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# VITRIFICATION OF HIGH LEVEL WASTES IN FRANCE

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## 1. HISTORICAL BACKGROUND

High level radioactive wastes in the form of fission product solutions are generated in nuclear fuel reprocessing plants. The solidification of these liquid wastes by a vitrification process was first considered in France over 25 years ago. Since that time, considerable research and development work has been conducted to derive suitable materials and processes. Significant milestones in this program include the following :

1957 : Beginning of laboratory studies

1960 : Startup of the first cell in the VULCAIN series. These cells were used to produce glass blocks of a few kilograms containing actual radioactive solutions.

1963 : Startup of GULLIVER, a radioactive glass fabrication facility based on a gel process yielding 5 kg glass blocks.

1969 : Startup of the VULCAIN pilot plant, using a pot vitrification process. From 1969 to 1973 the facility produced about 12 metric tons of glass, corresponding to 820 tons of fuel irradiated in French graphite/gas reactors. (VULCAIN resumed operation in 1979 and 1980 to vitrify FBR wastes).

1978 : Radioactive startup of AVM, the vitrification facility at the Marcoule UP1 reprocessing plant.

## 2. VITRIFICATION AT THE UP1 REPROCESSING PLANT

The UP1 reprocessing plant began operation at Marcoule in 1958. It reprocesses spent fuel from the plutonium production reactors as well as from commercial naturel uranium/graphite/gas reactors and MTRs.

The plant uses the Purex process and generates highly radioactive wastes in the form of acidic fission product solutions that are stored on-site in stainless steel tanks. Table 1 indicates some of the properties of these solutions.

## 2.1. The Glass Medium

Glass formulations have been devised for each type of solution to meet special requirements, including the following :

- suitable chemical composition,
- maximum permissible temperature in the interim storage facility,
- large liquid-to-glass volume reduction,
- ease of manufacture under industrial conditions,
- chemical stability with regard to environmental agents,
- physical stability under self-irradiation.

Typical glass compositions and properties are shown in Table 2.

## 2.2. The Vitrification Process and Facility

The batch process pot vitrification technique used in the PIVER pilot vitrification plant provided a substantial amount of technical data on radioactive glass manufacture, casting and production phenomena. This information was useful in subsequently designing a continuous process to meet the Marcoule throughput requirements and to reduce the volume of previously stored wastes. This development resulted in the construction of AVM, the Marcoule Vitrification Facility.

The vitrification technique is based on a two-stage process (Figure 1) In the initial calcination step the feed solution is continuously supplied to a rotary kiln where it is solidified. In the next step the calcined products are blended with suitable raw materials in an induction-heated melter to produce the desired glass at a temperature in the 1100-1250°C range.

The molten glass is cast every eight hours into stainless steel canisters that are introduced into the vitrification cell.

Gas generated in the melter and the calciner is extracted through the rotary kiln. The primary components are steam, nitrogen compounds and dust particles. Most of the latter are soluble in nitric acid and are trapped in a dust remover and then fed back into the calciner. The gas stream then flows across a condenser and a standard treatment system comprising an absorption column, a washing column, an absolute filter and an extraction blower.

The maximum plant capacity is 36 $l.h^{-1}$, and the maximum glass output is about 16-18 $kg.h^{-1}$.

Each canister is filled with 360 kg of glass (150 l) corresponding to three castings. Several hours after filling, the canister is transferred to another station in the vitrification cell where the lid is welded on using a plasma torch.

After welding, the canisters are cleaned by high pressure water jetting in a separate cell, from which they are then transferred to an air-cooled storage facility where they are stocked on metal racks. Forced-air cooling is initially provided but subsequently switched off to permit natural convection cooling (Figure 2). The storage facility was designed to prevent the glass temperature from exceeding 600°C.

As of January 1984, a total of 715 $m^3$ of fission product solutions have been vitrified in the Marcoule facility corresponding to 138 million curies (967 filled canisters).

## 3. VITRIFICATION AT THE UP2 AND UP3 REPROCESSING PLANTS

Another French nuclear fuel reprocessing center began operation in

1966 at La Hague, in Normandy. Initially limited to reprocessing spent fuel from commercial graphite/gas reactors, it was completed in 1976 by a "High-Activity Oxide" (HAO) head-end facility designed to reprocess Light Water Reactor (LWR) fuel. The nominal HAO plant capacity is about 400 metric tons per year. In order to meet French and foreign throughput requirements, the decision was made to design and build two additional plants on the same site : UP2 and UP3, each with an annual capacity of 800 metric tons. UP2 is already partially in use, and should be in full operation by 1989. UP3 is scheduled to be ready for operation in 1987.

High level radioactive wastes are stored on-site in stainless steel tanks. The quantity of wastes produced from reprocessing spent graphite/gas reactor fuel is diminishing and being replaced by LWR fuel reprocessing wastes. Consequently, vitrification process development work is primarily concerned with the latter.

The average characteristics of LWR fission product solutions are as follows (per metric ton of uranium) :

a) Volume of concentrated solution : 300 l

b) Chemical composition :

| | |
|---|---|
| . free acidity | 2 N |
| . $HNO_3$ | 38 kg |
| . U | 0.65 kg |
| . Pu | 0.05 kg |
| . Am | 0.32 kg |
| . Np | 0.43 kg |
| . Cm | 0.03 KG |
| . Fission products | 26.04 kg |
| . Fe | 6.0 kg |
| . Misc.(P, Ni, Cr) | 2.3 kg |

c) Total activity

| | |
|---|---|
| . $\beta$ , $\gamma$ activity | 530 000 Ci |
| . $\alpha$ activity | 2 800 Ci |

d) Radionuclide spectrum

| | |
|---|---|
| . Ru + Rh | 32 000 Ci |
| . Cs + Ba | 222 000 Ci |
| . Sr + Y | 134 000 Ci |
| . other $\beta\gamma$ emitters | 142 000 Ci |
| . Am | 800 Ci |
| . Cm | 1 980 Ci |
| . Pu and other $\alpha$ emitters | 20 Ci |

It was decided that the fission product solutions would be mixed with alkaline solutions and dissolution residues for vitrification.

The alkaline solutions are produced by solvent purification in the first extraction cycle and the plutonium purification cycle. They are concentrated and stored in a special tank. After three years of cooling their nominal characteristics per metric ton of uranium are the following :

a) volume of concentrated solution : 198 l

b) chemical composition :

| | | |
|---|---|---|
| Na | 8.3 | kg |
| U | 0.7 | kg |
| Pu | 0.003 | kg |

Their beta-gamma activity ranges from 500 to 600 Ci and the alpha activity is about 1 Ci (per metric ton of uranium). The principal beta and gamma emitters are $^{137}$Cs and $^{90}$Sr, while alpha contamination is primarily due to plutonium.

The dissolution residues result from centrifugal clarification of the fission product solution. The fine particles are backwashed and stored in a special tank. This type of fines includes both zircaloy and undissolved fission products, especially platinoids and molybdenum. After three years of cooling their nominal characteristics per metric ton of uranium are the following :

a) Volume of concentrated solution : 135 liters

b) Chemical composition :

| | |
|---|---|
| . Fission products (Ru,Rh,Pd,Mo,Tc) | 3.1 kg |
| . Zircaloy scrap | 2.2 kg |
| . Pu | 0.005 kg |
| . U | 0.093 kg |

c) Total activity

| | |
|---|---|
| . $\beta, \gamma$ activity | 63 365 Ci (mainly from $^{106}$Ru + Rh) |
| . $\alpha$ activity | 2 Ci (mainly from Pu) |

## 3.1. The Glass Medium

The glass formulations developed to solidify LWR waste solutions must meet the same requirements as those used in the UP1 facility at Marcoule. However, allowance must be made for a major difference : the high fission product content of the solutions processed in UP2. This implies a trade-off with regard to the glass composition. Thus, a high percentage of fission product oxides in the glass permits a high volume reduction factor, but this in turn has two major drawbacks : the high specific activity results in substantial heat release ; and the percentage of centrifuged elements other than fission products diminishes accordingly, resulting in lower amounts of silica, aluminia and other oxides which enhance the properties of the glass.

For this reason the fission product oxide content was limited to about 11-13 wt.%. Table 3 shows the composition of a glass formulated to meet various requirements. The vitrification process developed at Marcoule was adopted, therefore requiring a number of related properties compatible, among others, with a continuous fabrication process and ensuring safe containment for interim storage and long-term disposal.

### 3.1.1. Glass Properties Related to the Fabrication Process

Three important aspects must be considered with respect to the fabrication process described above :

. the corrosiveness of the molten glass with regard to metals,
. the viscosity of the molten glass,
. volatilization during glass fabrication.

The corrosiveness of the glass is of considerable importance, since it determines the lifetime of the melting furnace and thus affects the quantity of the secondary solid wastes produced. It is difficult to modify this corrosiveness (e.g. by reducing the $Na_2O$ content) without significantly affecting other properties, and viscosity in particular. It is preferable to select a material with a favorable cost/lifetime ratio ; laboratory corrosion studies have shown the advantages from this standpoint of using Inconel 601.

Suitable viscosity is essential in any process involving molten glass transfer, as for casting. The maximum viscosity at the casting temperature has been set at about 400-500 poises. Once again trade-offs are necessary among the $Na_2O$, $B_2O_3$ or $Al_2O_3$ content values, since a lower viscosity (obtained by increasing the $Na_2O$ and $B_2O_3$ content or reducing the $Al_2O_3$ content) is incompatible with the chemical resistance of the glass.

The volatility of certain non-radioactive elements can raise problems, but above all ruthenium is capable of clogging outgassing lines by $RuO_2$ buildup. In order to assess this volatilization experiments must be conducted with radioactive samples using the same equipment setup. These experiments were carried out at Marcoule using tracers in the ATLAS one-half scale continuous vitrification mockup. A reduction in ruthenium volatility could be achieved either by denitrating or by sugaring the process solution. Sugar hydrolyzes in an acid medium, yielding levulose and glucose, which is a reducing agent. An adequate amount of sugar in the calciner ensures a sufficiently reducing environment to prevent the formation of ruthenium oxides complexes, forming $RuO_2$ directly in the unit. The results showed that a process solution sugar content of 30 $g.l^{-1}$ reduces the volatilization to an acceptable value of less than 2%, compared with almost 30% in an unsugared solution in the same process equipment (Figure 3).

Candidate glasses for continuous melt process operation are submitted to measurements and analyses in order to improve their properties and reach a final selection.

### 3.1.2. Glass Properties Related to Interim Storage and Long-Term Disposal

Determination are carried out on non-radioactive laboratory samples, non radio-active industrial-scale blocks, or on radioactive blocks weighing several kilograms.

#### 3.1.2.1 Physical Properties

The following physical properties are measured :

- specific gravity
- viscosity versus temperature
- electrical resistivity
- characteristic temperatures
- specific heat
- thermal conductivity versus temperature
- expansion coefficient versus temperature
- compression modules
- microhardness
- Young's modulus
- biaxial flexure strength
- fracture toughness (KIC)

A number of characteristic values are indicated in Table 4. The biaxial flexure strength is on the same order as for Pyrex glass, while the Young's modulus and fracture toughness values are higher than for Pyrex. The presence of metal particle inclusions (0.7 wt.%) does not affect these two values.

#### 3.1.2.2 Homogeneity

Glass homogeneity is evaluated using microscopes, electron probe analyzers, scanning or transmission electron microscopes, X-ray diffraction, etc.

The examinations completed to date only on non-radioactive samples show good homogeneity even for molybdenum. Figure 4 shows the molybdenum distribution in the glass formulation presented in Table 3.

### 3.1.2.3 Thermal Stability

Thermal stability is evaluated in the following ways :

#### 1. Glass Crystallization Property Measurements

Glass samples are subjected to a 15-20 hour heat treatment at 30°C temperature intervals up to 1200°C to induce microcrystallization phenomena for which the following points are measured :

- occurence temperature range
- crystalline density
- maximum crystal growth rate
- maximum growth temperatures
- upper and lower crystallization temperatures.

The crystalline phases are identified when possible, although this is made difficult by the small crystal fraction (well below 1%).

#### 2. Crystalline Phase Development Tests

The glass blocks are held for 100 hours at the previously determined maximum crystallization temperatures in order to confirm the presence of crystals in massive samples, to obtain crystal growth, to quantify the crystalline density by X-ray diffraction or image analysis, and to identify the crystalline phases formed.

In most cases, complex molybdic microcrystallization occurred, containing primarily sodium, rare earth or strontium molybdates, spinels (mixed Cr, Ni, Fe oxides), cesium and uranium oxides. Figure 5 shows a typical example. Crystallization generally remains very low, never exceeding a few percent.

## 3. Examination after Extended Isothermal Treatment

Samples are held for 6 months or 1 year at a temperature 50°C above the transformation point, and at 450°C (the maximum currently permissible glass core temperature for interim storage). Crystalline phases are again identified and quantified.

## 4. Induced Crystallization Effects on Mechanical Properties and Alterability

In the selected glasses with their low crystallization rates, the appearance of crystalline phases generally did not modify their mechanical properties. With regard to their fission product containment power, crystallization raises the cesium leaching rate by about a factor of 5, slightly increases the strontium leaching rate and does not affect or even reduces the leaching rates for other fission products.

## 5. Crystallization Effects of Metal Fines

Metal fines included in the lattice can act as clustering agents ; also, by creating structural discontinuities, they constitute an interface with lower surface energy from which cristallization will tend to develop.

The amount of metallic fines in LWR glass is estimated at 0.7 wt.%. Examinations of laboratory samples containing 1% platinoid inclusions have shown that after induced crystallization heat treatment the glass contained precipitations of the metal fines, but no significant changes in the matrix or in the quantity of crystalline phases were found in comparison with glass containing no fines.

## 6.Volatility Effects

Constant temperature holding can volatilize certain radioactive chemical species. This problem must be considered during the first years after disposal. The slightly volatile species can condense on the cooler walls of the container and can be relatively leachable.

The overall mass entrainment in time is low at temperature below 1050°C : the mass loss after 8 hours is less than 0.6% (Figure 6). Planned tests will determine the entrainment of radionuclides such as $^{137}Cs$ and $^{106}Ru$ as a function of time and temperature.

### 3.1.2.4 Chemical Stability

The following examinations are carried out.

#### 1. Matrix Alterability Measurements

This parameter represents the sum of the leaching rates for all of the glass components. For analytical purposes they are measured at 100°C over a period of about 100 days under dynamic (Soxhlet) or static leaching conditions. The result is expressed in terms of the sample weight loss and by measuring the mean mass leaching rates of the major components. Changes in the pH are noted and the surface etching layer is analyzed.

The test results indicate that the mean alteration rate at 100°C with currently available glasses is about $10^{-4}$ g of glass per $cm^2$ per day, or about $10^{-6}$ and $g.cm^{-2}.d^{-1}$ at room temperature under dynamic conditions with water renewal. Under static conditions the mean alteration rate is always 3 to 5 times lower, and the pH modification remains balanced. For example, the mean alteration after 28 days for the glass defined in Table 3 is $1.43 \times 10^{-4}$ $g.cm^{-2}.d^{-1}$ for dynamic leaching compared with 0.50 x $10^{-4}$ $g.cm^{-2}.d^{-1}$ for static leaching. (at 100°C)

Moreover, the glass leaching is not congruent, i.e. each oxide reacts in a specific way and certain oxides (e.g. rare earths, actinides, Zr, Fe and sometimes Al) tend to remain in the interface layer.

#### 2. Alterability under Pressure

At 100°C, the leaching rates are practically unaffected by a pressure of 100 bars.

## 3. Leaching Resistance and Containability of Radioactive Glasses

Glass blocks are manufactured under active conditions with reconstituted solutions by a batch vitrification process and cast in graphite molds to permit mold removal. Leach tests are carried out on the following samples :

- $\beta\gamma$ glasses with slight Pu enrichment (400 - 1000 Ci $\beta\gamma$)
- $\alpha$ glasses with separate trace amounts of Pu, Am and Np
- $\alpha$-doped glasses.

The containability, corresponding to the activity released from the material by water action is expressed in terms of dilution equivalents, and amounts to the following values :

| RADIONUCLIDE | APPROXIMATIVE VALUE ($g.cm^{-2}.d^{-1}$) |
|---|---|
| $^{137}$Cs | $1.5 \times 10^{-7}$ |
| $^{90}$Sr | $5.0 \times 10^{-8}$ |
| $^{106}$Ru | $5.0 \times 10^{-8}$ |
| $^{144}$Ce | $3.0 \times 10^{-8}$ |
| $^{125}$Sb | $1.2 \times 10^{-7}$ |
| $^{60}$Co | $1.0 \times 10^{-7}$ |
| actinides | $10^{-7}$ to $10^{-9}$ |

For a glass block of the type planned for the La Hague industrial reprocessing center corresponding to 1300 kg of fuel, the resulting activity release versus time is shown in Figure 7 for values of this magnitude.

The leaching rate was found to be significantly temperature-dependent : compared with baseline values recorded at 25°C, the fission product leaching rate increased 10 times at 70°C, 30 times at 100°C and 180 times at 150°C. The increases were less significant for the actinides : at 70°C the leaching rates were unchanged in glasses doped with $^{238}$Pu, $^{241}$Am and $^{244}$Cm. This is no doubt attributable to the hydrolysis kinetics of these oxides and to their low solubility when hydrated.

### 4. Hydrolized Layer Studies

These experiments are carried out under conditions similar to those of the Materials Characterization Center. These long-term (up to 12-month) static leaching tests are designed to study the hydrolized layer, and the effects of the pH or of various corrosion products or geological inputs in the water.

### 5. Geological Disposal Parameter Test

The purpose of this test is to study the effects of geological disposal parameters such as the leachant composition, flowrate, temperature and pressure. Glass samples are placed on a screen at the top of a stainless steel tube filled with a mixture of materials representative of the repository environment (sand, granite, corrosion products, alumina, illite, bentonite, etc). The alteration will be measured under static conditions at intervals of 7 days, 28 days, 3 months, 6 months.

The reference conditions are specified as follows :

|  |  |
|---|---|
| . temperature | 90°C |
| . pressure | 100 bars |
| . water flowrate | $200\ l.m^{-2}.yr^{-1}$ |

Tests will also be conducted at 150°C and 150 bars.

This study is currently in progress with non-radioactive glass samples.

### 6. Geological Repository Simulation with Small Glass Blocks

Samples 70mm in diameter and 80mm high surrounded by environmental materials are placed inside a test enclosure. Granitic water is allowed to stand for one month in a second identical enclosure above the first one, before it is introduced into the leaching vessel. The standard test conditions are 100°C at 100 bars. Water samples are taken at 2-month intervals.

Six identical test setups are currently in use with non-radioactive glass samples. Plans call for installing 4 more units in hot cells for testing glasses doped with $^{238}Pu$, $^{241}Am$ and $^{237}Np$.

## 7. Leaching Tests on Industrial Glass Blocks

These tests are designed to assess the alterability of industrial size glass blocks subjected to the least favorable cooling scenario, i.e. while the container is still in the cell after casting. The relative increase in surface area under these conditions is by nearly a factor of 10.

Glass blocks initially measuring 300-350mm in diameter and 500mm high are leached in a stainless steel Soxhlet device under static or dynamic conditions. For the dynamic tests the glass is continuously immersed in water flowing out through an overflow pipe. The large amount of water involved permits tests of very long duration provided the sampled water volume is replaced.

Static and dynamic tests lasting 100 days have been completed to date on a non-radioactive LWR glass block. The test results confirm the incongruent nature of the leach rates : molybdenum, boron, lithium and sodium losses are relatively higher than for silicon and aluminium.

In general, the measured alteration rates are on the order of $10^{-4}$ $g.cm^{-2}.d^{-1}$ and the correlation with the Soxhlet laboratory tests is good, especially in static conditions.

Static leaching losses for various elements compared with silicon are the following : cerium = 1000 times lower, lanthanum = 130 times lower, strontium = 30 times lower, iron = 30 times lower.

The water pH evolution curves show that the equilibrium point is about 10.4 in dynamic conditions and 9.6 in static conditions.

A one-year static leaching test with a 95 kg glass block is now in progress.

### 3.1.2.5. Irradiation stability

An important consideration is to evaluate the glass behavior under self-irradiation and to detect any modification in its properties. For this purpose, glass samples will be irradiated in a β flux to a dose on the order of $10^{12}$ rads. It is unlikely, however, that any significant changes will appear, based on previous tests with Marcoule glass irradiated to $10^{11}$ rads which showed that irradiation effects were practically nil.

In the near future, glass samples doped with $^{237}$Np, $^{238+239}$Pu, $^{241}$Am and $^{242+244}$Cm will be prepared, and self-irradiation effects will be evaluated from the following standpoints : overall leach rate changes, homogeneity, density, crystallization, energy storage, helium release and its consequences. At the same time, specific leaching properties of the actinides will be measured and their physicochemical form will be studied in the leachates.

## 3.2. Vitrification Process and Facilities

Two identical vitrification facilities are planned for the site : R7, to process the UP2 throughput, and T7 for the UP3 plant. Both will implement the same process used at Marcoule. R7 is now under construction, and is scheduled to become operational late in 1986 or early in 1987.

### 3.2.1 Prototype Unit

A prototype unit was built and operated at Marcoule. It differs from the AVM facility in three areas : the component dimensions, the throughput capacity and some improvements in process equipment.

The dimensional changes are summarized in the following table

| | | AVM | R7 PROTOTYPE |
|---|---|---|---|
| CALCINER | diameter | 250 mm | 800 mm |
| | Heated length | 2.5 m | 3 m |
| | Wall thickness | 12 mm | 12 mm |
| | Rated heating power | 70 kW | 94 kW |
| MELTING FURNACE | Shape | cylindrical | Elliptical |
| | Dimensions | 350 mm Dia | 3000 mm major axis<br>350 mm minor axis |
| | Height | 1.0 m | 0.8 m |
| | Number of heating inductors | 4 | 4 |
| | Power rating | 100 kW | 200 kW |
| | Frequency | 10 kHz | 4 kHz |

The throughput capacity was increased according, from 40 $l.h^{-1}$ to 60 $l.h^{-1}$ for the liquid evaporation, and from 15 to 25 $kg.h^{-1}$ for glass production. The gas treatment system was also modified proportionately.

The principal equipment modifications include the following :

. calciner :
- provisions were made to replace the rotating seals without replacing the end-fittings
- the heating power distribution was improved by the adoption of four non-identical zones ;
- a compressed air driven backup motor was added.

. melting furnace : a separate drain tube was provided in addition to the casting duct

. frit feed unit : the slide valve was replaced by a pinch valve

As of november 1, 1983, the prototype unit had logged a total of 3500 operating hours on the basis of which the operational parameters were determined.

This total included periods of calcination only, as well as periodes of full process operation. The facility was used to solidify simulated LWR solutions, producing 5200 kg of calcinate and 18.4 metric tons of glass under satisfactory conditions.

### 3.2.2 The R7 Facility

R7 differs from the AVM facility in a number of fundamental respects. To begin with, the liquid waste material itself is different : as mentioned earlier, it consists of an LWR solution to which are added fine metallic particles in suspension and solvent rinsing solutions, representing a total of about 660 liters per metric ton of uranium.

A significant design difference in R7 (Figures 8 and 9 ) is the process layout with three independent vitrification lines, each with the same equipment as the Marcoule prototype. Each line includes a dismantling cell which, unlike the AVM facility, is separate from the vitrification cell. Another important difference is that the glass is not cast in the vitrification cell but in a separate cell. The canister cover melting station is thus set up outside the vitrification cell. After two castings (instead of 3 as in the AVM facility) totalizing 150 liters, the canister (Figure 10) exits via a passageway accessible from all three vitrification cells. All the canisters are wipe-tested for possible contamination before they are transfered to the storage area. If evidence of contamination is found, the canisters are decontaminated using high pressure water jets.

The containers inside their transport casks are transfered to the storage area by a traveling crane, where they are deposited inside tubular steel storage pits suspended from a metal framework beneath the concrete slab. Forced-air cooling is provided for a maximum specific power of 25 W per liter of glass to limit the glass core temperature to 450°C.

A quality control program is implemented throughout the fabrication and storage operations. The major quality control provisions are outlined in Figure 11.

R7 has been designed by SGN Company (Société Générale pour les Techniques Nouvelles).

## 4. PROSPECTS

A new generation of high melting point glass formulations is under development in order to improve the properties of the vitrified blocks. This will also require the use of new types of melting furnaces ; studies are now in progress in this area.

Plans call for implementing the existing technology in the T7 vitrification facility at La Hague, and also in a vitrification facility for solidifying high level liquid wastes from the COGEMA fast breeder fuel reprocessing plant : a single vitrification line is planned for this unit. Similarly, an identical vitrification facility will be installed at Marcoule to meet the requirement of the CEA's "TOR" pilot reprocessing plant for FBR fuels.

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| Reactor System | Fuel type | Burn up | Concentration rate | Acidity (M) | Chemical composition g.l$^{-1}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Al | Na | Mg | Fe | Ni | Cr | F | Fission products uranium and actinides |
| MTR | UAl/PuAl | 500 MWd.kg$^{-1}$ | 12m$^3$.t$^{-1}$ | -1.8 (depleted) | 81 | 2-3 | | 1-2 | | | 10-12 | low |
| GG (defense) | SICRAL | 1000 MWd.t$^{-1}$ | 30 L.t$^{-1}$ | 1.5-2.0 | 30-35 | 19-23 | 4 | 15-17 | 1-2 | 1-2 | 8 | 22-27 |
| GG (commercial) | SICRAL | 4000 MWd.t$^{-1}$ | 100 L.t$^{-1}$ | 1.0-1.5 | 10-12 | 2-5 | 3 | 8 | 1 | 1 | 5 | 37-42 |

**Table 1** : Characteristics of UP1 Fission-Product Solutions

|  |  | Waste type |  |  |
|---|---|---|---|---|
|  |  | Defense | MTR | Defense and Commercial |
| Composition (weight%) | $SiO_2$ | 38.1 | 37.0 | 38.4 |
|  | $Na_2O$ | 17.8 | 19.4 | 17.1 |
|  | $B_2O_3$ | 16.4 | 15.4 | 17.3 |
|  | $Al_2O3$ | 12.3 | 23.2 | 11.0 |
|  | $Fe_2O_3$ | 4.2 | 1.7 | 3.2 |
|  | MgO | 4.1 | - | 5.1 |
|  | NiO + $Cr_2O_3$ | 1.0 | 0.2 | 0.8 |
|  | F | 2.0 | 1.8 | 1.5 |
|  | Fission product and actinide oxydes | 4.0 | 1.3 | 5.6 |
| Current volume reduction (related to the liquid) |  | 7.0 | 3.5 | 6.0 |
| Glass volume per ton of fuel |  | 13 to 15 liters | 3.4 $m^3$ | approx. 10 liters |
| Viscosity at 1100°C (Po) |  | 150 | 430 | 130 |
| Thermal conductivity at 100°C (W.m$^{-1}$°C$^{-1}$) |  | 1.25 | 1.25 | 1.25 |

**Table** 2 : Characteristics of Some UP1 Glasses

| | |
|---|---|
| $SiO_2$ | 45.2 |
| $B_2O_3$ | 13.9 |
| $Al_2O_3$ | 4.9 |
| $Na_2O$ | 9.8 |
| CaO | 4.0 |
| $Fe_2O_3$ | 2.9 |
| NiO | 0.4 |
| $Cr_2O_3$ | 0.5 |
| $P_2O_5$ | 0.3 |
| $ZrO_2$ (filings) | 1.0 |
| $Li_2O$ | 2.0 |
| ZnO | 2.5 |
| Actinide oxides | 0.9 |
| F.P. Oxides | 11.0 |
| Metallic particles | 0.7 |

**Table 3** : Possible Glass Composition for Solidification of High Level LWR Waste (values in weight %)

| | |
|---|---|
| Specific gravity | 2.75 |
| Viscosity at 1100°C | 8 Pa.s (80 poises) |
| Transformation temperature | 502°C |
| Mean expansion coefficient | $8.3 \times 10^{-6}\,°C^{-1}$ |
| Thermal conductivity at room temperature | $1.1\ W.m^{-1}\,°C^{-1}$ |
| Young's modulus at room temperature | $8.4 \times 10^{10}$ N.m |
| Stress intensity factor | 0.95 MPa.m1/2 |

**Table 4** : Some Physical Properties of the LWR Glass Designated in Table 3, (free of metallic particles)

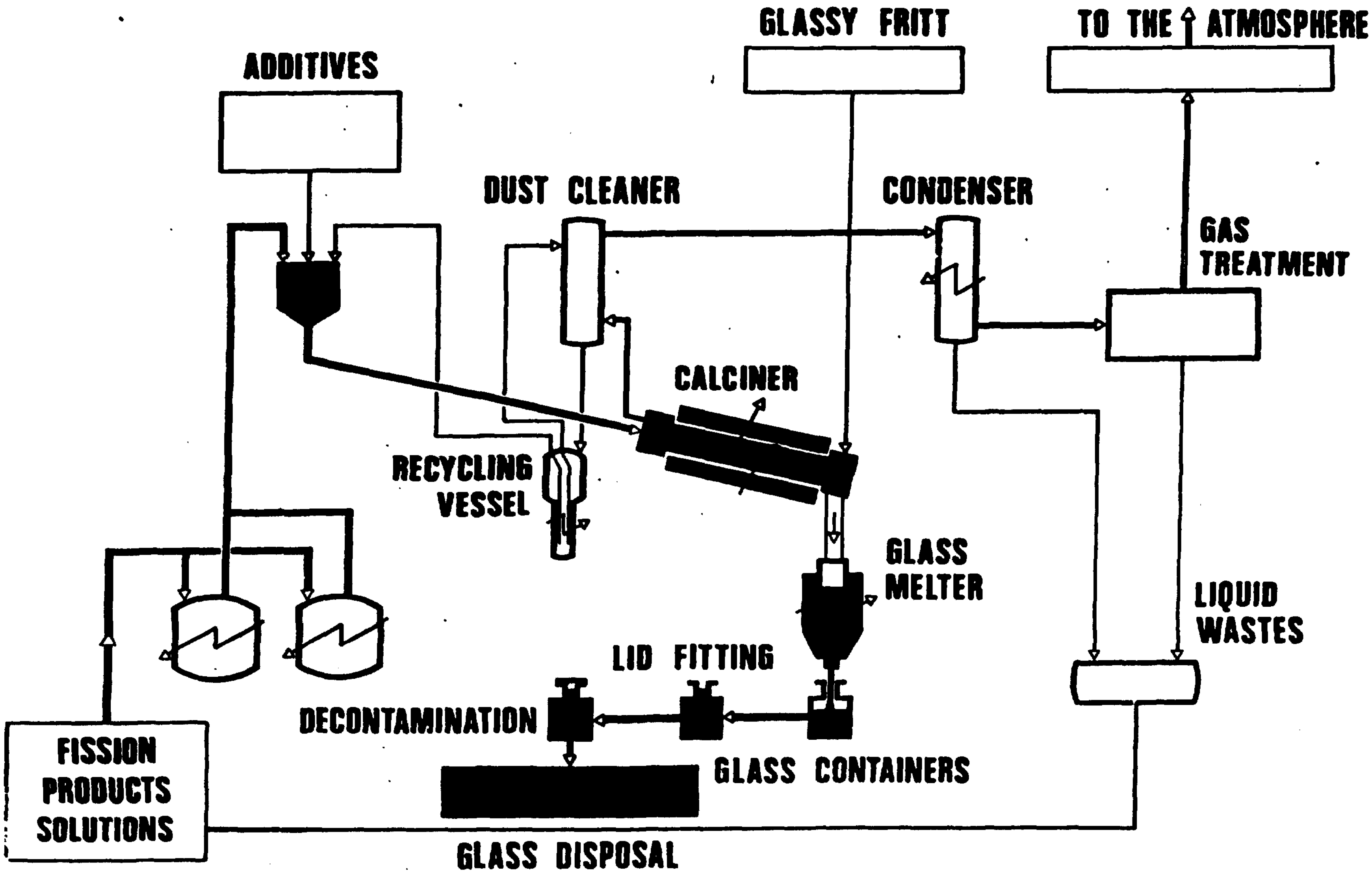
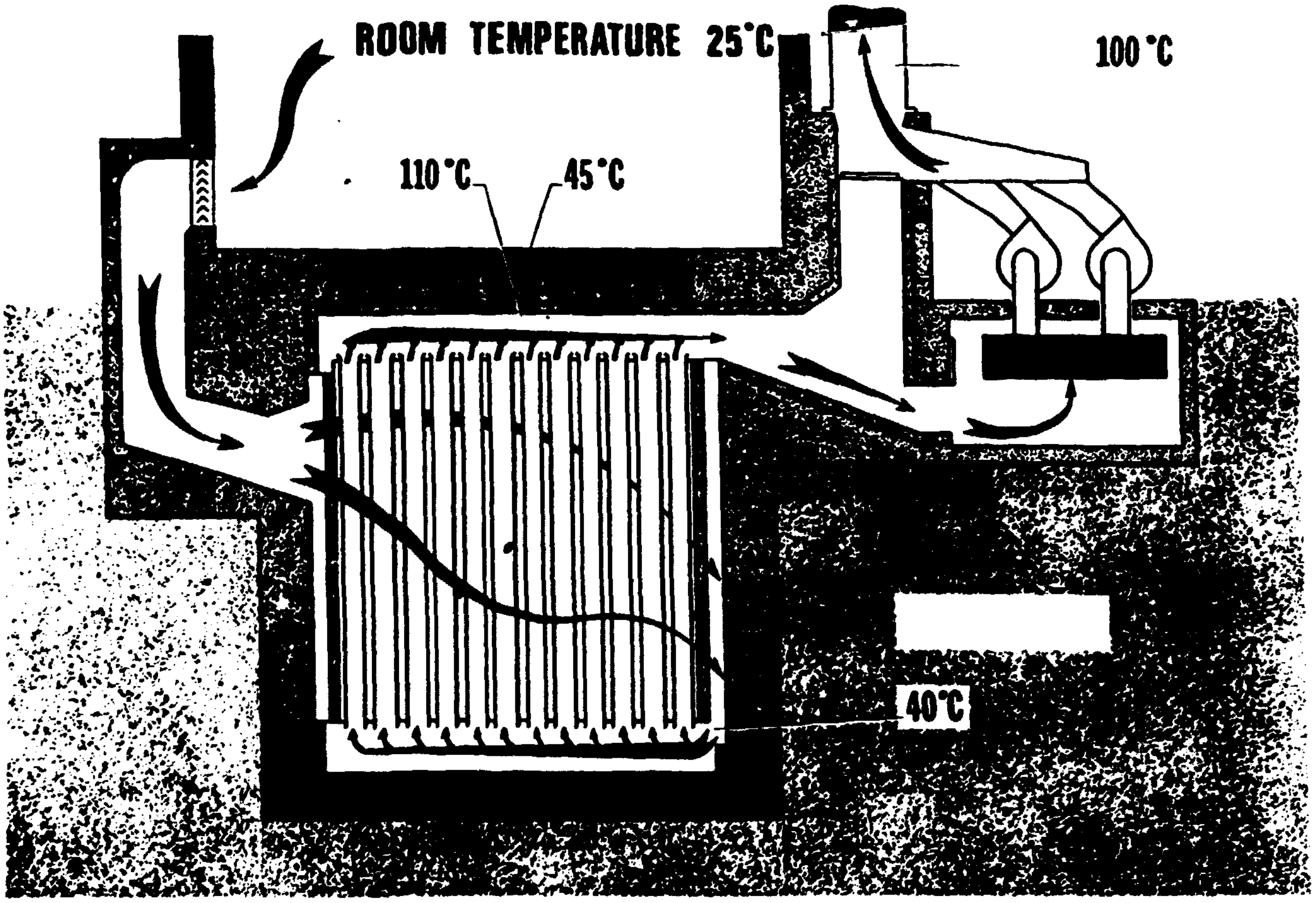
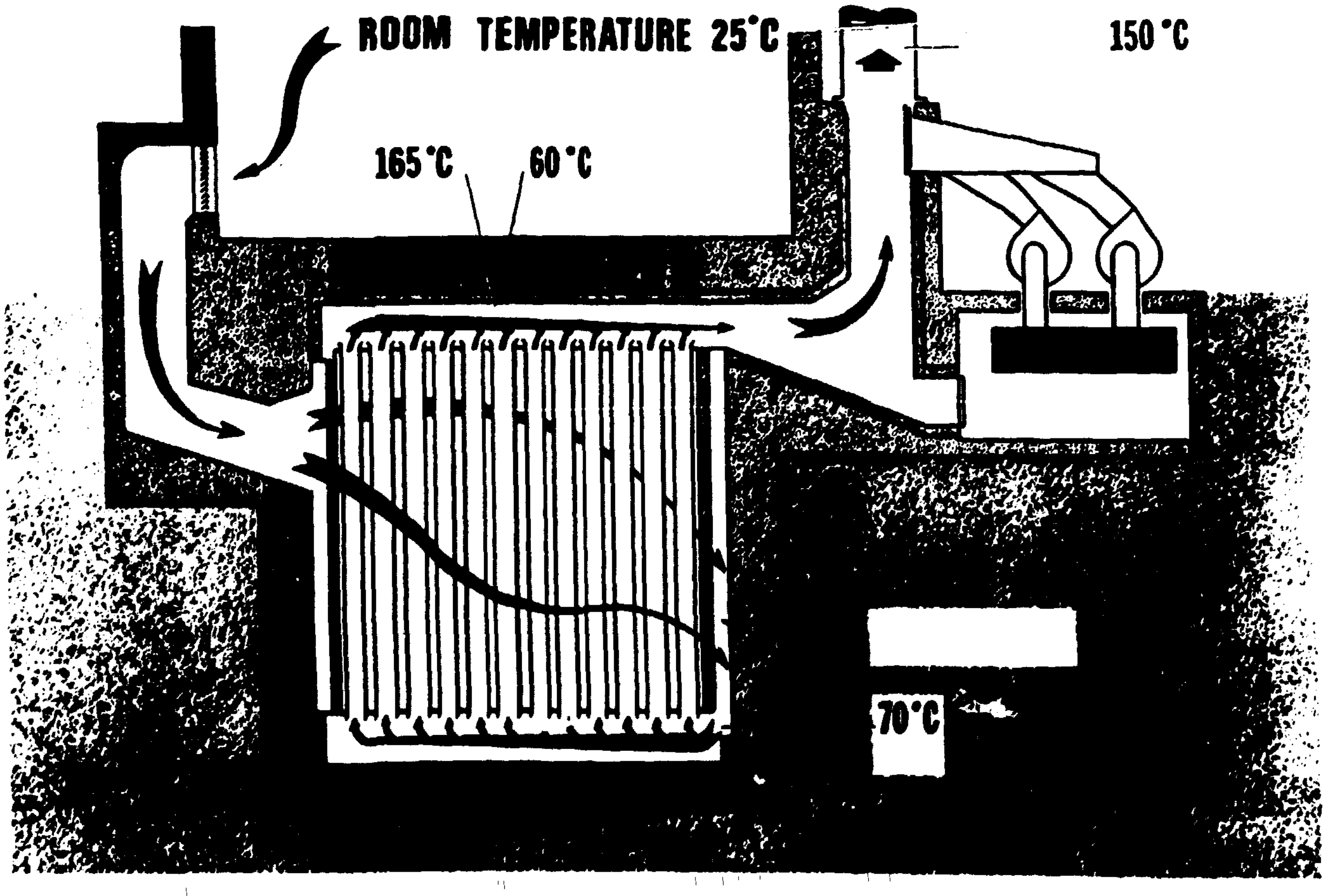


FIGURE 1 : MARCOULE UP1 CONTINUOUS VITRIFICATION PROCESS SCHEMATIC

FORCED AIR COOLING



NATURAL CONVECTION COOLING



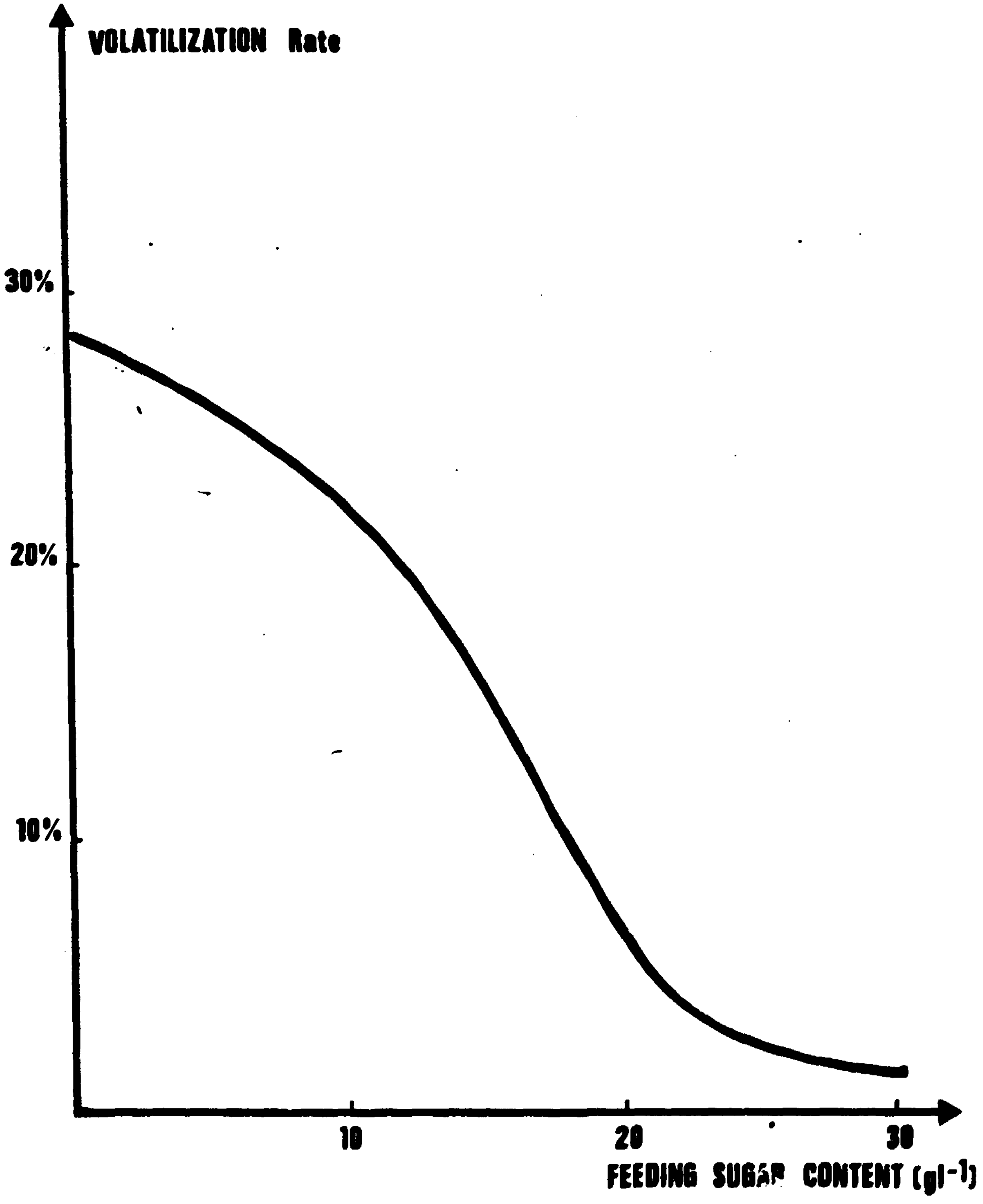


FIGURE 3: VOLATILIZATION OF $^{106}$Ru EFFECT OF SUGAR

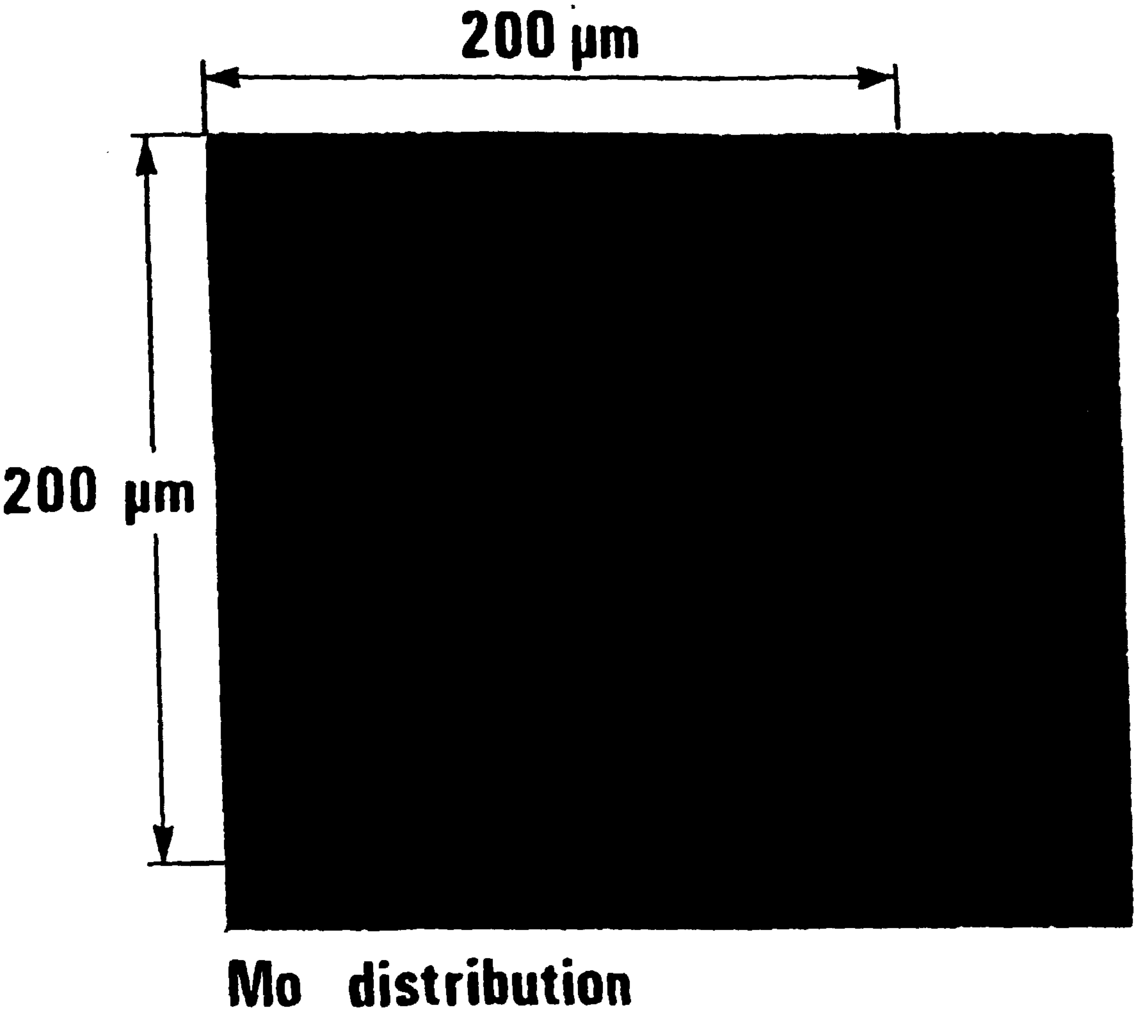


FIGURE 4 : SCATTERING OF Mo IN A LWR TYPE GLASS

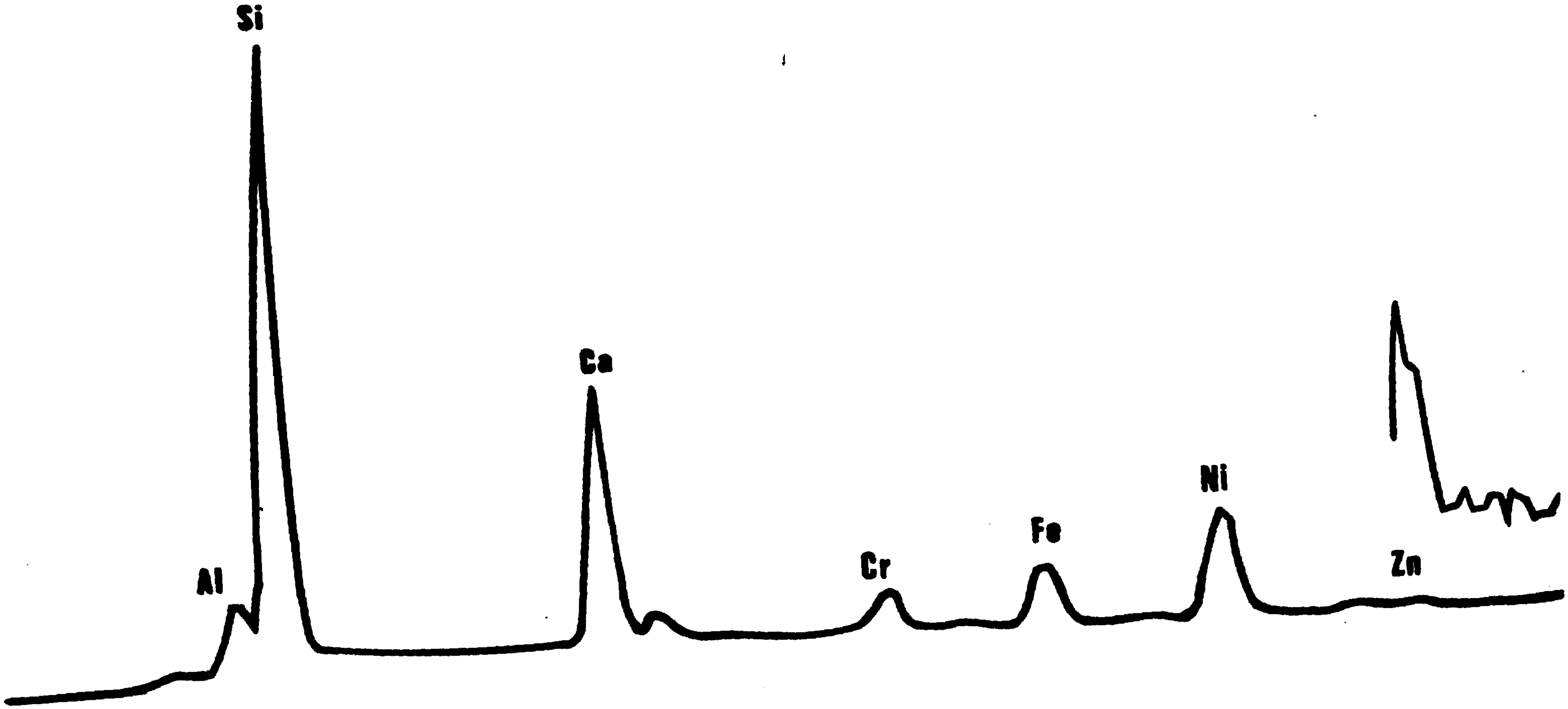


FIGURE 5 : IDENTIFICATION OF A CRYSTAL DEVELOPPED DURING THE DEVITRIFICATION TREATMENT OF A LWR TYPE GLASS

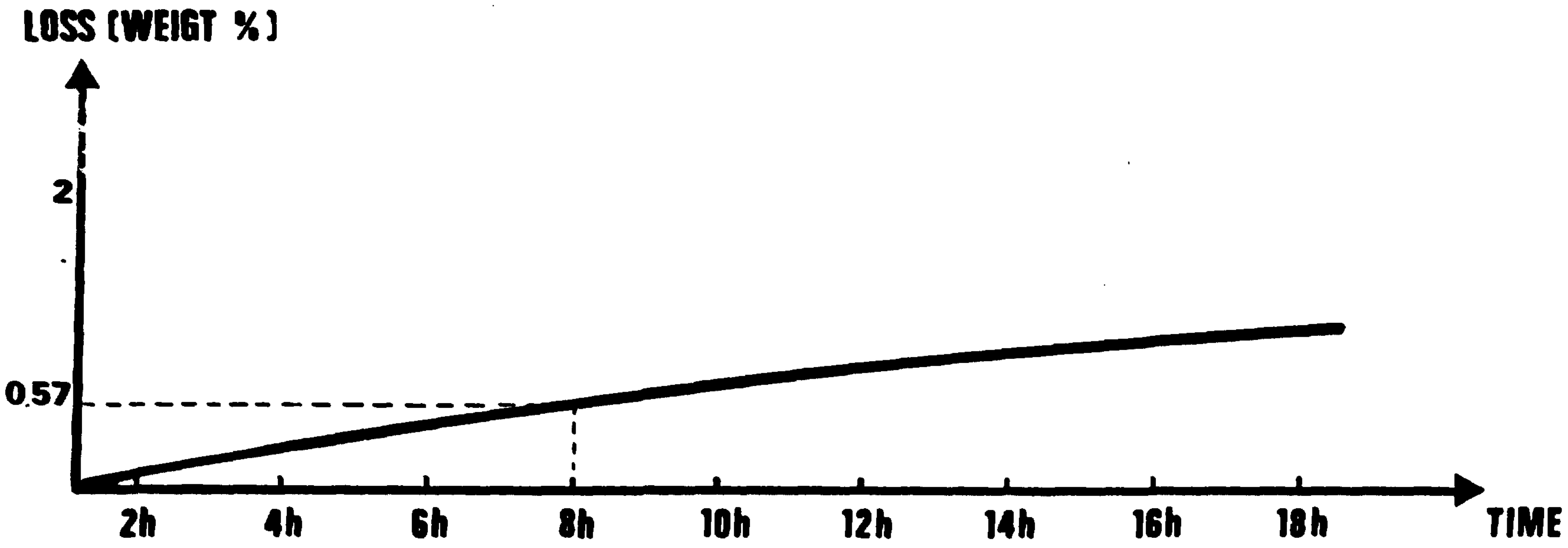


Figure 6 WEIGHT LOSS BY VOLATILIZATION OF A LWR TYPE WASTE SUBMITED AT A STEADY TEMPERATURE OF 1054°C

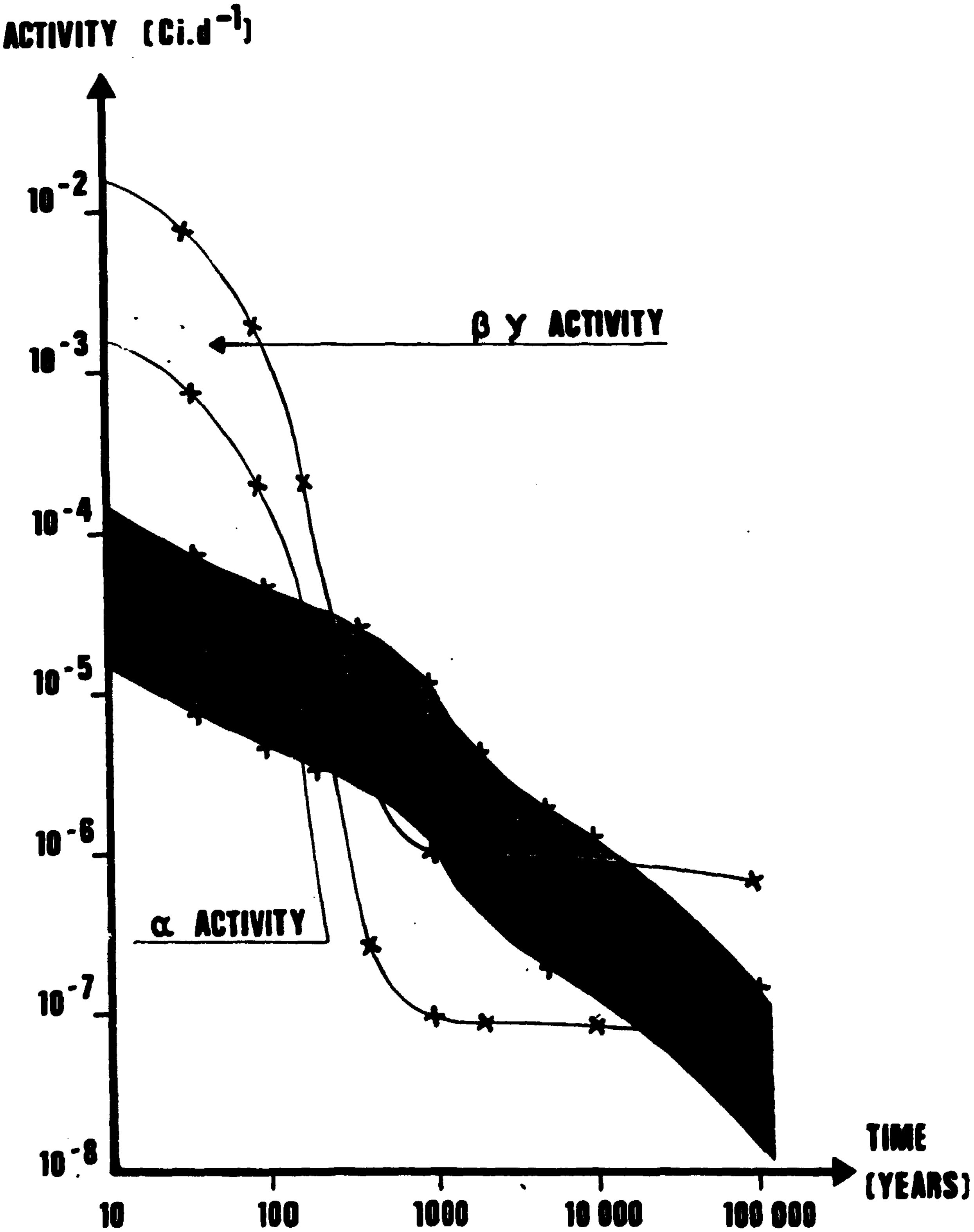


FIGURE 7 : **APPRAISAL OF THE RELEASABLE ACTIVITY VERSUS TIME BY A UP2 GLASS BLOCK**

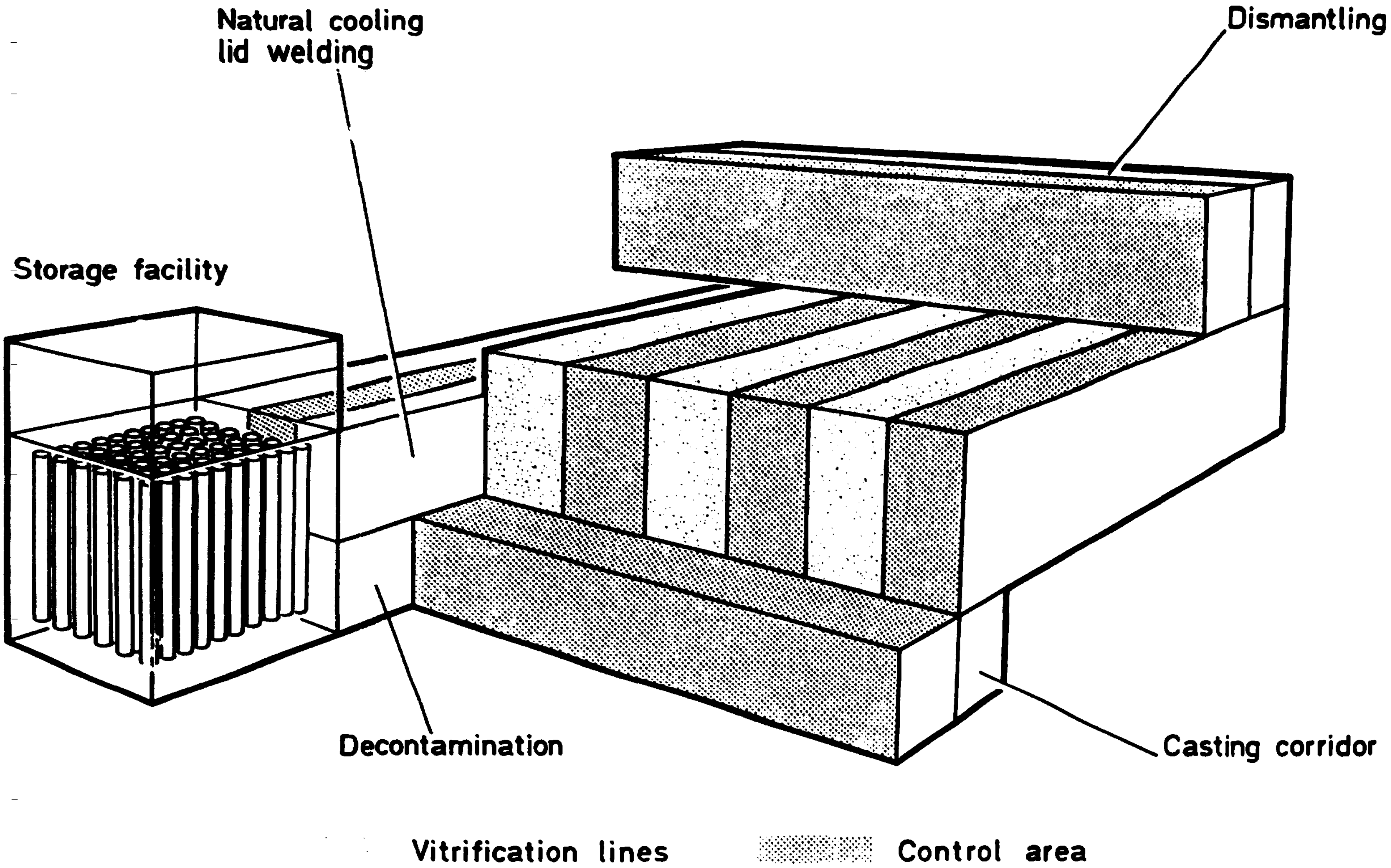
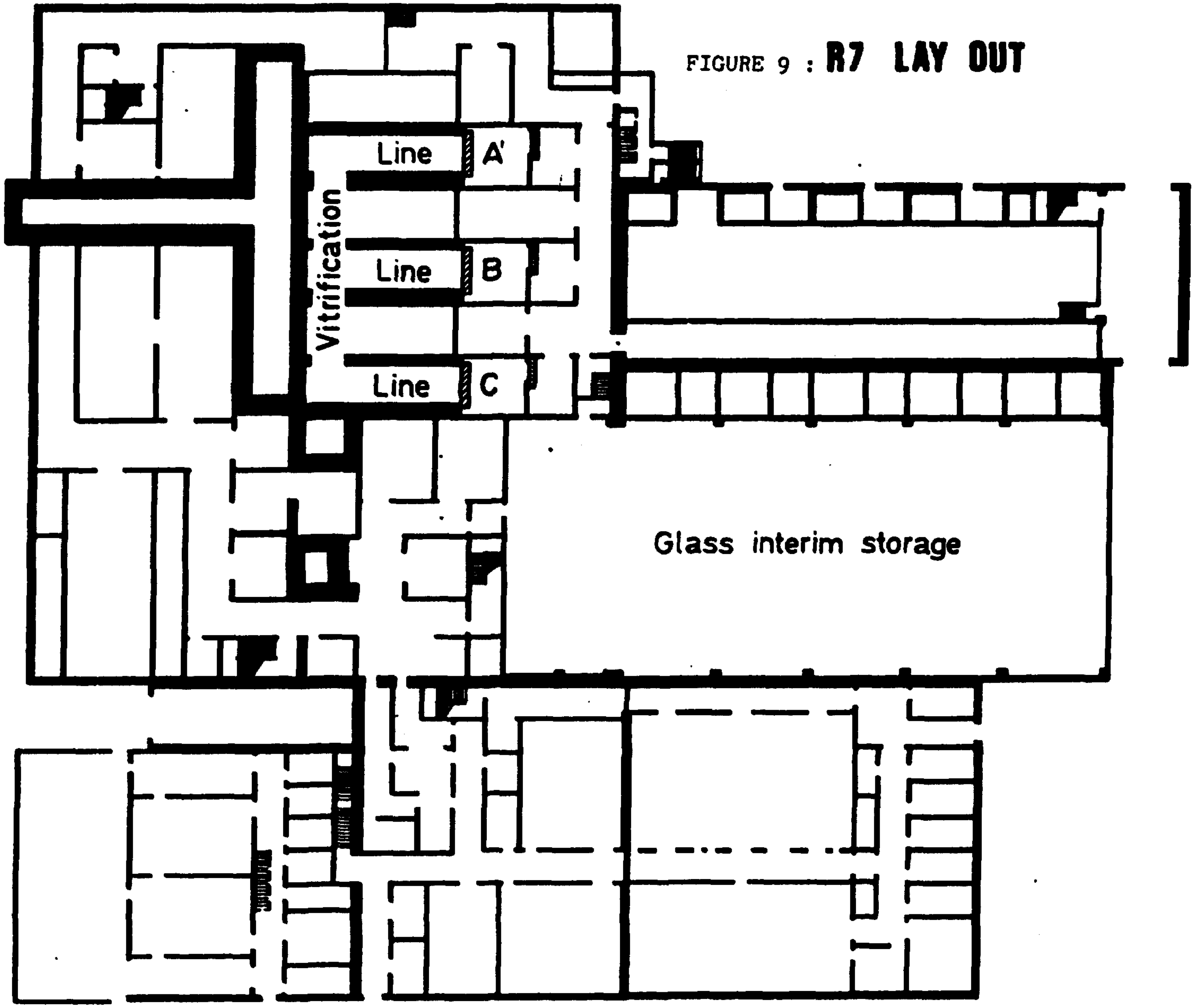


FIGURE 8 : LAY OUT OF THE LA HAGUE VITRIFICATION PLANT (R$_7$ AND T$_7$ )

FIGURE 9 : **R7 LAY OUT**



## FIGURE 10 : R7/T7 GLASS CONTAINER

**Container glass volume: 150 l.**

**( all dimensions in mm )**

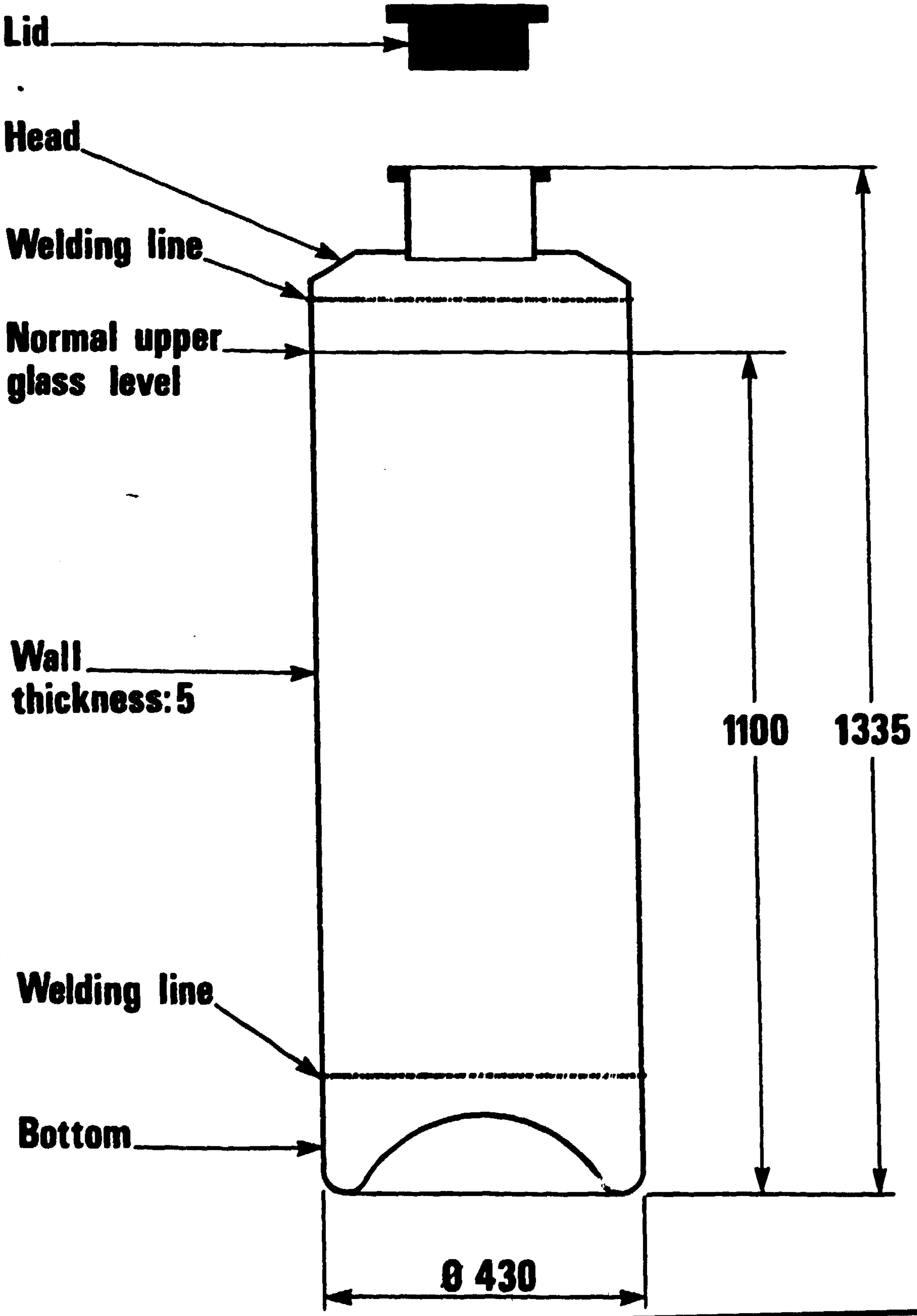


FIGURE 11 **R7 MAIN FUNCTIONS AND QUALITY CONTROL**