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THE FRENCH STATUS OF HIGH LEVEL RADIOACTIVE WASTES SOLIDIFICATION

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ABSTRACT

Research and Development carried out in France for a long time about solidification of High Level Radioactive Wastes have been mainly directed toward the glassy state. Investigations about borosilicates lead up to choose glass as a final form for the fission products solutions stored in both reprocessing plants.

Works related to various techniques to make use of this type of material started also a long time ago.

A two steps continuous process was selected owing to satisfactory results rised from a long term prototype running with respects to the glass manufacturing as well as the remotely handling ability.

AVM, the Marcoule Vitrification Plant has been running since 1978. Further Vitrification Plants related to the La Hague reprocessing plant are under design.

In Marcoule the radioactive glasses coming from AVM are put for decades in an interim storage facility located in the same building.

For glass containers to be issued in La Hague (AVH) from L.W.R reprocessing, several storage and disposal routes are being considered.

HISTORICAL BACKGROUND

The french research and development relating to the immobilization of high level radioactive wastes started in 1957.

At first, screening studies involving investigations about glasses and synthetic minerals as micas were carried out. It appeared very soon it was impossible to meet any wanted crystalline stoechiometrical composition owing to the numerous elements expected to be present in the wastes, so the research was directed exclusively towards vitrification.

The main milestones to point out are :

- 1960 : starting of Vulcain, a shielded cell designed for manufacturing and testing radioactive glass blocks. Since that time, various further improved types of Vulcain have been built successively.

- 1963 : Gulliver, a facility designed to fabricate fully radioactive glass blocks by means of a gel process, starts up.

- 1969 : first radioactive run of Piver, a fully radioactive industrial pilot plant based on a pot vitrification technique. The operation of an experimental engineered storage begins subsequently.

- 1978 : AVM (Marcoule Vitrification Plant) The industrial vitrification facility associated to the onsite reprocessing plant which is based on a continuous process begins to provide an industrial engineered interim storage with 360 kg radioactive glass blocks.

SOLIDIFICATION

GLASSES

The glass compositions must cope with the various existing high level radioactives wastes in terms of fission products, actinides and mainly non radioactive elements.

The french wastes compositions fall roughly into five categories :

- Commercial : from FBR reprocessed spent fuels
  from LWR reprocessed spent fuels
  from Gas Graphite Reactions spent fuels

- Defense : from Gas Graphite Reactions spent fuel (low burn up)

- Miscellaneous : from MTR reprocessed spent fuel.

The composition of the liquids are plotted on Table 1. The glass compositions depend on various factors and an optimization must be made to take them into account. These factors are :

- physico chemical properties of the glasses as regard to the long term disposal.

- maximum allowable temperature in the interim storage facility.

- maximum throughput of the available relevant industrial process equipment.

- physico chemical properties of the glasses with respects to the constraints due to the vitrification technique.

- the liquid-to-glass volume reduction .

An example of glass compositions, all borosilicates, associated to several types of liquid wastes is given in Table 2.

Investigations about the glasses are carried out in order to characterize them. The characteristics are connected to the fabrication process and to the long term disposal.

The properties relating to the babrication are :

- melting point

- corrosive effect of the molten glass upon ceramic and metallic materials ;

- viscosity in the range of the casting temperature

- release of volatile elements during the manufacture.

The composition governs the corrosiveness, the melting point and the viscosity. Because the two last are assigned to given values, the scope left for acting upon the corrosiveness is narrow and it is necessary to use suitable materials to contain the molten glass. On the other hand, it is possible to modify the volatilization rate of some elements. In particular the release rate of ruthenium, which is the most disturbing one, can be shorten by various chemical ways as the use of a low acidic medium or a reducing agent (sugar for example). To investigate in that field, a semi industrial equipment (Atlas) has worked with tracers (Ru, Te, Tc, Cs, Se) for over 2 years at Marcoule (see Figure 1) and already provided essential data which gave important contribution to the design of future vitrification plants.

With respect to the long term disposal, investigations are performed on radioactive and non radioactive glasses in order to evaluate :

- the thermal stability : crystals growth rate, crystals content, identification of crystalline phases ;

- the stability under radiation : change of structure, helium build up ;

- the chemical stability : leach resistance to various media under various conditions of pressure and temperature ;

- the mechanical stability versus time and particularly the tendency to fracturation.

Some characteristics are given in Table 3. As the incorporation into the glass of undissolved metallic particules issued from the reprocessing could be an interesting way to cope with, the effect of such materials upon the glasses properties is also under investigation.

FABRICATION TECHNIQUES

The pot vitrification process, already described (1) is a very attrative technique but it has to be restricted to the needs of small reprocessing facilities owing to its low capacity. The continious process has been also reported (1) (2). It lies on separated steps for calcination (in a rotary kiln) and for vitrification. AVM was based on this technique as well as facilities presently under design for the sake of BNFL, EUROCHEMIC, GWK and COGEMA. The latter will operate AVH the La Hague Vitrification Plant actually composed of 2 facilities R_7 and T_7 respectively associated to the reprocessing plants UP_2- 800 and UP_3-A. Both involve three lines including each, a rotary kiln (maximum throughput 60 $l.h^{-1}$ routine throughput 50 $l.h^{-1}$) and a metallic melter heated by induction at 4000 cycles.

The calciners are tubes about 4 m long. The calcination furnaces are made up of 4 heating zones. The 2 first zones, 32 Kw each, are longer than the 2 other (16 Kw each).

The cross section of the melter enables a large surface area of the molten glass (25.5 dm2). Therefore, compared to AVM the throughput is increased. The routine one will be 25 $kg.h^{-1}$ per furnace. The maximum one is 35 $kg.h^{-1}$ (AVM : 18 $kg.h^{-1}$).

The melting furnaces are made up with 4 main coils. There are one deduster and one condenser in each line which are located closely to the calciner. Downstream the condenser, the rest of the off gas treatment equipment is common to the three lines. There is no rethenium trap owing to the use of sugar added to the processed solution.

The lay out of the facilities differs from the AVM one. In particular the glass is cast in a separate cell (see Figure 2). Two casts will be performed per 8 hours shift in a 42 cm diameter container.

PROSPECTS

The progress of the design of R7 and T7 will give the possibility to start with LWR wastes solidification in 1987. In the meanwhile, as regard to the glass composition, the research will be directed toward the devise of higher melting point glasses in order to enhance the chemical properties. This will bring the necessity to pay attention to the volatilization phenomena and to give up metallic melters.

Some prototypes of ceramic melters involving heating by induction in the glass using high frequency current have been tested and improved. Such type of furnaces will contribute in addition to increase the melting capacity in order to meet higher reprocessing throughputs.

REFERENCES

1. R. Bonniaud, C. Sombret, Status of research in the field of solidification of high level radioactive wastes in France, 77th annual meeting of the American Ceramic Society, Washington DC, USA (May 1975).

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TABLE 1 : Characteristics of the french fission products solutions

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 $MWd.kg^{-1}$	12 $m3.t^{-1}$	~ 1.8 (depleted)	81	2-3		1-2			10-12	low
GG	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	SICRAL	4000 $MWd.t^{-1}$	100 $l.t^{-1}$	1.0-1.5	10-12	2-5	3	8	1	1	5	37-42
LWR	UO_2	33000 $MWd.t^{-1}$	500 $l.t^{-1}$	1.5	1	18-22		12	1	1		70
FBR	UO_2/PuO_2	60000 $MWd.t^{-1}$	1200 $l.t^{-1}$	1.0-1.5		20		15-20	1-3	2-3		25-28

TABLE 2 : Example of glass compositions

		COMPOSITION (in weight %)									
		SiO_2	Na_2O	B_2O_3	Al_2O_3	Fe_2O_3	MgO	CaO	NiO + Cr_2O_3	PF and actinides oxides	F
GG	Defense	38.1	17.9	16.4	12.3	4.2	4.1		1.0	4.0	2.0
	Defense and commercial mix up	38.4	17.1	17.3	11.0	3.2	5.1		0.8	5.6	1.4
MTR		37.0	19.4	15.4	23.2	1.7			0.2	1.3	1.8
LWR		47.5	12.0	15.0	3.0	5.0		4.0	0.5	13.0	
FBR *		40.7	18.2	18.2	13.9	0.9			0.3	7.8	

* This example relates to a part of a core of Phenix reactor reprocessed at the pilot reprocessing plant of Marcoule. The glass was made in Piver.

TABLE 3 : Some characteristics of possible glasses for the vitrification of the HLW generated by the reprocessing of LWR spent fuels

Viscosity at 1100°C	80 to 220 poises	
Transition point (Tg)	490 to 560°C	
Crystallisation range	620 to 840°C	
pH steady state after a 25 days period leaching with water	flowing at 100°C (Soxhlet)	= 9.0 to 9.6
	static test	= 9.3 to 9.7
Weight loss at 100°C after a 25 days period leaching with water	flowing at 100°C (Soxhlet)	= 1 to 4 x 10^{-4} $g.cm^{-2}.d^{-1}$
	static test	= 0.5 to 1.0 x 10^{-4} $g.cm^{-2}.d^{-1}$

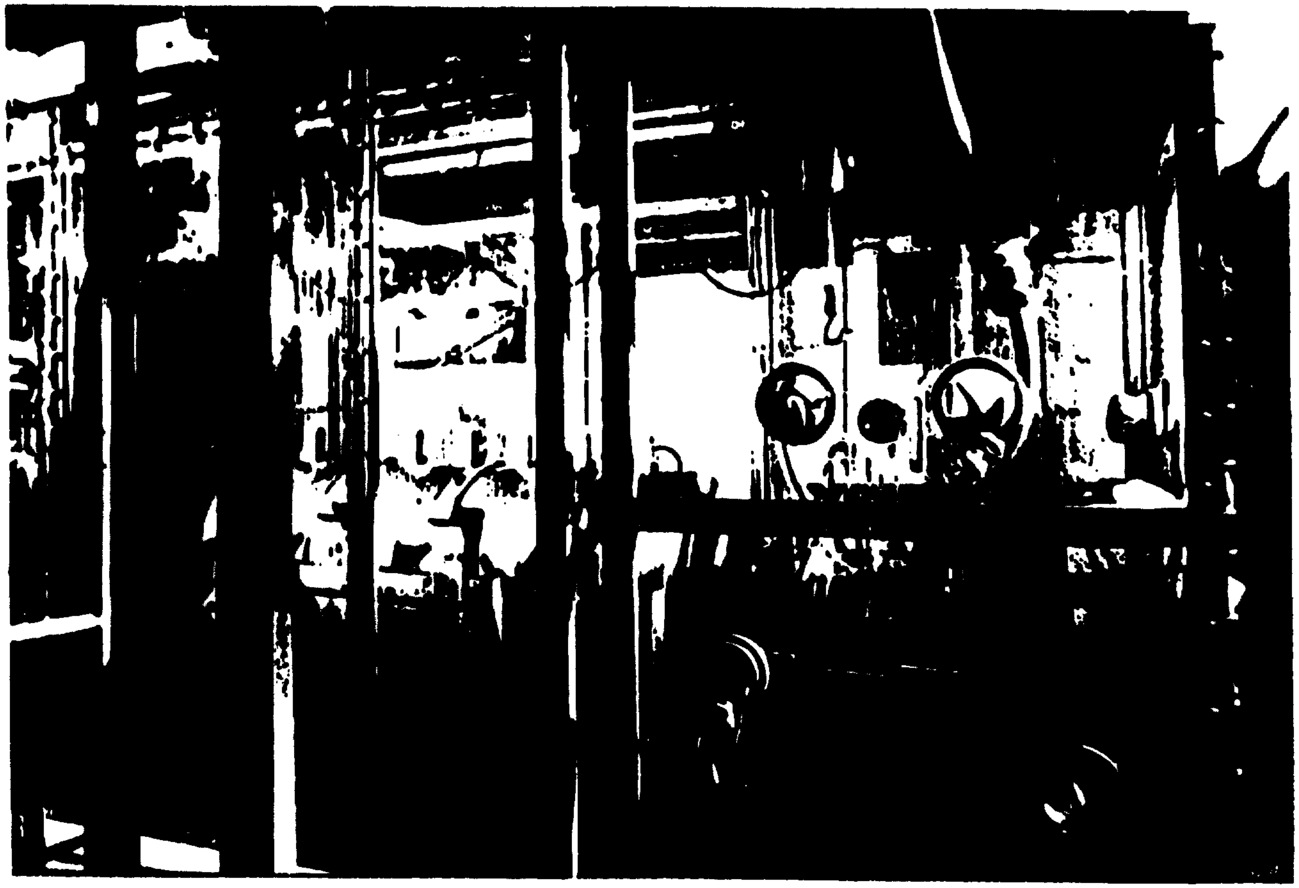

FIGURE 1 : ATLAS facility, a continous vitrification equipment used for investigation about volatilization

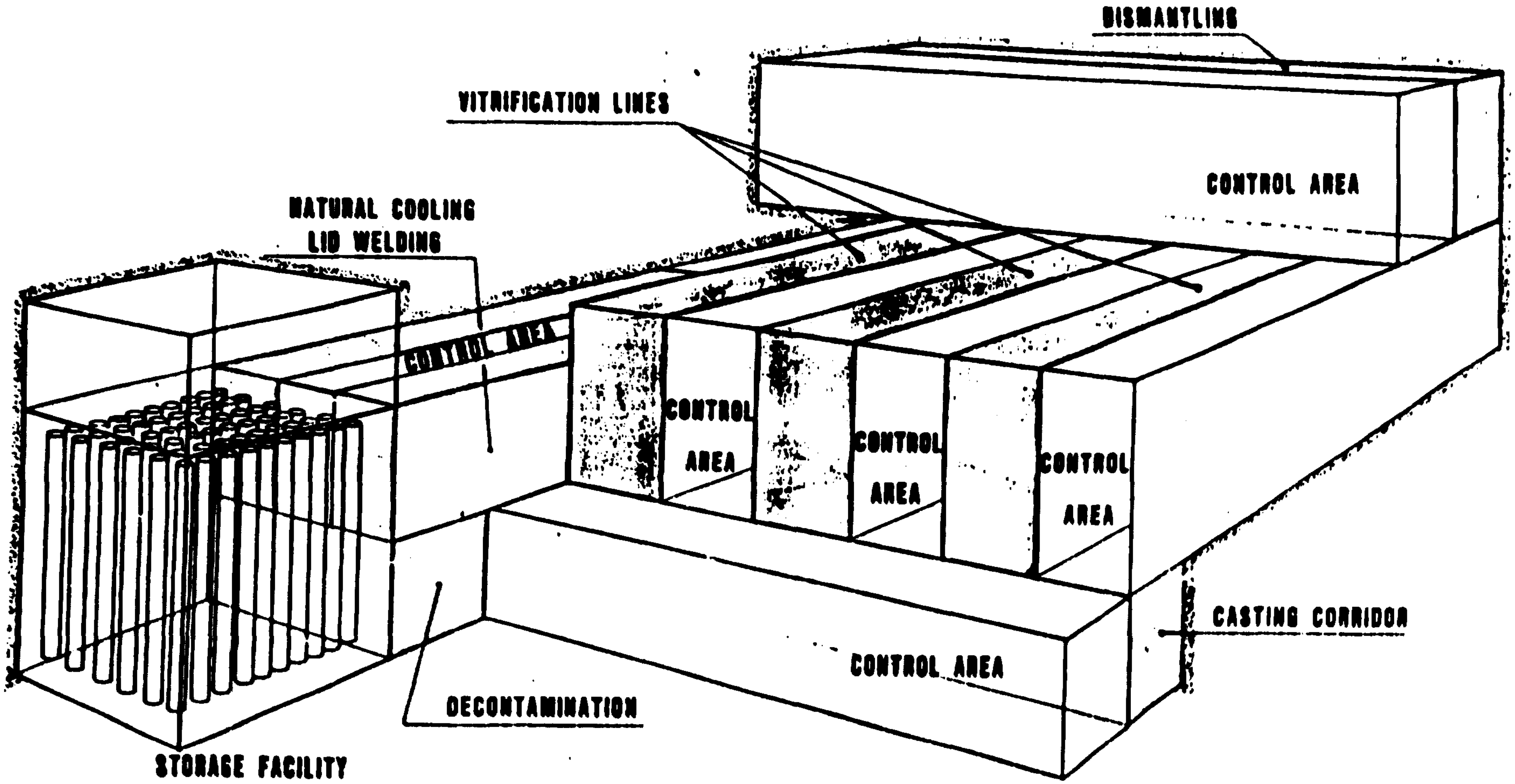

FIGURE 2 : lay out of the La Hague Vitrification Plant (R_7 and T_7)