(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 242 890
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 87200213.4

(51) Int. Cl.[4]: G21F 9/36 , G21F 5/00

(22) Date of filing: 11.02.87

(30) Priority: 26.02.86 IT 1955086

(43) Date of publication of application:
28.10.87 Bulletin 87/44

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR LI LU NL SE

(71) Applicant: ENIRICERCHE S.p.A.
Corso Venezia 16
I-20121 Milan(IT)

(72) Inventor: De Angelis, Bernardo
Via N. Tilli 51
I-00171 Roma(IT)

(74) Representative: Roggero, Sergio et al
Ing. Barzanò & Zanardo Milano S.p.A. Via Borgonuovo 10
I-20121 Milano(IT)

(54) Barrier against the release of radionuclides from vitrified radioactive wastes and process for accomplishing it.

(57) Barrier against the release of radionuclides from vitrified radioactive wastes, constituted by Al, Ti, Zr oxides, and process for the application thereof inside the metal containers used for the storage of the radioactive wastes immobilized inside glass matrices.

EP 0 242 890 A2

"BARRIER AGAINST THE RELEASE OF RADIONUCLIDES FROM VITRIFIED RADIOACTIVE WASTES AND PROCESS FOR ACCOMPLISHING IT"

The present invention relates to a barrier against the release of radionuclides from vitrified radioactive wastes and to the process for accomplishing it.

The liquid radioactive wastes are, presently, concentrated to dryness, incorporated inside solid materials (glass, ceramic, cement) and then stored inside underground cavities, wherein they are out of contact, as extensively as possible, with such agents, as water, which tend to disperse the radionuclides. Processes are known, according to which the radioactive wastes undergo solidification inside ceramic matrices constituted by mixtures of Ti, Al, Zr, Ca, Ba oxides. Such crystalline materials display the advantage of incorporating a large amount of radioactive material (up to 70%) and of being endowed with a high corrosion strength, but suffer from the disadvantage of requiring high costs. The most widespread processes consist in dispersing the wastes inside monolithic shapes of glass, which are in their turn inserted inside metal containers.

Such processes are basically of three types. The first type, ICGM - "in-can glass melting" - consists in placing both the dried radioactive wastes and the glass inside the metal container and melting all of the material. The second type, JHGM - "joule-heated glass melting" - involves the melting of both the wastes and the glass inside a furnace, and the subsequent introduction of the obtained molten material inside the container. The third type, GC -"glass-ceramic" - differs from the second one only in that the container undergoes a high-temperature treatment, so that a partial glass crystallization may occur.

These processes show low costs, both thanks to the wide availability of the raw material, glass, and due to the simpleness of the processes. However the possibility exists, in the long term, of tightness losses, by the glass, caused by the corrosive water action - the leaching.

It was surprisingly found that the insertion of a barrier, constituted by a layer of suitably selected oxides, between the glass and the metal container, obviates such drawbacks. The oxides used are Al_2O_3, TiO_2, ZrO_2, either individually taken, or taken as couples, in any percentages, or taken all together, in any percentages and in any crystalline forms. The process for the accomplishment of such a barrier comprises the following steps:

1) coating the inner surface of a metal container with a, preferably aqueous, suspension of oxides selected from Al_2O_3 and/or ZrO_2 and/or TiO_2, so to form a layer having a thickness comprised within the range of from 0.05 to 10 mm, preferably of from 0.1 mm to 3 mm.

2) concentrating to dryness, heating up to a temperature comprised within the range of from 110 to 170°C, preferably of 150°C.

3) pouring into the metal container, processed as described under (1) and (2), the glassy substance, as well as the radioactive wastes in either solid or molten form.
(In case the glassy substance and the wastes are poured into the container as solids, they are molten inside the container and are then solidified according to the ICGM and GC processes).

4) covering the upper portion by using the following procedures:

a) smear the upper glassy surface with a powder of the oxides as per point (1) and mechanically press such a powder, so to form a compact layer having a thickness equal to that applied onto the inner container surface.

b) place above the glassy surface a metal cover, the inner surface of which has been previously processed as described under (1) and (2).

The process comprises moreover, as an important step besides the above mentioned four steps, a fifth step consisting in keeping the layer of oxides (the oxide powder applied onto the glass surface being included) and the molten glass in contact at a temperature of from 950°C to 1350°C for a time period ranging from a few minutes up to many hours (in particular, of 2-3 hours).
The purpose of the oxide layer is to act as a further obstacle to the contact of water with the glass, and to bring in the nearby of, and within, the surface layers, Al^{3+}, Ti^{4+}, Zr^{3+} ions, in as much as such ions give rise to the formation, on the same glass, of a passivating layer, which decreases the leaching rate, up to nullifying it. From this viewpoint, the efficaciousness of the protection is not impaired by the presence of cracks or of a dusty consistency.

The purpose of the following Examples is to illustrate the invention; they are not to be considered in a limitative sense.

Example 1

The inner surface of an AISI 316 stainless-steel container having a square cross section of 2.5 x 2.5 cm, 1 cm high, is painted, by means of a brush, with Ceramabond by AREMCO, an Al_2O_3 -based ceramic paint; it is then dried at 120°C. After being filled with Pyrex type glass, it is placed inside a muffle. The container is heated to 1000° and is kept at this temperature for half an hour. The muffle is turned off and the sample is extracted when the temperature is of 350°C.

The Al_2O_3 layer results compact.

Example 2

The inner surface of a 3.5-cm high steel cylinder of 3.5 cm in diameter is painted, by a brush, with an aqueous solution of alpha-Al_2O_3 (Alcoa Al6), containing 2% polyvinyl alcohol as bonding agent. After being dried at 150°C, the cylinder is filled with minced Pyrex and is maintained at 1050°C for 2 hrs. After turning off the muffle, the sample is extracted when the temperature has decreased to 200°C. The coating results unbroken.

Claims

1. Barrier against the release of radionuclides from vitrified radioactive wastes, constituted by Al, Zr, Ti oxides, characterized in that said elements are either individually present, or present as couples, or present all together, in any percentages and in any crystalline forms.

2. Barrier according to claim 1, having a thickness comprised within the range of from 0.05 mm to 10 mm, preferably of from 0.1 mm to 3 mm.

3. Process for the accomplishment of the barrier according to claims 1 and 2 consisting in coating with a suspension of Al, Ti, Zr oxides the inner surface of a metal container, drying at a temperature comprised within the range of from 110 to 170°C, preferably of 150°C, pouring into the container the glass and the radioactive wastes, either in solid or in molten form, covering the upper portion of the the mass of glass and radioactive wastes, after melting it if it was in solid form, with the powder of the oxides used for coating the bottom and the walls of the metal container, maintaining the molten oxides and glass in contact for a time period of from a few minutes up to many hours at a temperature of from 950°C to 1350°C.

4. Process according to claim 3, characterized in that the glass and the radioactive wastes, coated with the oxides, are solidified according to the ICGM or GC processes.

5. Process according to claims 3, 4 and 5 characterized in that the upper portion of the mass of glass and radioactive wastes is covered with the oxides applied onto the inner face of the cover of the metal container, by the same procedure as used to coat the inner surface of the same container.