to is the saturation of the ceramic intermediate porous pieces in radioactive waste containing ammonium nitrate 63.04 grams per liter, mercury nitrate 1.07 grams per liter, ammonia 5.05 to 19.3 grams per liter and aluminum nitrate 8.25 grams per liter. The relatively large content of aluminum absorbed by the ceramic pieces, and the subsequent oxidation of this aluminum to alumina, causes the pieces to be more refractory than are pieces which have a smaller aluminum content, and consequently they are more difficult to vitrify. When dealing with radioactive wastes of the character mentioned, it is necessary to modify the initial composition of the ceramic pieces so that they will vitrify after the composition has been changed by saturation and drying, or else subject the pieces to relatively higher firing temperatures until vitrification is achieved. Such modification of the initial composition has been mentioned previously; for example, the reducing of the clay content and increase of the feldspar content.

The heating rate will depend upon the size and shape of the ceramic pieces but should not be excessively rapid. In a period of from 24 to 36 hours, the temperature should be raised gradually from room temperature to the maximum which may range from 1200° C. to 1400° C., held at the maximum temperature for about one hour, and then gradually cooled.

The final step of my process is a safety measure designed to minimize possibility of leaching. For this purpose, I glaze the waste-saturated and dried ceramic pieces and re-fire them at a temperature high enough to mature the glaze. The glaze may be applied automatically by spraying the pieces after they have cooled subsequent to the previously described firing of the saturated, dried pieces to vitrify them. In place of a separate glazing step, I may produce self-glazing ceramics by introducing materials such as sodium chloride into the furnace wherein the saturated and dried ceramic pieces are being fired to produce vitrification. Sodium chloride and other materials vaporize and react with the ceramic to produce self-glazing during the vitrification-firing procedure.

The resultant product is completely vitrified and non-absorptive, in which the radioactive materials are combined with the ceramic material in the form of insoluble silicates and other insoluble or slightly soluble minerals from which the components cannot be leached out by ground waters or otherwise.

By using the compositions referred to herein and subjecting them to the described processes, I have produced intermediate products, namely, pre-fired shapes having

high water absorptive properties, and end products which are radioactive waste-saturated ceramic pieces, completely vitrified, characterized by zero porosity and absorptiveness and by non-leaching by ground waters or otherwise.

As pointed out herein, the invention is not limited to the specific examples described herein with respect to ingredients, proportions of ingredients, and temperatures, which may be varied within the ranges stated.

As to the form of the product, the spherical or ball shape has the advantage of being high-volume and easy to handle. Balls can be piled in towers which form ideal heating beds through which air can be blown. Air from such a bed can be used directly for space heating. The radioactive ceramics emit only gamma rays which do not irradiate dust particles coming in contact with the bed, and consequently no danger exists in using air from such a bed for air heating purposes.

#### I claim:

1. A method for disposing of radioactive waste which comprises the steps of mixing ceramic materials, adding water to the mixture, shaping the mixture into porous pieces which can be handled, pre-firing the pieces at temperature sufficient to destroy the ion-exchange capacity of the ceramic materials and to harden the pieces and prevent slaking on absorption of water while retaining maximum absorptive properties, saturating the pieces with radioactive waste material by absorption, drying the saturated pieces, and finally firing the saturated dried pieces at temperatures sufficient to produce complete vitrification and to convert the material to an insoluble state.

2. A method for disposing of radioactive waste which comprises the steps of mixing ceramic materials, adding water to the mixture, shaping the mixture into porous pieces which can be handled, pre-firing the pieces at temperatures between 800 and 1100° C. to harden the pieces to permit handling and to prevent slaking on absorption of water while retaining maximum absorptive properties, saturating the pieces with radioactive waste material by absorption after said pre-firing procedure, drying the saturated pieces, and firing the saturated pieces at temperature to produce complete vitrification and to convert the material to an insoluble state.

3. A method for disposing of radioactive waste which comprises the steps of mixing ceramic materials, adding material which will be destroyed and produce air cells in the ceramic materials at low firing temperatures, adding water to the mixture, shaping the mixture into pieces which can be handled, pre-firing the pieces at temperatures sufficient to destroy the ion-exchange capacity of the ceramic materials and to harden the pieces and prevent slaking on absorption of water while retaining maximum absorptive properties, saturating the pieces with radioactive waste material by absorption, drying the saturated pieces, and finally firing the saturated dried pieces at temperatures sufficient to produce complete vitrification and to convert the material to an insoluble state.

4. The method defined by claim 3, in which the saturation and drying of the ceramic pieces is repeated a plurality of times until the absorption of waste material is in excess of 140% by weight.

5. A method for disposing of radioactive waste which comprises the steps of mixing ceramic materials, adding water to the mixture, shaping the mixture into pieces which can be handled, pre-firing the pieces at temperature sufficient to destroy the ion-exchange capacity of the ceramic materials and to harden the pieces and prevent slaking on absorption of water while retaining maximum absorptive properties, saturating the pieces with radioactive waste material by absorption, drying the saturated pieces, repeating the saturation and drying of the saturated and dried pieces, and firing the saturated dried pieces at temperatures sufficient to produce complete

vitrification and to convert the material to an insoluble state.

6. The method defined by claim 5, in which the ceramic materials comprise kaolin calcined at 1000° C., bentonite, feldspar, talc and whiting.

7. The method defined by claim 5, in which the ceramic materials comprise kaolin calcined at 1000° C., bentonite and pre-melted ground glass.

8. The method defined by claim 5 which includes the step of treating the ceramic mixture to increase porosity before shaping it into pieces which can be handled.

9. The method defined by claim 5, in which the pre-firing of the formed pieces is done at temperatures between 800 and 1100° C.

10. The method defined by claim 5, in which the dried saturated pieces are subjected to firing at temperatures not exceeding 1400° C. to produce complete vitrification.

11. The method defined by claim 5, which includes the step of machining the shaped pieces to predetermined forms before pre-firing them.

12. The method defined by claim 5, in which the saturation and drying of the ceramic pieces is repeated a plurality of times until the absorption of waste material is in excess of 140% by weight.

13. The method defined by claim 5, which includes cooling the vitrified pieces, applying glazing material to the pieces and re-firing them to mature the glaze.

14. The method defined by claim 5, in which the final firing of the saturated dried pieces is done in the presence of glaze producing material.

15. A method for disposing of radioactive waste which comprises the steps of mixing ceramic materials, adding water to the mixture, shaping the mixture into porous pieces which can be handled, pre-firing the pieces at temperature sufficient to harden the pieces to permit handling and to prevent slaking on absorption of water while retaining maximum absorptive properties, saturating the pieces with radioactive waste material by absorption after said pre-firing procedure, drying the saturated pieces, repeating the saturation and drying steps a plurality of times until the absorption of waste material is in excess of 140% by weight of the ceramic pieces, and firing the saturated dried pieces at temperature to produce complete vitrification and to convert the material to an insoluble state.

16. A new product of manufacture in the form of hardened pieces which can be handled, composed of ceramic material and radioactive waste material absorbed therein and chemically combined therewith in the form of insoluble silicates and minerals from which the components cannot be leached out by water, in which the weight of the radioactive solids is in excess of the weight of the ceramic material, characterized by complete vitrification and absence of water absorptiveness.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

|           |                  |               |
|-----------|------------------|---------------|
| 2,616,847 | Ginell           | Nov. 4, 1952  |
| 2,918,700 | Hatch            | Dec. 29, 1959 |
| 2,918,717 | Struxness et al. | Dec. 29, 1959 |

##### OTHER REFERENCES

- U.S. Atomic Energy Commission Report AECU—3618, "Preparation of Radiation Sources From Fission Products, by the Clay Process," by J. E. Schoolmeester et al., Aug. 1957, pages 2-4 Technical Information Service Extension, Oak Ridge, Tenn. (Copy in Scientific Library.)
- "Sewage and Industrial Wastes," vol. 28, No. 6, June 1955, page 791, article entitled "Problems of Radioactive Waste Disposal," by C. P. Straub. (Copy in Scientific Library.)