(54) Title: GLASS FOR THE CONTAINMENT OF RADIOACTIVE ELEMENTS AND HIGHLY TOXIC AND HAZARDOUS WASTES AND PROCEDURE OF CONTAINMENT BY SAID GLASS

(57) Abstract: The present invention relates to a glass for the confinement of radioactive elements and of highly toxic and hazardous waste, comprising 35-45% by weight of B₂O₃, 17-22% by weight of ZnO, 15-20% by weight of B₂O₃, 15-20% by weight of SiO₂, 4-8% by weight of Na₂O, characterized by a softening temperature (for which the viscosity is 1066 Pa-s) comprised in the range 570°C - 620°C, a process for the confinement of radioactive elements and of highly toxic and hazardous waste by means of said glass and the uses of said glass for the safety of an element of irradiated nuclear fuel, damaged as a result of an exceptional accidental event, or for conditioning by incorporation into the matrix of confinement of radioactive waste of low and medium activity and/or highly toxic and hazardous non-radioactive waste.

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The present invention relates to a glass for the confinement of radioactive elements and of highly toxic and hazardous wastes and a method of confinement of radioactive elements and of highly toxic and dangerous wastes that makes use of said glass as containment matrix.

More in particular, the invention relates to the development of a glass with particular chemical-physical and nuclear properties, for use in a process of securing, by incorporation of an irradiated nuclear fuel element, damaged as a consequence of an exceptional accident event.

The invention concerns also the possibility that said glass can be used for the conditioning of particular radioactive waste with low/medium activity and highly toxic and hazardous waste.

The present invention relates to the field of management of nuclear installations and in particular the management of irradiated nuclear fuel, damaged as a result of exceptional accidents such as, for example, those that have caused the loss of coolant in a reactor or in a pool of storage of irradiated fuel.

At the current state of knowledge, when a fuel element (in the following of the present specification also indicated as "fuel assembly" or more simply "assembly") presents micro fissures, due for example to corrosion, it is removed from its seat, placed in a containment vessel of stainless steel (also referred to as "containment bottle" or "canister", the following terms being used interchangeably in the following specification), sealed with gasket and relocated for temporary storage in a pool or at dry.

One such solution, in the case of severely damaged fuel element, with loss of containment represented by the metal sheath of the assembly, is insufficient, for safety reasons, for long-term storage, because a possible loss of containment from the canister would expose the personnel and the environment to unacceptable radiological risks as a result of the resulting extensive contamination.

In order to remedy this problem and increase the security level of the canister, some solutions have been proposed in the past, and are hereinafter briefly described.
In patents US4650518 (1987) and US5832392 (1998), as a containment barrier uranium alloys are proposed, involving the use of specific and particularly expensive technologies; in US4950426 (1990) as a filler for the containment vessel (canister) a granular material is used composed of sand, bentonite and an organic liquid able to absorb radioactive substances; thus an incoherent matrix, the function of which as a barrier is not fully effective in case of damage to the containment vessel.

In the "Journal of Non Crystalline Solids", Vol. 84, n. 1-3 of September 1986 in the article "Systems approach to nuclear waste glass development," Jantzen described the different solutions according to the prior art in the field of packaging of high-activity liquid waste, the so-called HLLW-High Level Liquid Waste (or HLW) through the well-known process of vitrification. In particular, the publication describes the main glass matrixes under study or already in the industry. Additionally, the document refers to a process of vitrification of HLW at a temperature of 1150° C. Due to the required temperature, the solutions are not simple to implement in a plant, since they could impair the integrity of the metallic sheaths of the fuel.

DE 2524169 describes methods for the incorporation of highly radioactive waste in which, in order to avoid phenomena of devitrification in glassy artifacts containing a high radioactivity (or containers of large size), and therefore characterised by a high heat output of radioactive decay, radioactive wastes are first incorporated in granules of glass, which in turn are embedded in molten pure metals or metal alloys. In this way it is increased the coefficient of heat transmission by reducing the maximum temperature at the center of the container. The process thus requires two separate phases of confinement of radioactive waste, first with granules of glass and then with molten metal that incorporates both the waste and the granules, resulting in a considerable complication of the plant, necessary for the fact that the glass described in this patent does not have suitable characteristics to ensure a correct and long lasting confinement of the waste.

GB 1006194 describes glass compositions containing about 5% of PbO, 18% B₂O₃, 60% ZnO, 15% SiO₂, 2% CuO, which are found to have softening point between 600 and 700 °C and which, at such temperatures, de-vitrify in about 1 hour. These glass compositions are
used as sealants for seals between glasses (for example for cathode ray and vacuum tubes). The formation of crystals in the step of devitrification, however, makes these compositions unsuited to confinement of radioactive and highly toxic and hazardous waste.

EP03903750 relates to the disposal of nuclear waste, and in particular to the operations needed to prevent that any radioactive contamination caused by leakages from the canister containing high level liquid waste (HLW) could arrive to the environment, or that water which has entered in the module containing the canister, and thus contaminated, could arrive to the environment. In particular, EP03903750 describes a granular filler to be placed in the empty spaces between the various canister within the module (and a special design of the module itself), forming the absorbent for spills and leaks ("sawdust effect" for the wet, but with the added ability to capture and sequester radioactive ions). This filler is constituted by a combination of sand, bentonite clay, montmorillonite, lime and zeolite, and remains in granular form for all the time, additionally it is located outside of the canister and is used for disposal in deep geological disposal.

Finally, U.S. 4737316 describes glasses that, in the state of mesoporous sponge contained in a metal container, act as ion exchange inorganic filters for purification of radioactive liquids. Once saturated, such glasses are admixed with some components (melting frits, which lower the viscosity or form a low melting eutectic) and inserted, metal casing included, in a furnace at temperatures between 1250 - 950 °C (depending on the filtering glass and additive used), so that the whole sinterises and gives life to a compact waste. The final sintered product has a good chemical resistance and is then disposed of in a geological repository or other depending on the degree of radioactivity. The glass therefore acts as a filter for the radioactive liquid, or as a fondant, which works at high temperatures with considerable complications in the plant, the temperature being higher than the critical temperature for the integrity of the metallic sheaths of the fuel.

In this context it is proposed the solution according to the present invention, with the aim of providing a new proposal of solution to the problem of long-term and safe storage of severely damaged fuel elements, consisting in the incorporation of the whole damaged fuel element in a specifically developed containment matrix comprised of glass
with low softening point, which constitutes an additional barrier (in addition to the external canister) against the dispersion of radioactive material. As will be detailed in the following of the present specification, such a solution is at the same time effective, safe, economic and simple to implement in a plant.

These and other results are obtained according to the present invention by proposing a special glass as a function of specific needs inherent to the particular operating conditions related to the process of securing, through incorporation into a containment matrix, an element of irradiated nuclear fuel, damaged by an exceptional accidental event.

The glass according to the present invention is characterised by low softening temperature, good thermal transmission, appropriate coefficient of thermal expansion, in relation to the material of the sheath of the fuel, and by the property of "barrier" after cooling.

Purpose of the present invention is therefore to provide a glass for the confinement of radioactive elements and of highly toxic and hazardous waste and a method of confinement of radioactive elements and of highly toxic and hazardous waste that makes use of said glass as a containment matrix that can overcome the limits of the solutions of the prior art and get the previously described technical results.

Further object of the invention is that said glass and said method can be realized with substantially low costs, both as regards production costs and as regards operative costs.

Another object of the invention is to propose a glass for the confinement of radioactive elements and of highly toxic and hazardous waste and a method of confinement of radioactive elements and of highly toxic and hazardous waste that makes use of said glass as containment matrix that are simple, safe and reliable.

It is therefore a first specific object of the present invention a glass for the confinement of radioactive elements and of highly toxic and hazardous waste, comprising 35-45% by weight of PbO, 17-22% by weight of ZnO, 15-20% by weight of B2O3, 15-20% by weight of SiO2, 4-8% by weight of Na2O, characterized by a softening temperature (for which the viscosity is 10^6 Pa-s) comprised in the range 570°C - 620°C.

According to the present invention, said glass can include in addition the following oxides in a total amount of less than 5% by weight
K_2O, CaO, Li_2O, CeO_2, these quantities being expressed with reference to
the total oxides present.

Preferably, according to the invention, said glass comprises in
addition an amount of less than 30% of inorganic fillers.

More preferably, said inorganic fillers are selected from LAS
(Litia-Alumina-Silica) glass-ceramic and silica glass.

It is a second specific object of the present invention a process
of securing of an element of irradiated nuclear fuel, damaged as a result of
exceptional accidental event, wherein said nuclear fuel is placed in a metal
containing which is subsequently filled with solid particles with a diameter of
100-300 μm made of glass as defined in claims 1-4, said container being
then heated up to obtain the complete softening of the glass.

It is further a third specific object of the present invention a
containment vessel or canister comprised of a metal body, divided into two
parts: a lower part apt to contain an irradiated nuclear fuel element,
damaged as a result of an exceptional accidental event, or radioactive or
highly toxic or hazardous waste, and an upper part of useful volume equal
to 25-35% of the volume of the said lower part which remains free after the
insertion of said fuel element or said waste.

It is then further specific object of the present invention the use
of said glass for securing of an irradiated nuclear fuel element, damaged
as a result of an exceptional accidental event, by incorporation into a
containment matrix, or for conditioning by incorporation into a containment
matrix of radioactive waste of low and medium activity and/or of highly
toxic and hazardous non-radioactive waste.

The present invention will be now described, for illustrative but
not limitative purposes, according to a preferred embodiment thereof, with
particular reference to the following illustrative examples and to the figures
of the accompanying drawings, in which:

- Figure 1 shows a cross-sectional elevation view of a canister
and an irradiated nuclear fuel element of type BWR, damaged by
exceptional accidental event, positioned inside it to be subjected to
confinement in glass according to the present invention;

- Figure 2A shows a plan view of the canister of Figure 1, from
the section line AA of Figure 1;

- Figure 2B shows a cross-sectional view of the canister and
nuclear fuel element of Figure 1, from the section line BB of Figure 1;
In particular, the glass according to the present invention presents some peculiar features, such as: softening temperature, chemical composition, thermal conductivity, chemical resistance and density, as well as other chemical, thermal and mechanical properties that will be described below.

With reference to the softening temperature, the glass according to the present invention has a softening point or "softening point" (temperature at which the viscosity is equal to $10^{6.6}$ Pa·s), which ranks in the temperature range of 570-620°C, which ensures that the whole process of the present invention can be carried out under temperature conditions that are not critical for the structural components of the fuel element.

Regarding its chemical composition, the glass according to the present invention has the following weight percent composition of the main oxides:

- PbO: 35-45%
- ZnO: 17-22%
- B$_2$O$_3$: 15-20%
- SiO$_2$: 15-20%
- Na$_2$O: 4-8%

In order to improve specific physical-chemical properties, such as optimizing adhesion of the glass to the different metal alloys, chemical resistance, etc., in addition to the main oxides specified above, in the
compositions an amount of less than 5% of the following "minor" oxides can be used: $K_2O$, $CaO$, $Li_2O$, $CeO_2$. 

In order to improve some thermal properties (coefficient of dilation) and chemical properties (resistance to acid/base attack), the glass according to the present invention is preferably loaded up to 30% by weight with an inorganic fraction.

The glass according to the present invention is able to ensure at the same time an excellent resistance to dissolution in an aqueous environment and a softening temperature sufficiently low to make it possible the incorporation of damaged fuel elements at temperatures below the critical temperatures for the integrity of the metal sheaths. Moreover, even after staying at high temperatures for a long time, the glass according to the present invention does not give rise to crystals of detectable size.

Making reference to the thermal conductivity, the thermal properties of the glass according to the present invention are particularly relevant in the case of nuclear materials with significant generation of thermal energy.

The confinement system used in the implementation of the process of securing of a damaged irradiated nuclear fuel element, as better illustrated in the following description, is based on the use of this glass material that, initially in solid incoherent form, is brought above the softening temperature to obtain a homogeneous melt, and subsequently cooled to obtain a homogeneous solid able to confine its contents.

Since the thermal characteristics of any glass are strongly temperature dependent, and that the process described above requires highly variable thermal conditions for the system (from room temperature to softening temperature in the first step, and from the softening temperature to room temperature in the second step), a physical-mathematical model has been used to calculate the thermal conductivity (phononic and radiative component) of the glass at different temperatures.

The model was constructed starting from experimental evidence concerning the glass material, both in massive form and in the form an incoherent grit, acquired at room temperature as well as at some other significant temperatures.

In the case of the glass according to the present invention, the thermal conductivity adopted was assumed conservatively coincident only
with the conduction component of the glass, equal to 0.6W/(mK) at room
temperature, completely neglecting the contribution of heat transfer due to
to irradiation inside the glass itself.

As far as other chemical, thermal and mechanical properties is
concerned, the glass according to the present invention meets the
following minimum requirements.

Resistance to compression: greater than 5 MPa (determined in
accordance with ASTM C39/C 39M-05).

Resistance to thermal cycles: in accordance with UNI
11193:2006 - § 5.2.2, after 30 thermal cycles of 24 hours from -40°C to
+40°C at relative humidity equal to 90±5%, no cracks are generated and
medium resistance to compression is at least equal to 5 MPa, and in any
case not less than 75% compared to the initial, determined in agreement
with ASTM C39/C 39M-05.

Consistency of the product: the dissolution rate in water at
90°C, determined according to the methodology described in ASTM
C1285-02, but, differently from the provisions of the norm, where it is
provided for the measure on powder material, operating on monolithic
samples of dimensions 9x4x1 mm, is less than 1 g/m² day.

As far as the chemical resistance of the glass according to the
present invention is concerned, in the case in which the fuel element
confined by the process object of the present invention is stored in a pool
of storage, in the case of damage to the canister structure of AISI 316
steel, for example due to corrosion or accidental damages, the layer of
glass according to the present invention that surrounds the assembly may
come into contact with the water of the pool. It is therefore important that
the glass is not severely attacked by water, so as to ensure that the
radioactive material of the element confined inside the glass remains
effectively isolated from the external environment.

For this purpose, the glass according to the present invention
was specially developed to ensure a very low dissolution rate in water at
90°C, comprised between \(1 \cdot 10^{-5} + 4 \cdot 10^{-5}\) g/cm² days (value determined in
accordance with ASTM C1285-02).

Finally, the density of the glass according to the present
invention is between 4.1 and 4.4 g/cm³.
With reference to the process for the securing of a damaged irradiated nuclear fuel element, the glass according to the present invention was developed for the process of described below.

The process consists in the insertion of a damaged irradiated nuclear fuel element in a canister and the subsequent incorporation in the glass according to the present invention, maintaining safety maximum temperatures inside the same element.

The damaged fuel element, removed from its position in the reactor or in the storage pool, is placed, under water head, inside of a canister, which is then closed with lid and seals. The canister is then transferred, after surface decontamination in an equipped area of the pool, indicated below as conditioning and vitrification unit.

After draining and drying with nitrogen, the canister and the inside of the fuel assembly are filled with micro particles of said glass.

The vitrification unit is then closed, emptied and dried.

By the use of radiant plates in the unit (necessary, in particular, for fuel elements having long cooling times and to ensure an optimal homogeneity of heating of the whole assembly) then the heating from outside of the canister is performed, thereby raising its temperature almost uniformly.

Above the softening temperature of the glass, the last reduces its viscosity to such an extent as to allow the total filling with glass material of the free volume of the canister and the assembly, resulting in complete incorporation of the fuel element.

After controlled cooling, the solidified glass material encompasses the entire fuel element, constituting, together with the stainless steel canister, a double containment barrier against losses of radioactivity.

This process has been the subject of experimentation on laboratory scale and of quantitative modelisation with computation codes qualified for the various stages of heating, incorporation and cooling of irradiated nuclear fuels, with thermal power corresponding to different decay times after removal from the reactor.

Example. Securing a damaged irradiated fuel element of type BWR

By way of not limiting example, the process (and the relative equipment) forming the object of the present invention can be summarized
in four steps, given below with reference to a nuclear fuel element of type BWR and to operations in a pool, under shielding water head.

Step 1: arrangement of a damaged fuel element in a canister

The first step involves the removal of the damaged fuel element from the reactor (or from the pool of storage) and its insertion into a stainless steel canister (shown in its entirety in the attached figures), sealed with a lid and seals.

Only with the aim of optimization of the process, always with reference to the attached figures, the canister may present some peculiar properties, such as the prismatic shape of its lower part 1, in order to obtain a uniform incorporation of the fuel element, and an upper cylindrical body 2.

These elements, however, are not binding on the invention, being possible to make the canister with other geometries, methods and techniques.

In the present example, the canister for fuel elements of type BWR (said fuel elements being indicated in the figures by the reference number 3) is constituted by a body made of AISI 316L stainless steel of total height of 5000 mm, divided into two parts: a lower part 1 with 160x160 mm square cross section, for a height of about 4500 mm, containing the fuel element of type BWR, also with prismatic shape, with 134x134 mm square section, active length of 4115 mm, which rests on a support 13 on the bottom of the canister, and an upper part 2 with circular section $\Phi_1 = 260$ mm, $h = 500$ mm, with flange and lid, of volume equal to about 30% of the free volume of the lower part 2 (prismatic body), after filling with the fuel element, and that constitutes a reserve volume for the micro particles of glass. This volume, filled with glass particles, is used to compensate for the reduction of volume during the steps of softening and solidification.

The body of the whole canister is completely sealed and conditioned, designed to withstand maximum working temperatures of about 700°C.

The canister, always under water head, is closed with a lid 4, using the gripping element 5, the dowel pins 6 and the clamping bolts 7, the lid is provided with a suitable gasket 8, resistant to operating temperatures and fixed at the same lid by means of a clamping ring.
The canister with the damaged fuel element 3 inside (type BWR in this example), is transferred, via the gripping element 5, in a decontamination unit (not shown), where decontamination of the external walls is performed.

After decontamination, the canister is transferred in the conditioning and vitrification unit shown in Figure 5, placed in an equipped area of the same pool of storage.

Similar containers can be provided for other types of nuclear fuels.

Step 2. Preliminary conditioning of the canister

By pre-conditioning of the canister it is meant emptying of water, drying inside of the canister and loading with particles of glass.

The containment vessel or canister, always under water head, is introduced in the above said conditioning and vitrification unit and then connected, via the "quick connector" 8 and 9, provided with guide system 10 for insertion, with the systems (not shown) for pressurization and emptying of water that is present, using for emptying a discharge pipe 11 of 1 inch.

In the hypothesis of damage of the sheath of the fuel, the water removed from the canister will be heavily contaminated, and therefore will be sent to the radioactive liquid treatment.

Then, the subsequent drying inside the canister is performed, using a stream of nitrogen through the emptying pipe 11 and the "quick connector" 9. The off-gas is sent to the system for treating radioactive effluents, via the pipe 8.

The connections of the canister with the emptying/treatment system and with the systems of nitrogen feed and aspiration of off-gas occur by rapid connectors ("quick connector") and flexible pipes.

The canister is then connected to an external tank and the pool is filled with glass particles, with a diameter of 100-300 μm, through a dedicated pipe and a "quick connector" 12. The reduced medium size (100-300 μm) of the particles is particularly important since they must completely fill the free volume of the canister, through the grates of the fuel element.

The used glass is the glass according to the present invention, specifically designed for the process of the invention.
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As previously said, the upper part 2 of the canister, equal to about 30% of the free volume of the same, is used to compensate for the reduction in the volume of glass particles as a result of their softening.

In the filling operation with the glass particles, the canister is connected to the system of treatment of off-gas via "quick connector". Appropriate vibrating systems will ensure complete filling of the free volume with the glass particles.

At the end of the filling with the glass particles, revealed by measuring the level of glass, the canister is disconnected, remaining active only the ceramic filter acting as a relief valve.

It must be kept in mind that, in the following step of heating, the whole canister temperature will be increased to approx. 600-700 °C, and this forces to use only gaskets and connectors that are resistant to this temperature.

All the conditioning operations of the canister are carried under water head, in conditions of radiation safety for the operating staff, operating from the upper operating deck of the pool of storage.

Step 3: Incorporation of the damaged fuel element in a confinement matrix obtained by the softening of the glass particles

The process of softening of the glass material loaded around and inside of the damaged fuel element constitutes the third step of the process, and takes place in the same conditioning and vitrification unit (shown in Figure 5), in the pool of storage, under the water head.

This apparatus consists of a cylinder of AISI 316 14 stainless steel, with a lid 15, with gaskets 16 for high temperature, dowel pins 17 and clamping bolts 18, thermally isolated by thermal insulating casing 19 and placed on a base 20 on the bottom of the pool of storage.

Inside the conditioning and vitrification unit are located:
- guides 21 for the proper introduction and positioning of the canister;
- a plurality of electrical radiant panels 22 arranged on the inner surface at different heights;
- temperature sensors 23.

By the bottom pipe 24 the emptying of water being present in the space between the apparatus and the canister is performed, and then the introduction of nitrogen, with ventilation to the off-gas through the pipe
25. Not having been in contact with active/contaminated parts, the water drained has the same radioactivity of the pool of storage.

The canister is then heated externally by means of the radiant panels 22, placed on the inner wall of the unit.

The use of radiating panels 22 is required to compensate for the different distribution of the axial residual power of decay, for the purposes of the optimization of the whole process.

The increasing of the temperature on the outside of the canister up to about 650 °C is measured by the temperature sensors 23 mentioned above, and the temperature is maintained constant by means of the modulation of power supplied by radiant panels 22.

This modulation also takes account of the residual thermal power of the fuel element, which will have as effect a rise of temperature at the center of the element, under conditions of residual power of 3 kW (for an element BWR) corresponding to about 6 months of cooling of a fuel of a reactor BWR operating at nominal power of 1200 MWe, with a medium burn-up of 30.000MWd/tonU, the temperature will reach maximum values in the range of 720 °C.

At these levels of temperature a further reduction of the viscosity of the whole vitreous mass is obtained, which consequently will compact, recalling glass material from the top of the canister.

In this case, when the required power to the radiant panels 22 reaches almost constant values, with a maximum temperature of the wall of the canister of about 650 °C, the vitreous mass inside of the canister has reached the condition of fusion. By maintaining these conditions for an appropriate period of time, a condition of generalized fusion of micro glass particles inside the whole canister is obtained.

An indirect measure of the generalized fusion occurred can be made through the measurement of the level of the glass particles in the upper cylindrical body.

Step 4. Cooling of the canister

Subsequently, the step of controlled cooling of the whole canister starts, first by gradual reduction of the irradiation of radiant plates, then by nitrogen inlet in the interspace between the canister and the walls of the same equipment, then with nitrogen and water and finally with water, so as to ensure to the glass conditions of integrity at the end of cooling. To avoid the cracks that may result from the contact of materials
with different coefficient of expansion, as mentioned, a certain amount of
inorganic filler with a very low coefficient of expansion is added to the
glass, such as for example silica glass or LAS (lithium alumina silica glass-
ceramic), in order to make the coefficient of expansion of glass similar to
that of Zircaloy of the sheaths of the fuel element. AISI 316 steel of the
external container, having a coefficient of expansion greater than that of
the materials contained in its inside, will induce in the glass a beneficial
compressive stress.

Finished cooling, the vitreous mass constitutes an intact and
compact protective casing around the same element.

The conditioning and vitrification unit is then opened, and the
canister removed and transferred, after integrity checks, to the storage,
awaiting reprocessing or long-term storage.

The process described allows for the "reconstruction" of the
primary containment, consisting of the fuel element originating from the
sheath in the Zircaloy fingers, and for the addition of an additional
containment barrier with respect to the use of only the steel canister,
preventing the release of radioactivity in the subsequent management of
irradiated fuel, both in normal working conditions, and in situations of
accidental leakage of secondary containment, or of damage to the
canister.

In Figures 5, 6A and 6B it is schematically shown the
conditioning and vitrification unit, with reference to a BWR fuel, similar
solutions can be envisaged to implement the process, or for other types of
nuclear fuels, without substantial changes to the process forming object of
the invention.

As said, the unit of vitrification is constituted by a metal cylinder,
of AISI 316 stainless steel, provided with a lid 15 to seal, having a
diameter Φ = 380mm and H = 5500mm, thermally isolated, enclosed in a
casing of aluminium or steel.

The unit is immersed in the pool in its deepest point, and is
anchored to a support plate.

The unit is connected to the end of a discharge pipe 24, through
submersible pump connected to liquid effluents treatment plant, and head
to a pipe 25 of the intake and treatment of off-gas.
Inside the cylindrical body plates 21 are welded with opening having square section, for positioning "in phase" of the canister of the fuel element.

Thermal panels of radiant energy 22, distributed axially (in example eight in number in the diagram of figure 5) with electrical power supply are positioned at various heights of the body of the conditioning and vitrification unit.

Sensors 23, the type pyrometers, measure continuously the temperature of the outer wall of the canister and allow the control of the process.

Temperature profiles to 'interior of the canister to various powers decay'

'S analysis of the profiles of the temperatur in the' interior of the canister for various thermal inputs of radioactive decay has been developed on a model of the canister using a computer code qualified to finite elements, ANSYS 12.1, which were introduced features thermophysical of glass and the geometry of the system.

The geometry used for the simulation models of the processes of heating and cooling includes:

- A volume of homogeneous glass, internal to 'element of the fuel, which are contained within the fingers of fuel;
- The fuel rods are fully taken into U02 (conservative estimate);
- The sheath of the 'fuel element is in zircaloy;
- A volume of glass to 'external sheath of element of the fuel;
- A volume of steel on the prismatic portion of the vitreous canister.

For a temperature to 'external canister of 650 ° C, at the center of 'element, you will have, as mentioned earlier, a maximum temperature of 720 ° C, in' hypothesis of residual power of 'element offuel of 3 kW / assemblies, corresponding to 6 months of cooling a fuel rector of a BWR operating at nominal power of 1,200 MWe, with a burn - up 30,000 average MWD / Tonu.

In the condition of refrigeration in the water of the canister, after the 'incorporation into the glassy matrix and subsequent raff redamento checked, the maximum value of temperature, to the 'interiorof the 'fuel element is slightly greater than 310 ° C, assuming the temperature of 'water in the pool of 30 ° C.
Similarly, in the case of raffeddamento in the air, it was considered that the heat transfer to the 'outer environment is due both to the phenomenon de ll'irraggia chin to that of convection.

Conservatively, for the evaluation of the contribution due to 'radiation, has assumed the shiny steel surface of 'element vitrified (and missivita reduced). Despite limited performance Deil 'air' s removal of heat, the contribution due to the 'irradiates m ent allow to obtain, in the cooling phase in air in the long term, a maximum temperature at the center of 'element slightly lower 235 °C.

Advantages of the process object of the 'invention

The present invention starts from the well-established practice of using a stainless steel containment vessel for the development of safety in spent nuclear fuel strainer, mainly as a result of harsh events.

This container or canister has been suitably modified to allow the nglobamento in a matrix constituted by the containment of glass according to the present invention of an irradiated fuel element severely damaged as a result of incidental exceptional events, such as, for example, those that have resulted the 'direct exposure of radioactive material (tablets or pellets the rr Aggia Tedi U02, Pu 0 2, and oxides of pr odott the fission) to 'water raffieeddamento. Said glass matrix is formed at maximum temperatures in 'intomo of 700 °C, in order to preserve the characteristics of the outer steel canister and sheaths in the Zr caloy of the 'fuel element.

With this process, extremely cheap, simple and safe from an operational point of view, "reconstructs" an 'effective barrier containment, through the 'incorporation of whole element of fuel damaged (and the 'any exposed material) in a glassy matrix that goes to constitute a barrier against the dispersion of radioactive material, both during normal operating conditions, that following further incidental events.

It adds that the walls of the canister, which may for example wicked of cracks caused by corrosion or loss of property, an 'additional proof glass barrier, resulting in increased levels of security.

Moreover, in addition to the above, the advantages of the process object of the present invention are:

- Reversibility, ie possibility of separation of the 'element of fuel from the encapsulating matrix, for example by heating to temperatures above the softening;
- Radiological safety during the operations of cutting, in case of reprocessing;
- Increased content of liquid and solid waste, in the case of damaged fuel reprocessing.

A further application of the present invention relates to the 'Option and management of irradiated fuel, referred to as "once-through cycle."

This option provides for the conditioning of the fuel irradiated in a special container (subject to their eventual thickening), "long-term dry storage in cask or in statistical structure engineers, followed by the deposit definitivo in a deep geological formation.

It is precisely in the "conditioning" of the fuel that this process can find its optimum application, introducing an additional barrier, the glass, between the fingers of the radioactivity present to 'internal' fuel element el'environment.

In addition, having a glassy material conductivity coefficient greater than the thermal gas, such as' air or helium (for the' air is stagnant bout c 0,027 c bout against 0.6 W / m K for the glass), we have an improvement of the disposal of the residual power of decay and, in case of loss of seal of the canister outside, the glass also keeps protected I 'fuel element with respect to oxidative phenomena.

Utilization of the inventive glass for the conditioning of radioactive waste in particular low-and intermediate and non-radioactive waste highly toxic and hazardous

The glass according to the present invention, or sviluppat for 'use in the process of the invention as a containment barrier for elements of fuel from nn eggiati, can be ottimizzato or for the 'use, for the purposes of the 'incorporation of radioactive waste of low and media activities, where the consolidated cementation processes, normally used for this type of product, prove inapplicable or difficult to apply, as in the case of radioactive waste containing high cone entrazioni of organic compounds, or not convenient.

In this case, the 'use of a glass of low-temperature softening which the glass according to the present invention for the 'incorporation of rejection (after a possible treatment concentration and calcination dry), allows to overcome the 'incompatibility with the cementitious matrix and at the same time to avoid the problems of off - gas and use of complex
equipment vitrification, which is present in the use of glassy matrices usually used in the treatment of radioactive waste.

Similar application can affect non-radioactive waste highly toxic and dangerous, for which it is necessary, for reasons of safety, the isolation in a matrix durable and inert with respect to chemical agents - biological environmental, just as the glass according to the present invention.

In all these cases, the use of glass according to the present invention allows the incorporation of the waste at temperatures lower than 700 ° C, with all the consequent advantages from the point of view of the plant, the economic and security.

The present invention has been described at the illustrative but not limitative purposes, according to its preferred embodiments, but it is understood that variations and/or modifications can be apport to you by those skilled in the art without departing from the scope of protection, as defined by the appended claims.
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CLAIMS

1) Glass for the confinement of radioactive elements and of highly toxic and hazardous waste, comprising 35-45% by weight of PbO, 17-22% by weight of ZnO, 15-20% by weight of B₂O₃, 15-20% by weight of SiO₂, 4-8% by weight of Na₂O, characterized by a softening temperature (for which the viscosity is 10⁶⁶ Pa·s) comprised in the range 570°C - 620°C.

2) Glass according claim 1, which additionally comprises the following oxides in a total amount of less than 5% by weight K₂O, CaO, Li₂O, CeO₂, these quantities being expressed with reference to the total oxides present.

3) Glass according to claim 1 or 2, which comprises in addition an amount of less than 30% of inorganic fillers.

4) Glass according to claim 3, wherein said inorganic fillers are selected from LAS (Litia-Alumina-Silica) glass-ceramic and silica glass.

5) Process of securing of an element of irradiated nuclear fuel, damaged as a result of exceptonal accidental event, wherein said nuclear fuel is placed in a metal container which is subsequently filled with solid particles with a diameter of 100-300 μm made of glass as defined in claims 1-4, said container being then heated up to obtain the complete softening of the glass.

6) Containment vessel or canister comprised of a metal body, divided into two parts: a lower part (1) apt to contain an irradiated nuclear fuel element (3), damaged as a result of an exceptional accidental event, or radioactive or highly toxic or hazardous waste, and an upper part (2) of useful volume equal to 25-35% of the volume of the said lower part (1) which remains free after the insertion of said fuel element (3) or said waste.

7) Use of glass defined in claims 1-4 for securing of an irradiated nuclear fuel element, damaged as a result of an exceptional accidental event, by incorporation into a containment matrix.

8) Use of glass defined in claims 1-4 for conditioning by incorporation into a containment matrix of radioactive waste of low and medium activity.

9) Use of glass defined in claims 1-4 for conditioning by incorporation into the matrix of confinement of highly toxic and hazardous non-radioactive waste.
INTERNATIONAL SEARCH REPORT

PCT/IT2013/000327

A. CLASSIFICATION OF SUBJECT MATTER

INV. C03C3/074 G21F5/008 G21F9/30

ADD.

According to International Patent Classification (IPC) onto both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C03C G21F C03B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

See patent family annex.

Date of the actual completion of the international search: 26 May 2014

Date of mailing of the international search report: 03/06/2014

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Authorized officer: Deckwerth, Martin
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