WASTE VITRIFICATION: MORE THAN ONE STRING TO ITS BOW

Vitrification has long provided the nuclear industry with a safe long-term conditioning technology for high-level radioactive waste. Scientific and technological progress – the cold-crucible process in particular – have now opened up new ways to ensure volume reduction, extend the range of waste that can be incorporated, increase durability, and combine with combustion technologies. Excluding specific radionuclides that are managed by other processes would allow the production of "light glass" packages whose radiotoxic inventory would return in a few hundred years to the level of the initial ore.

Thierry Foulon/CEA

The CFA2001 advanced cold-crucible facility at CEA/Valrhô-Marcoule, developed by CEA and Cogema to demonstrate the feasibility of direct-induction cold-crucible melter technology, as part of an initiative to develop a simple, single-step vitrification process. The waste solution and glass frit are fed at the upper level, the cold crucible is in the middle, and the canister into which the melt is poured stands on the floor.

Extensive vitrification experience

By the late 1950s, CEA managers were already aware of the problem posed by waste from atomic **fission** (see box B, ***Waste from the nuclear power cycle***), and launched programs to solve it. These programs were fully integrated into **fuel**-cycle studies. Many nuclear plants have since been built, and spent-fuel **reprocessing** has been implemented on an industrial scale. Work has begun to develop industrial processes for waste reprocessing and **containment**, together with the exploration of containment materials to immobilize **radionuclides** (see box G, ***Conditioning, a vital phase***) and reduce the waste volume.

Research and development programs have been carried out to meet partners' needs, step by step, investigating both containment materials and the processes required to make them, with a strong technological component. Laboratory studies focusing on the fabrication and characterization of **radioactive** glass packages were initiated in the first series of shielded cells at Saclay, and are now being pursued in the recent **Atalante** DHA (high-level waste) facility at Marcoule. The first batch-vitrification process was developed in the Piver pilot **fission-product** vitrification facility at Marcoule in 1969. Today, the continuous two-step vitrification process is used by Cogema at La Hague. Tomorrow simplified processes using the liquid-fed cold-crucible melter will take over.

Glass was chosen for highly radioactive waste because it was the only mineral capable of including in its disordered structure all the elements found in fission-product solutions, including **minor actinides** (figure 1). Crystalline materials such as mica or feldspar were found to be too selective with respect to a given element. In addition, glass is not very sensitive to radiation because of its disordered structure.

The *continuous two-step vitrification process* was selected in the 1970s to vitrify Marcoule fission-product solutions. The Marcoule Vitrification Unit (AVM) was built to meet the need for increased production capacity. The process is well suited to the main criteria of importance when working in a hostile environment: it is modular and simple, allowing the use of remote manipulators for dismantling operations, and its reliability is ensured through the use of induction heating. Following further development work, this process was set up in the six vitrification lines of the R7 and T7 vitrification facilities at La Hague in 1989 and 1992 to contain high-level radioactive solutions from spent-fuel reprocessing in "**R7T7**" **glass**.

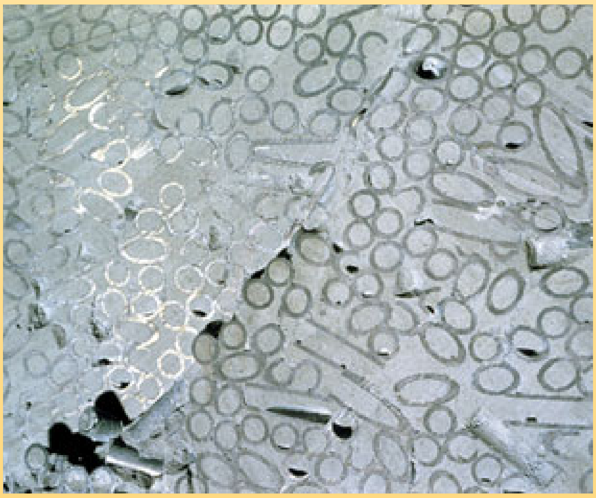
Conditioning, a vital phase

G

The purpose of conditioning waste is to mitigate any harmful effects by ensuring lasting, high-performance **containment** of the **radionuclides** inside it. Two complementary operations are carried out to this end. A material is used to immobilize the waste by encapsulating or blocking it in a **matrix** (cement, bitumen, glass, etc.), the type of which depends on the waste category. It is this matrix that fulfills the containment function. The encapsulated or immobilized waste is then placed inside a sealed **canister**, comprising one or more **envelopes**. The complete unit is known as a **package**. The canister allows the package to be handled and can also act as a containment barrier. The way in which these functions are shared between the matrix and the canister depends on the type of waste.

In storage or disposal conditions, waste packages are exposed to various internal or external hazards. First of all, radioactive decay of the radionuclides tends to disorganize the matrix containing them (**self-irradiation**). When radiation is emitted, **heat** is generated. For example, in glass used to contain waste with a high level of **activity**, the main irradiation sources are the result of **alpha** (α) disintegration from **minor actinides**, **beta** (β) disintegration from **fission products**, and gamma (γ) transitions emanating from β and α disintegrations. Most atom displacements are due to α disintegrations characterized by the recoil motion of a residual nucleus following the emission of an α particle that is transformed into a helium atom at the end of its path. **Recoil nuclei**, which deposit a large amount of energy over a short distance, lead to a cascade of atom displacements, thereby breaking many chemical bonds. This is the chief cause of potential long-term damage. Containment matrices must therefore resist heat and radiation damage.

Waste packages are also exposed to the action of water (**leaching**). For this reason, canisters must withstand corrosion, and containment matrices will be chosen for their resistance to water, i.e. their **chemical durability**.



CEA

Waste immobilized in a cement matrix.

Sidney Jezequel/Cogema

Vitrified waste canister being inspected in the R7 vitrification facility in the Cogema UP2-800 waste-reprocessing plant at La Hague (Manche département).

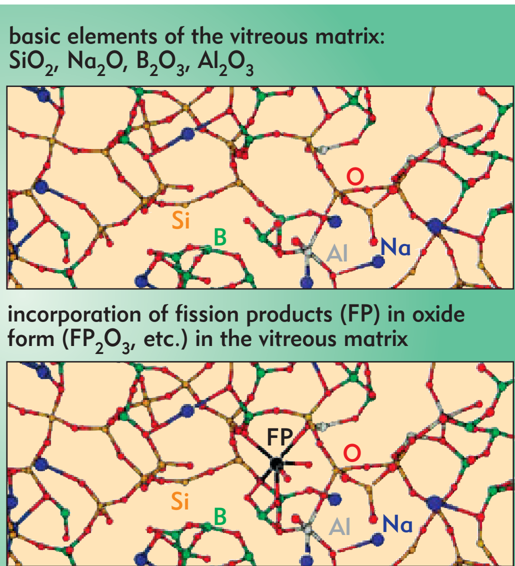


Figure 1. On the left, a block of containment glass. On the right, how elements are contained in a vitreous structure. Because of its amorphous structure, glass can easily accommodate the wide variety of elements found in spent fuel. Fission-product atoms are incorporated in the glass by forming bonds with its main components.

Performance levels required from materials

Containment materials must be capable of immobilizing radionuclides, ensuring thermal stability and good alteration resistance (**self-irradiation**, **chemical durability**, **leaching**; see box G, ***Conditioning, a vital phase***). In the case of glass packages, radionuclides form part of their disordered structure. This is true containment, not encapsulation. The glass-**formulation** methodology is intended to define a range of compositions around a reference formula to allow for slight fluctuations in the composition of the waste feed stream (figure 1). The glass properties must be guaranteed to ensure the satisfactory long-term performance of the waste **package**. The alteration behavior of the glass must also be assessed against the performance criteria required for interim **storage** or **disposal** purposes. In addition to experimental determination and comparison with natural materials, long-term predictive behavior models are being developed (see *Predicting the long-term behavior of waste packages,* and *Glass packages guaranteed for millions of years*).

A similar approach is adopted to develop ceramics or glass/ceramic materials specifically designed to confine certain chemically pure elements, suitable for waste management options in which some long-lived radionuclides would undergo **transmutation** and others would be conditioned separately. Under such conditions, the required durability would be on a similar scale to the time required for the **radioactivity** to disappear.

The current vitrification process in France

The current vitrification process (figure 2) is carried out in two steps: evaporation–calcination of fission-product solutions, then vitrification of the resulting calcine. The evaporation–calcination step is carried out in a rotating tube heated by a resistance furnace. The calcine, made up of elements from the solution in nitrate or oxide form, flows into an induction-heated metal pot. Glass former or glass frit is added to the calcine to produce the containment glass. Borosilicate glass consisting mainly of about 80% SiO_2 (silica), B_2O_3 (boric anhydride), Al_2O_3 (alumina), and Na_2O (sodium oxide) is fabricated at La Hague. Fission-product oxides are incorporated in quantities ranging from 12 to 18% of the R7T7 glass package (this value ranges from 6% to more than 20% depending on waste composition and type of glass. In the La Hague vitrification facilities, the metal pot is heated to 1,150 °C using a 200-kW power generator operating at a frequency of 4 kHz. The glass inside the metal pot is melted by conduction upon contact with the metal wall. Glass can react with metals at the process temperature, with the result that melting pots corrode and must be periodically replaced. They currently have an average lifetime of 5,000 hours with R7T7 glass. The melter lifetime has been extended considerably since the vitrification unit was commissioned, however, by modifying the composition of the nickel-based alloy from which the pots are made and by optimizing the management of the thermal power dissipated in the glass during the process. The unit also includes equipment for process off-gas treatment, comprising a particle separator, a condenser, and scrubbing columns.

Fission-product solution is fed at a nominal rate of 60 L/h to produce 25 kg/h of glass. Glass is poured every eight hours into a **canister** with a capacity of two 200 kg melts. The canister is then sealed by a welded cover and placed in dry storage until its temperature, due to the residual waste heat, is low enough for it to be sent to a long-term interim storage facility in view of possible geological disposal at a later date.

In the future, vitrification materials and processes must adapt to foreseeable changes in requirements. Higher fuel **burnup** values and new fuel-assembly designs will improve reactor performance. Further improvement of waste management implies greater waste-volume reduction, containment of solutions from reprocessing of legacy fuel, or vitrifying certain types of low- and intermediate-level waste (**LLW** and **ILW**). As regards vitrification, these trends result in greater quantities of metal in the waste, the presence of particular chemical elements (e.g. cerium Ce) or corrosive elements (such as sulfur S or phosphorus P) during glass fabrication, or increasing waste loading. The acquired expertise and the most recent studies show that these constraints can already be overcome, one example being the manufacture of refractory glass. A glass fabricated at a temperature of 1,300 °C has recently been developed to contain solutions generated by reprocessing research fuel. Such glass cannot be made in today's metal pots, which have a temperature limit of 1,150 °C. Technologies will have to be developed that are compatible with higher temperatures and that have good corrosion resistance with respect to liquid phases during the fabrication process. Direct-induction cold-crucible vitrification is an example of this technology (box).

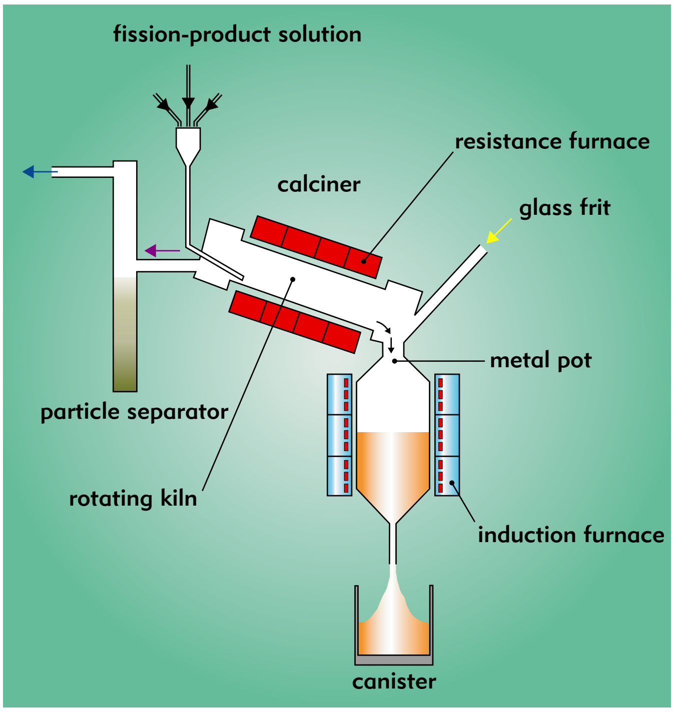


Figure 2. Continuous two-step vitrification process.

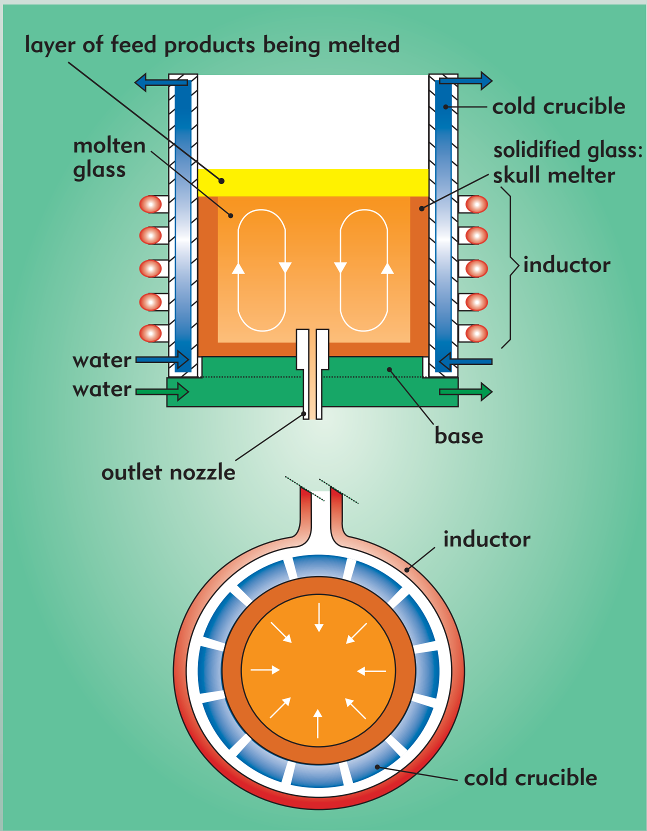
Industrial production around the world

Two types of vitrification process are currently used on an industrial scale world-wide. The Liquid-Fed Ceramic Melter (LFCM) process, which calls for large ceramic furnaces, is in use in the United States, Japan, and Russia. The two-step process described earlier and developed by CEA is used at La Hague in France, and in the United Kingdom in the Windscale Vitrification Plant (WVP) at Sellafield. In France, some 10,000 canisters have been produced to date, representing 4,000 metric tons (t) of glass, equivalent to 11 x 10^{20} Bq, or 30 x 10^{9} Ci, since the AVM was commissioned in 1978. Total production in the United Kingdom since 1990 amounts to some 2,000 t. Other pro-

Direct-induction cold-crucible vitrification

In this process, electric currents are induced directly in the material to be melted. The crucible must be as transparent as possible to the electromagnetic field. The induced currents can dissipate energy due to Joule effect in the material, causing it to melt. The melter load must be conductive to allow induction to occur. Glass is an insulating material at room temperature, but once melted its electrical resistivity drops to 10 Ω·cm, allowing induction. Two preheating methods were investigated to overcome the insulator/conductor barrier, i.e. to initiate induction in the glass: the first using microwaves, the other using a metallothermic method in which the **oxidation** energy of a metal is used to melt the glass locally. This was the method chosen.

The melter consists of a crucible placed on a base fitted with a pouring nozzle. The crucible and base consist of water-cooled metal segments. A mechanical stirring device is used to obtain a uniform molten glass bath. The inductor surrounding the crucible is connected to a high-frequency current generator; for a cold crucible with a 650 mm diameter, the generator power output is 280 kW at a frequency of around 300 kHz, to produce glass at a rate of nearly 50 kg/h. The production throughput can exceed 200 kg/h with a crucible 1.1 m in diameter (diagram).



The advantages of the direct-induction cold crucible are mainly due to the formation of a layer of glass that solidifies upon contact with the cold melter walls to form a “skull melter”. The skull prevents direct contact between the molten product and the cooled wall and creates a thermal insulation barrier. In this way, the crucible is not corroded by the molten glass, and the process can reach temperatures of more than 2,000 °C without damage to the cold crucible, which in turn cannot contaminate the molten material. Another advantage of this process is the formation of a cooler layer caused by feed products on the surface of the molten glass. This layer limits the volatility of elements from the melt. From the nuclear waste-reprocessing standpoint, the main advantage is the very long melter service life that reduces maintenance requirements and the quantity of secondary technological waste to be managed.

duction figures are nearly 1,500 t since 1995 for the United States, 2,500 t made from highly diluted solutions in Russia since 1986, and less than 100 t for Japan since 1995.

Cold crucible: bright prospects

Prospects for vitrification technologies already look good, especially in the USA, the UK, Italy, Korea, Japan, and France. Additional prospects will appear in China tomorrow, and perhaps in India. They should benefit from the latest technological breakthroughs. As regards the French process, the cold crucible is currently proposed as a replacement for conventional metal pots or even the calciner–metal-pot system, with a view to obtaining a simplified single-step process. A system can be devised in which the waste solution is supplied through a direct liquid-feed system to the surface of the bath at the same time as the glass frit. This would considerably reduce the size and maintenance requirements of the industrial equipment. The LFCM process remains useful for very large-capacity requirements, although it will raise technical problems at the end of the life cycle as regards processing the resulting technological waste.

The cold crucible can also be used to produce ceramic matrices (e.g. zirconolite or hollandite) intended for the containment of specific long-lived radionuclides extracted by advanced separation from the high-level waste stream generated by reprocessing spent fuel (see *Tailor-made matrices for long-lived radionuclides*). It would also be suitable for producing so-called *light* glass, which contains only some of the elements from the fission-product solution. The other radionuclides (e.g. minor actinides) would be reprocessed or confined in other materials. Glass packages produced in this way, without the most **radiotoxic** elements, would represent a **radiotoxic inventory** that would drop more

Erebus, a cold-crucible, magnetic-induction vitrification pilot facility installed at CEA/Valrhô-Marcoule, has been developed for long-lived intermediate- and high-level waste (type B and C). The gas treatment system (column with the porthole) can be seen at the rear.

Thierry Foulon/CEA

quickly than existing types of glass to the level of initial uranium ore. In addition, specifications regarding their chemical durability would become less stringent.

Finally, the cold crucible means that vitrification technology, with its proven performance levels, can be used to reprocess LLW and ILW (see *Working towards a universal container for category B waste*), either by vitrifying it directly or, in the case of oxidizable – often organic – products, by combining this technology with combustion devices such as plasma torches. In simpler terms, the heat given off in the crucible, combined with a flow of oxygen, is high enough to ensure the combustion of a variety of waste including ion-exchange resins, plastics, or graphite. The cold crucible is an ideal vector for incineration–vitrification processes as it allows both operations to be performed in the same chamber. One or more plasma torches can be added to increase incineration efficiency. The advantages of these two processes have been demonstrated separately. Studies are now under way to couple them to develop a process for reprocessing a wide range of LLW and ILW for inerting and volume-reduction purposes. This is one of the future industrial challenges that this technology will help to face.

Working towards second-generation processes

The industrial viability of vitrification processes has been amply demonstrated. Technical knowledge of materials and processes is now sufficiently advanced to consider the short-term possibility of setting up second-generation cold-crucible processes capable of adapting to new constraints. These processes will allow higher temperatures to be reached, generally leading to improved waste loading and therefore more effective volume reduction. They will also offer the advantage of handling a wider range of waste using simplified, compact instrumentation, making for reduced maintenance, and producing more diversified, long-lasting materials to offer more flexible answers to industrial requirements. Combination with combustion technologies will open the way to a wealth of new possibilities.

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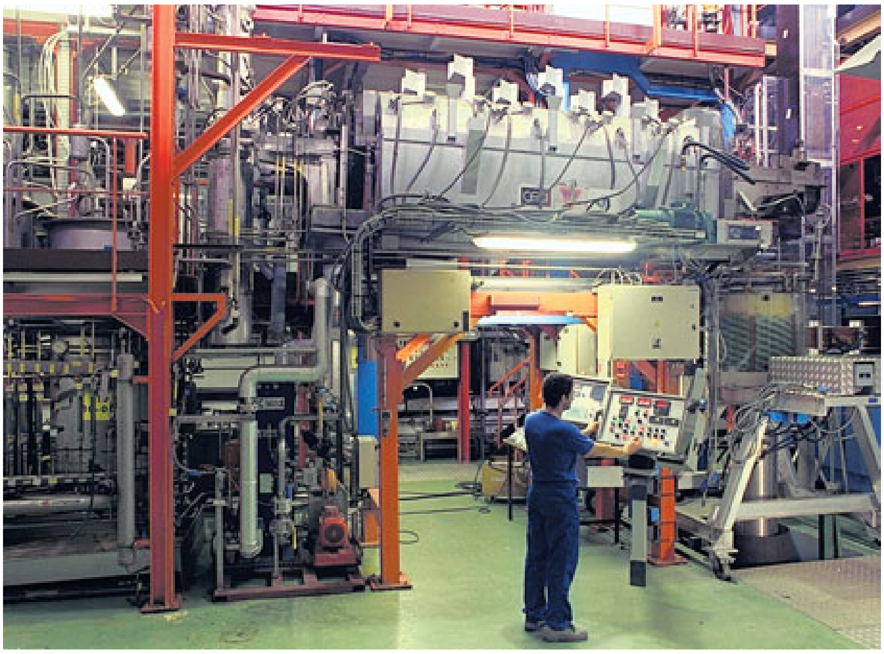
View of the PEV (evolving vitrification prototype) installed at CEA/Valrhô-Marcoule, showing the horizontal calciner and the cold-crucible melting furnace. An operator can be seen at the control station setting the pouring parameters.



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