Selecting a Plutonium Vitrification Process

Antoine Jouan
Commissariat à l'Energie Atomique
Centre d'Etudes de la Vallée du Rhône
Etablissement de Marcoule
BP. 171
30207 Bagnols sur Cèze, France

ABSTRACT

Vitrification of plutonium is one means of mitigating its potential danger. This option is technically feasible, even if it is not the solution advocated in France.

Two situations are possible, depending on whether or not the glass matrix also contains fission products; concentrations of up to 15% should be achievable for plutonium alone, whereas the upper limit is 3% in the presence of fission products. The French continuous vitrification process appears to be particularly suitable for plutonium vitrification: its capacity is compatible with the required throughout, and the compact dimensions of the process equipment prevent a criticality hazard.

Preprocessing of plutonium metal, to convert it to PuO_2 or to a nitric acid solution, may prove advantageous or even necessary depending on whether a dry or wet process is adopted. The process may involve a single step (vitrification of Pu or PuO_2 mixed with glass frit) or may include a prior calcination step - notably if the plutonium is to be incorporated into a fission product glass.

It is important to weigh the advantages and drawbacks of all the possible options in terms of feasibility, safety and cost-effectiveness.

INTRODUCTION

What can be done with the surplus military plutonium still held by the two power blocs to avoid its proliferation? This is clearly a strategic problem to be solved by the politicians, but there are also considerable technical problems.

Apart from its explosive capacity, plutonium is also extremely radiotoxic over a very long timescale; more so, for example, than the uranium fission products which are associated with it when it is produced in reactors (cf. figure 1).

Several options are available; some involve its destruction by fission in reactors, for example, while others advocate isolating it after confinement in suitable matrixes. Both of these categories have been recommended for research by the US National Academy of Sciences.

THE CHOICE BETWEEN BURNING AND VITRIFICATION

Which strategy should be applied?

- Controlled fission means consuming the plutonium in power reactors as their fuel. This is the MOx process, in which France and other countries, notably Britain, Germany, Belgium and Japan are currently engaged.

It seems only reasonable to benefit from the energy released by plutonium fission : one gram of plutonium, after all, is equivalent to a ton of oil - with no impact on global warming. Proven technology already exists in which Pu is used to fabricate mixed oxide (MOx)) fuel for use in power reactors.

MOx fuel was first used in 1963 in Belgium, with the BR3 demonstration PWR at Mol and in Germany at Obrigheim in 1970. In France, MOx fuel experience has developed progressively since the first irradiation in the Chooz plant in 1974, followed by the MOx program in light water reactors operated by the French electrical utility EDF at Saint Laurent des Eaux in 1987. Seven French nuclear power stations are currently operating with MOx fuel, and EDF intends to extend its use into 20 to 28 units by the end of the century.

In the longer term controlled fission will also involve using plutonium in fast reactors. Russia, in particular, is advocating this direction, even if it appears not to have the resources to do anything about it at the moment.

- Vitrification is the incorporation of plutonium into a relatively insoluble glass network from which recovery would be difficult. This is a technical possibility, even if many years of development would be necessary before it could become an industrial solution.

FRENCH EXPERIENCE IN VITRIFICATION

France has undeniably acquired considerable experience in the field of vitrification. Radioactive glass blocks weighing a few hundred grams were produced as early as 1957. In subsequent years laboratory facilities were established at Saclay and Marcoule producing increasingly large glass blocks until the process finally assumed industrial proportions. It is now nearly 30 years since 1968 when the CEA began operating a vitrification unit called PIVER using a batch or pot vitrification process in which a radioactive fission product solution was converted into glass in a single induction-heated metal melter, used for the evaporation, calcining and vitrification steps (figure 2). About 200 glass blocks weighing about 100 kg each were fabricated. Twenty years after it was commissioned, PIVER was named a Nuclear Historic Landmark by the American Nuclear Society on November 15, 1989 : "high-level waste vitrification prototype and its storage facility both began operating in 1969. PIVER successfully demonstrated one of the essential safety conditions of the nuclear power option : the safe disposal and storage of long-lived radioactive waste".

The transformation into an industrial process came in 1978 when COGEMA brought into operation its Marcoule Vitrification Facility, adjoining the UP1 reprocessing plant. This was followed by two other facilities of larger capacity at La Hague - R7 and T7, attached to the two reprocessing plants UP2 and UP3. COGEMA uses the "continuous vitrification" process in all these facilities, as does the British operator BNFL. This two-stage continuous process (figure 3) is designed to convert high level liquid waste from Purex reprocessing plants into borosilicate glass. The High Level Waste solution in nitrate form is fed at a metered rate into an electrically heated rotating calciner where the salts are evaporated and the nitrates are partially calcined to oxides ; the calcine is then supplied together with glass additives into an induction-heated metal crucible. The process thus converts the nitrate solution into a

dry oxide form suitable for glass production. The current R7/T7 melter design has a total volume of 200 liters and weighs less than 500 kg : glass is poured about 70 liters at a time every 6 to 8 hours. The results logged by the French vitrification units are summarized in Table 1. Over 5000 canisters have been produced representing nearly 2000 tons of glass containing more than 1500 million curies of fission products.

Table 1 - Operating statistics for French vitrification facilities (as of December 31, 1994)

Operating Statistics	Reprocessing Plant		
	UP1 (Marcoule)	UP2 (La Hague)	UP3 (La Hague)
Vitrification facility	AVM	R7	T7
Startup date	1978	1989	1992
Evaporation capacity ($l.h^{-1}$)	40	60	60
Glass fabrication rate ($kg.h^{-1}$)	10-15	20-30	20-30
Vitrified solution volume (m^3)	1800	1750	587
Glass production (metric tons)	806	806	344
Number of canisters produced	2275	2048	869
Volume reduction factor	5.7	5.6	4.5
Vitrified βγ activity(MCi)	384.3	745.7	380.4

The process continues to evolve. The CEA has been developing a new glass melting technique in recent years, using an induction-heated cold crucible melter (figure 4). This highly efficient heating technique could no doubt be used to vitrify plutonium ; compared with existing processes, it can produce more refractory glass or vitrocrystalline formulas with even better containment properties than the current fission product glasses if required. This process has two major advantages : temperatures of 1500°C can easily be reached and the melter is corrosion-free.

PLUTONIUM VITRIFICATION METHODS

Plutonium vitrification has not been a subject of major research in France to date ; only a few fission product containment glass blocks were fabricated in the 1970s with a few percent of PuO_2 to dope them with alpha emitters in order to investigate alpha irradiation damage in the glass. The incorporation of PuO_2 in sufficient quantities proved difficult because of segregation problems and PuO_2 was replaced by alpha emitters with shorter half-lives such as AmO_2 or CmO_2. Vitrification is as previously said routinely used in the COGEMA reprocessing plants at Marcoule and La Hague to produce containment glass for concentrated fission product solutions, but the glass contains only negligible amounts of Pu. Glass containing PuO_2 has been fabricated by KfK in Germany, but Pu vitrification has only been seriously investigated in the USA at Savannah River.

Broadly speaking, there seem to be two main ways to vitrify plutonium :

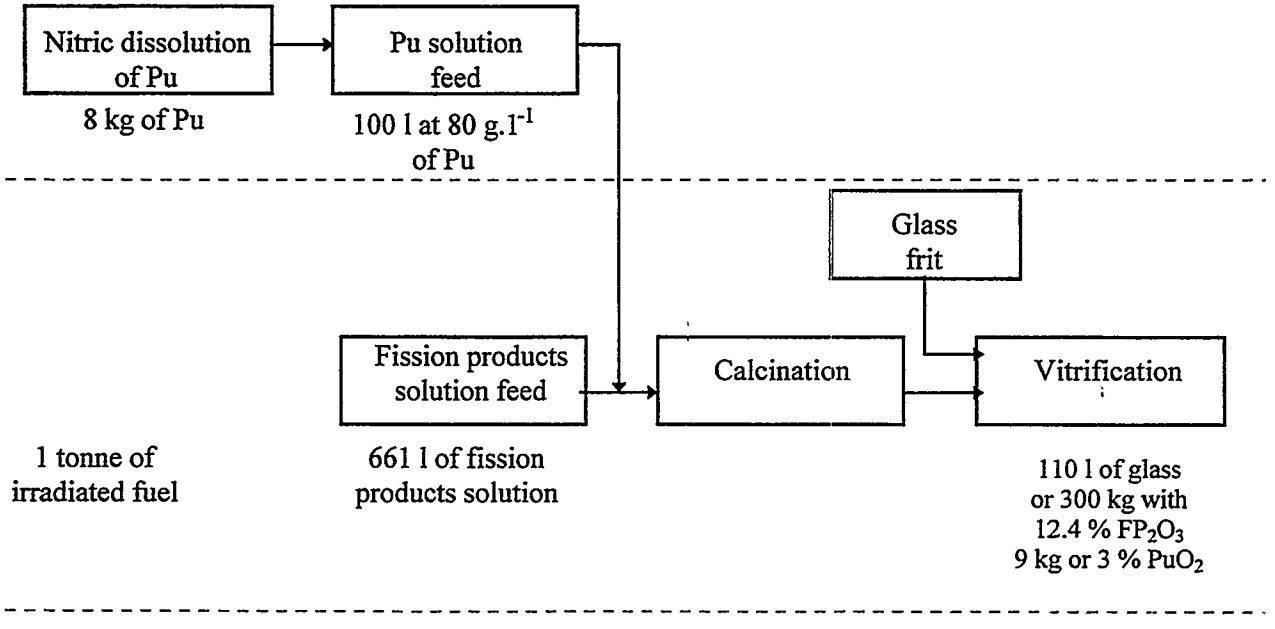
- The first is by incorporating it into borosilicate glass together with fission products, as recommended by the NAS. The intention here is to make recuperation as difficult as possible.

- The second involves determining the optimum formulation for incorporating PuO_2 alone into a glass matrix ; it should be noted that the maximum PuO_2 concentration in the glass would not only depend on its solubility in the glass, but could be limited by the risks of criticality and/or heat release in interim storage or after final disposal. The behavior of alpha emitting glass (helium production, leaching resistance) and its long-term behavior in repository conditions must also be investigated.

Let us now go into more detail on these two possible options :

- While the safer way may be to mix the plutonium with fission products in borosilicate glass, it is also the more difficult and subject to more constraints.

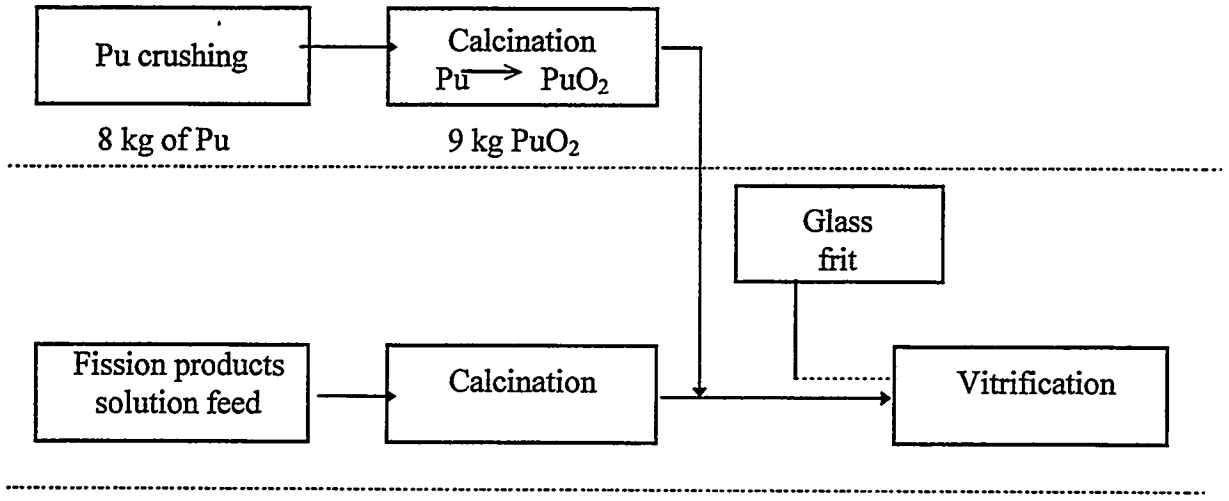
We are assuming that PuO_2 could be incorporated into fission products glass at a rate of 3% and, to use an example, let us consider the known process of the R7/T7 glass currently produced industrially at La Hague. The following simplified diagram shows what would probably be the most feasible method :



To ensure a homogeneous mixture and to avoid any plutonium segregation, the plutonium could be put into nitric solution and then fed into the calciner either parallel to or mixed with the fission products solution. Calcination would then change it into PuO_2. Closely mixed with the fission products calcinate, the PuO_2 would then be vitrified at the same time as the fission products oxides.

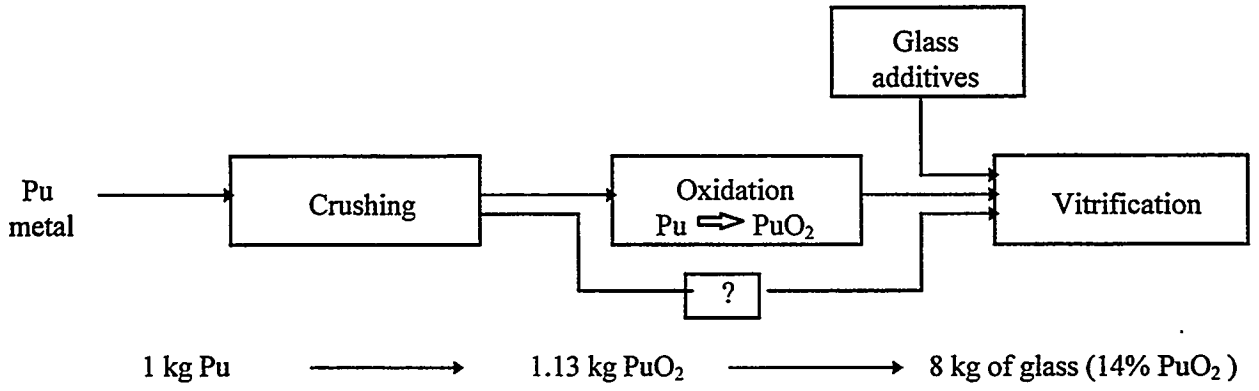
- Another possible technique could be the separate oxidation of the plutonium into PuO_2 followed by direct metered feeding at the vitrification stage. This would have the disadvantage of having to meter the feed in powdered form, certainly more difficult than a liquid feed, but would, on the other hand, be simpler and reduce the risks of criticality.

In any case, we would make 300 kg of glass for 8 kg of plutonium and using equipment like that at La Hague which produces about 800 canisters of 400 kg per year we could, theoretically, vitrify 8,5 metric tons of Pu in a year. Obviously, in reality the calculation is not as simple as that since the facilities at La Hague have not been designed to take account of criticality, particularly not for such an operation as this!



- Vitrification of plutonium on its own, without fission products would clearly result in the confinement of the PuO_2, but the plutonium could be more easily re-extracted.

Studies at Savannah River show the possibility of including 14% of PuO_2 in the lead-silicate formulae called "Löffler glass". In that case we could envisage the following scheme :



The metallic plutonium would first be crushed and the granulate or pulverized pieces would then be oxidized by heating in air at 500°C. Given the considerable reducing capacity of plutonium, we can even imagine the possibility of feeding Pu powder directly onto the surface of the glass melt where it would oxidize immediately in air or oxygen.

Disregarding the problems of criticality, it is easy to imagine a melter producing 50 $kg.h^{-1}$ of glass per hour which would thus vitrify 6.25 kg of Pu. Working at a rate of 4000 hours a year, 2 years would see the vitrification of 50 t of Pu in 400 t of glass. These are, of course, only hypotheses and there is still much work to do on glass formulations and their properties, as there is on safety aspects, above all criticality.

CHOICE OF EQUIPMENT

The main stages in the plutonium vitrification process, whichever option is chosen, PuO_2 alone or mixed with fission products, are the following :

- Pu crushing
- oxidizing Pu into PuO_2
- vitrification as such

Since the first two stages are already well known and in industrial operation, we now need only concern ourselves with the vitrification itself. A direct induction cold crucible melter (figure 5) would seem to have all the advantages needed for the delicate operation we are considering :

- it is completely static and its volume has been reduced to the minimum (about 60 cm diameter and 40 cm high) for an output of 50 $kg.h^{-1}$ of glass,

- all glass formulations are possible, including the most refractory, since there is no limit to the melt temperature,

- there is no risk of either corrosion or wear even at the highest temperatures,

- since the surface of the melt consists of a layer of ingredients for the vitrification, thus cold, any potential volatility is limited. This greatly simplifies the gas treatment equipment,

- the melt can be mechanically agitated, if necessary, which could prove useful to ensure that the glass is homogeneous,

- it enables the glass to be poured at any rate desired and started and stopped at will,

- the only contaminated wastes which could be produced in any possible incident would be easily dealt with owing to the absence of refractory and the nonadherence of the glass to the cold walls.

In passing, we might mention that a panel of international experts assembled by the Washington Hanford Company has recently selected this type of melter to vitrify the waste from Hanford.

Cold crucible technology is well understood by the CEA which, of course, developed it. It is already accepted in French non-nuclear industry and is being seriously considered for use in the nuclear field.

COMMENTS AND CONCLUSION

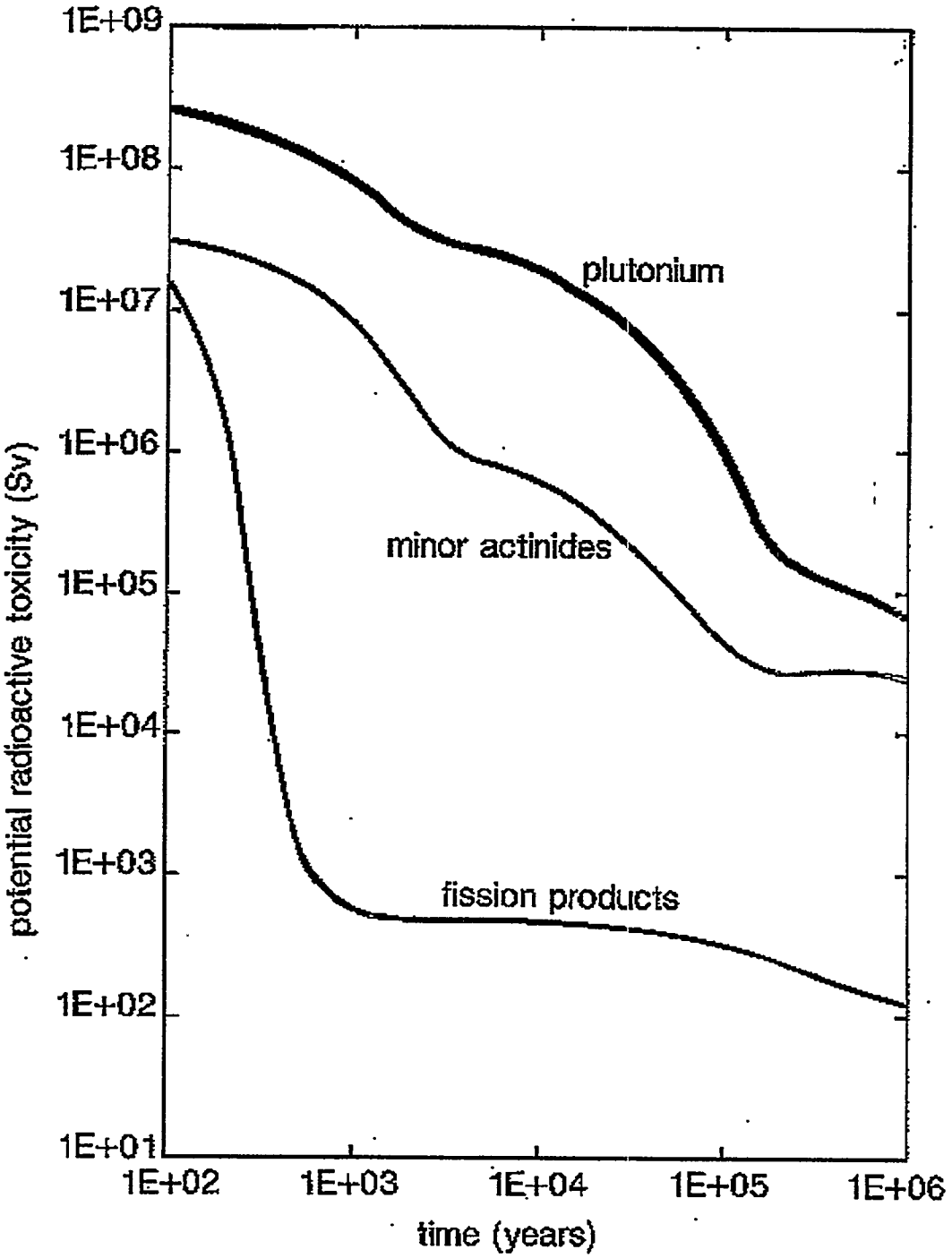
Apart from its attendant financial burdens, the vitrification of plutonium mixed with fission products will always remain a delicate operation compounding the problems of fission products and the criticality of plutonium, not to mention the political ramifications. It would, for example, be preferable for the both the plutonium and the fission products to come from the same country and that adequate controls be maintained on the vitrified product since it would contain weapons grade material ; otherwise, serious complications are no doubt inevitable.

The vitrification of plutonium alone, without fission products would obviously give a less secure product and would not entirely satisfy the criteria of the NAS. Although this process will also require the perfection of numerous techniques, it appears, nevertheless, to be simpler and certainly less costly. The chief reasons for this are that hot cells would not be necessary (the operation could, we think, be done in glove boxes) and that the quantity of glass needed would be much smaller. We estimate that it would probably be about ten times cheaper!

In any case, the vitrification of plutonium, the most energetic of all elements, seems anachronistic in a world where energy needs will continue to escalate.

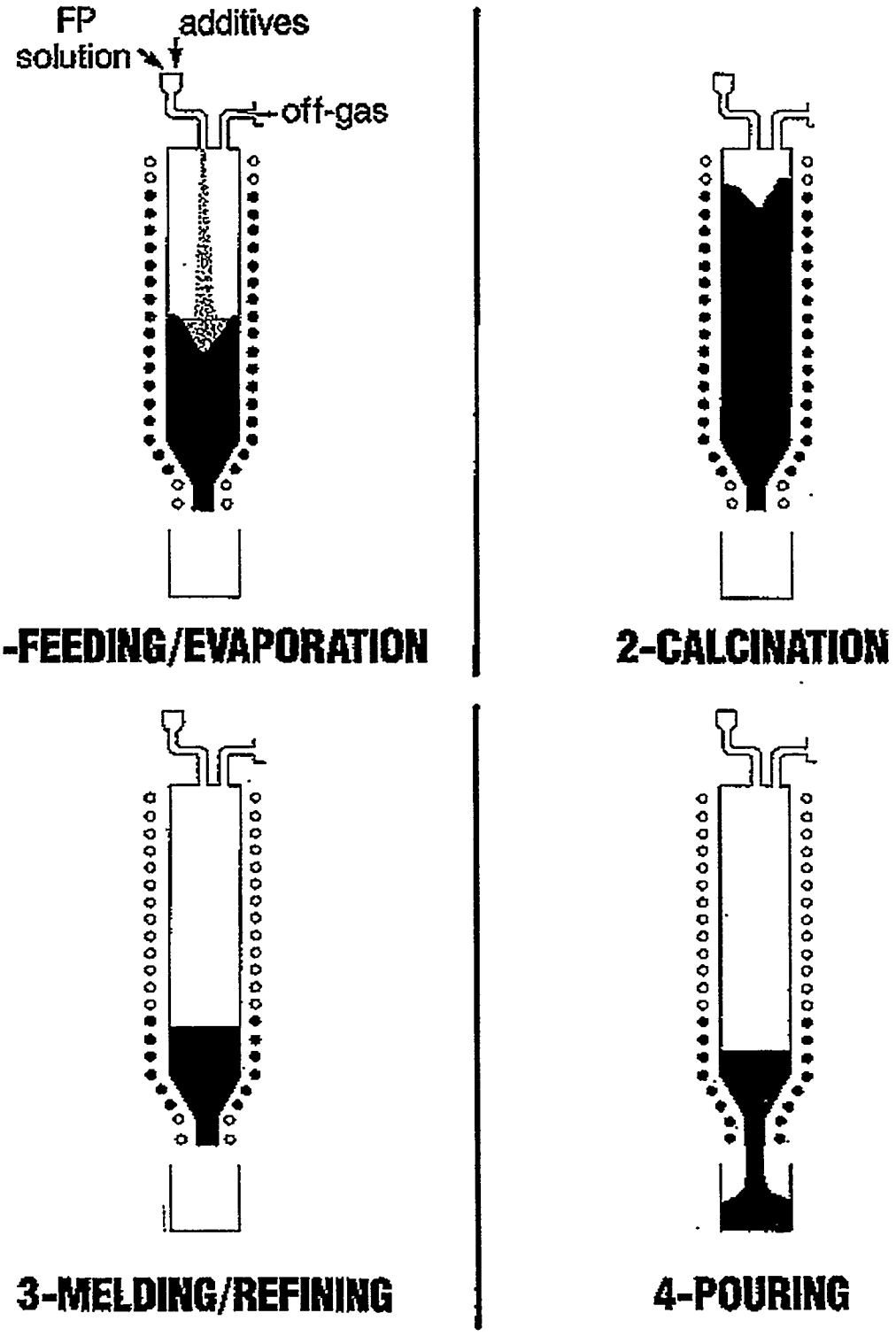
Man has been in effect extracting energy sources from the earth since the beginning of time, but this must surely be the first time he has ever considered getting rid of fuel by rendering them useless and burying them!

Would we not be better inspired to put this fabulous metal to good use?



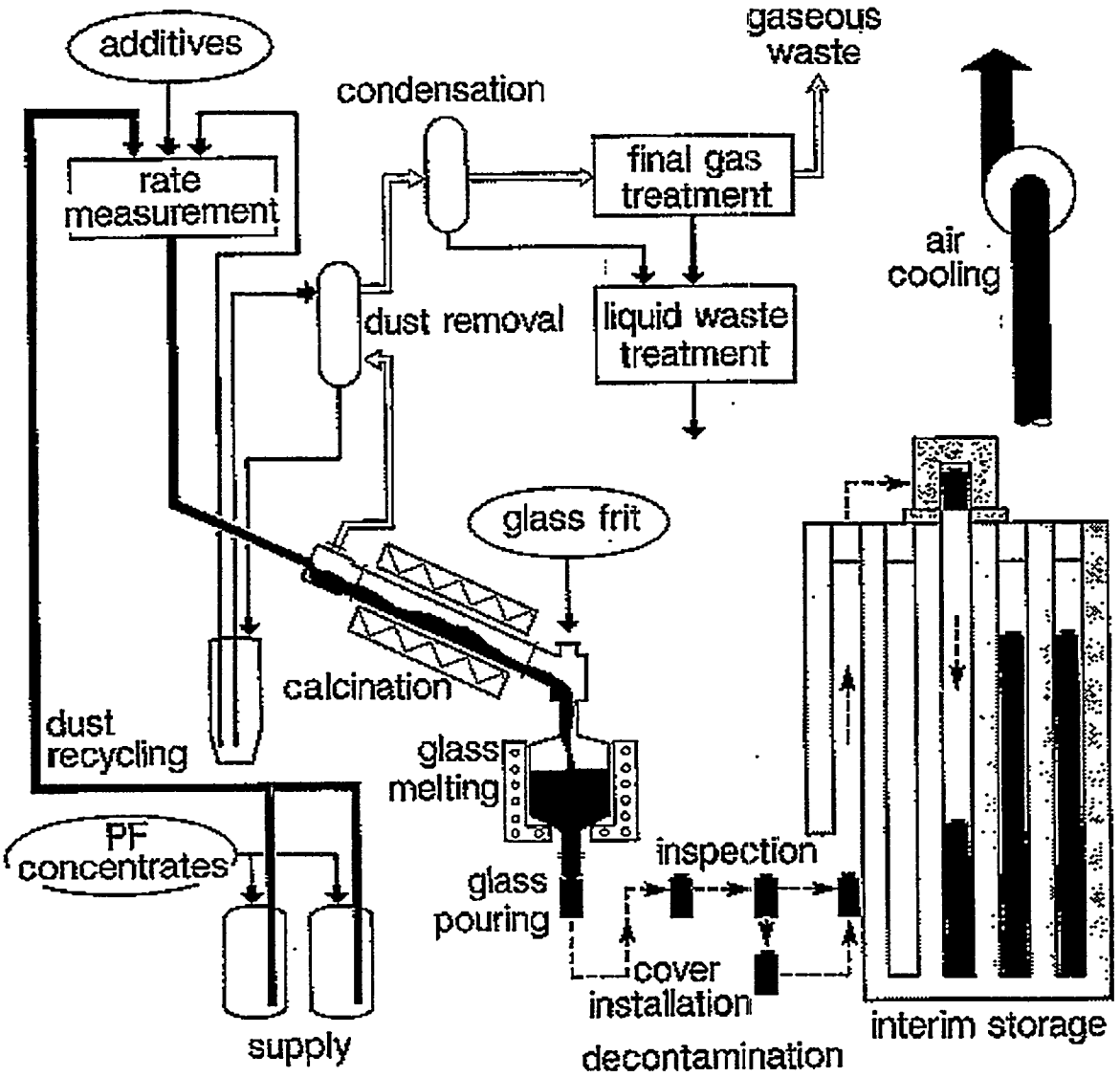
POTENTIAL RADIOACTIVE TOXICITY of ONE TON of UOX1 FUEL

FIGURE 1



POT VITRIFICATION PROCESS

FIGURE 2

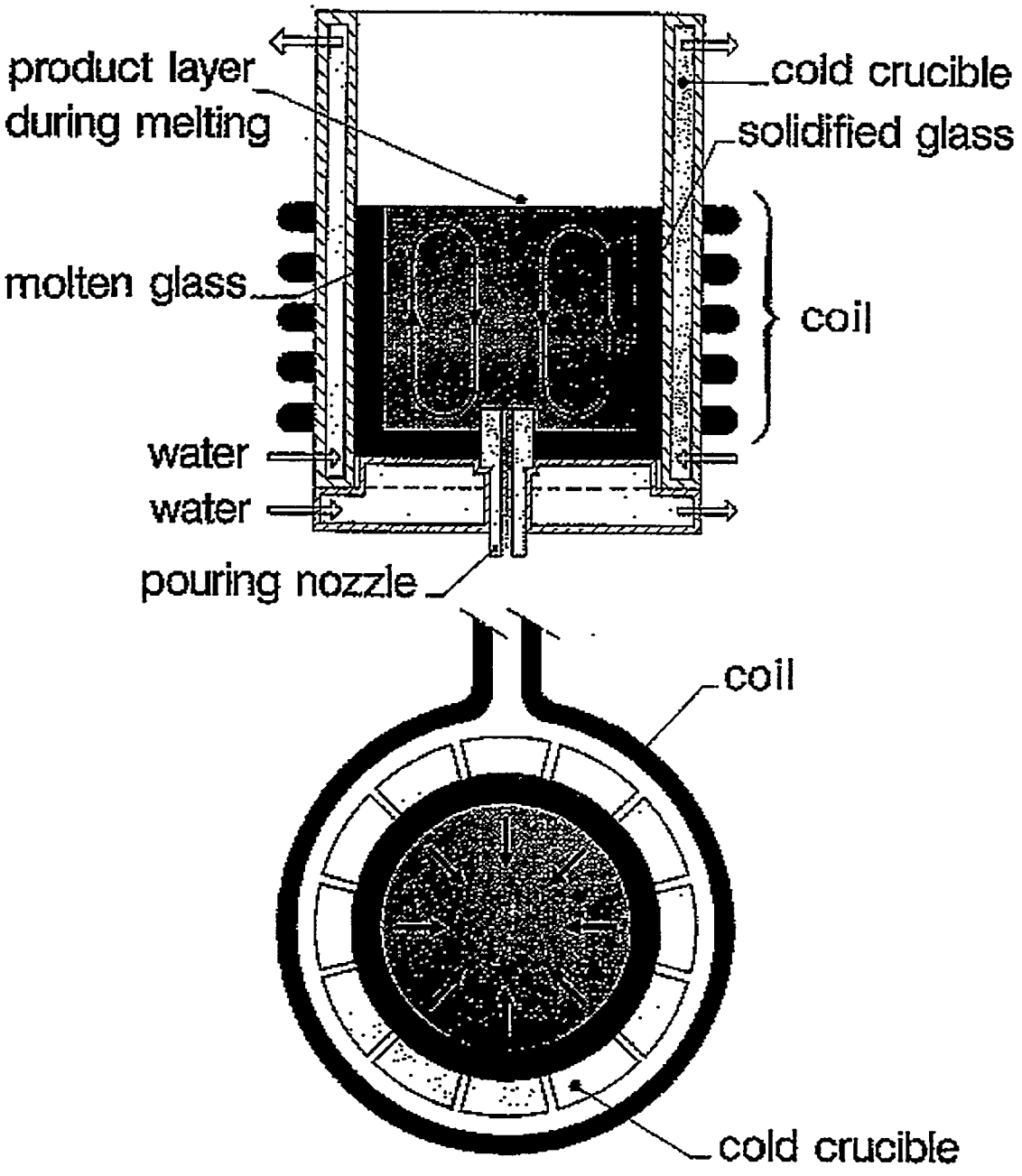


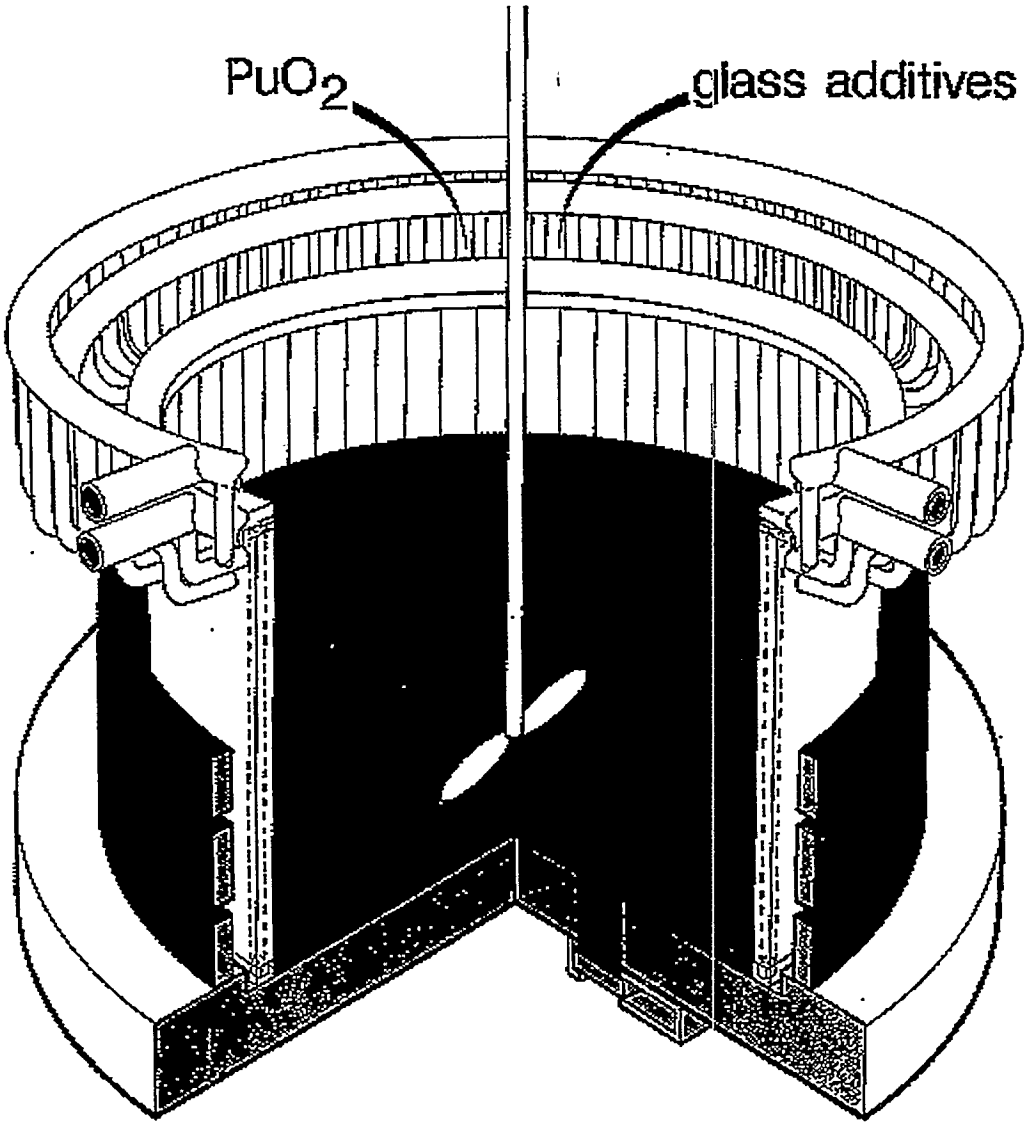
FRENCH TWO-STAGE CONTINUOUS VITRIFICATION PROCESS

FIGURE 3

FIGURE 4

COLD CRUCIBLE MELTING PRINCIPLE





SCHEMATIC VIEW of a COLD-CRUCIBLE PLUTONIUM VITRIFICATION MELTING

FIGURE 5