

STABILIZING SOLIDIFICATION I:  
A METHOD OF IMMOBILIZATION OF RADIOACTIVE WASTE  
INVOLVING VOLUME REDUCTION

K. Kinoshita  
Mitsubishi Heavy Industries, Ltd.  
Nuclear Fuel Cycle Engineering Department  
5-1, Marunouchi 2 Chome, Chiyoda-ku  
Tokyo, 100 Japan

E. Kakuya  
Mitsubishi Atomic Power Industries, Inc.  
Omiya Technical Institute  
1-297, Kitabukuro, Omiya  
Saitama, 330 Japan

ABSTRACT

Mitsubishi Heavy Industries, Ltd. (MHI) has developed a calciner/incinerator system aiming at an integrated treatment and a large volume reduction of radioactive liquid wastes and combustible solids including spent resins, etc. generated from a nuclear power plant.

It is preferable that the powdery products of calcination and incineration are treated into an immobilized form to ensure safe storage or disposal.

MHI has paid attention to utilizing in-waste glass network components, such as boron oxide in the calcination products of PWR liquid wastes and silicon oxide and alumina in the incineration ashes, as a method to obtain a greater volume reduction and a long-term stability of the wastes and has confirmed that a stable vitrified product can be produced by melting these wastes at a high temperature.

Furthermore, key parametric data necessary to enlarge the processing system have been obtained from a series of vitrification tests using a medium-size melter with a prospect of developing the system of practical use.

INTRODUCTION

Currently in Japanese nuclear power plants, all combustible miscellaneous solids are incinerated, and liquid wastes are generally solidified with materials like asphalt, cement and polymer in drums. As for the liquid wastes, the processing of them by a calciner or dryer is now being studied as an effective method of volume reduction.

However, considering that products of calcination or drying and incineration ("calcination/incineration products") are in a powdery form, they are to be immobilized for the long-term storage or disposal.

On the other hand, incombustible wastes are now drummed either with compressing to reduce the volume or without any processing. However, it is believed that there will be a need for higher safety and stability of the wastes for the ultimate disposal.

Glass components can roughly be divided into the following two types:

- Network Former  
Components that form the glass network structure and they are  $B_2O_3$ ,  $SiO_2$ ,  $Al_2O_3$ , etc.
- Network Modifier  
Components that irregularly enter into the glass network structure and they are  $Na_2O$ ,  $Cs_2O$ ,  $CaO$ , etc. Many of radionuclides in the wastes act as the elements of this type.

Table I shows the estimated annual quantities of to-be-vitrified wastes generated from 1200 MWe PWR twin units and of glass network formers contained therein.

It has been found that as the calcination/incineration products and the incombustibles such as heat insulations contain a large amount of the glass network formers as shown in Table I, a stable borosilicate glass monolith is obtainable if these wastes are mixed to have an appropriate ratio of such formers and melted at a temperature of about 1000 °C.

TABLE I

Glass Network Formers in the Wastes

Wastes for Vitrification	Generation	Network Formers			Network Modifier
		$B_2O_3$	$SiO_2$	$Al_2O_3$	
Calcination Product	20.0	13.8 (69)	-	-	6.2 (31)
Incineration Ash	2.5	-	1.3 (52)	0.5 (21)	0.7 (27)
Heat Insulations etc.	3.0	-	1.5 (51)		1.5 (49)
Total	25.5	13.8 (54)	2.8 (11)	0.5 (2)	8.4 (33)

( ): wt% Composition

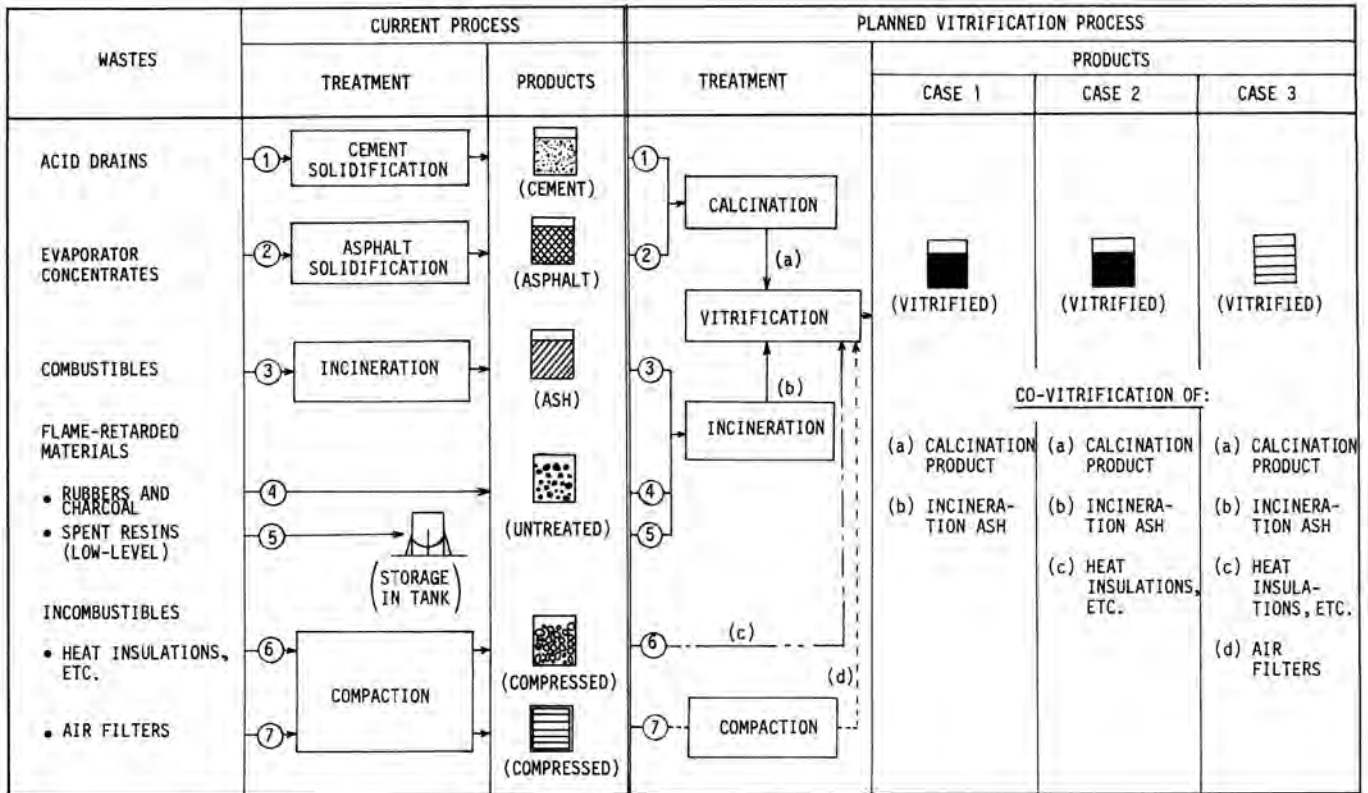


Fig. 1. Application of the Vitrification System to Power Plant Wastes

A vitrification system of low-level radioactive wastes is being developed based on the view and the result as described above.

For application of the vitrification system to actual power plant wastes, the following three cases are conceivable (Fig. 1):

**Case 1: Calcination/incineration products**

To melt and solidify the powdery wastes for stabilization

**Case 2: Heat insulations in addition to Case 1 wastes**

To melt and solidify Case 1 wastes together with incombustibles like heat insulations for the utilization of their glass network formers and for a greater volume reduction

**Case 3: Air filters in addition to Case 2 wastes**

To solidify compressed spent air filters with the melted, vitrified Case 2 wastes which penetrate into voids of the filters for immobilization and for a reduction in number of waste drums

**VITRIFIED PRODUCT EVALUATION TEST**

In preparation of the specimens for this test, simulated wastes were melted and solidified in mixing ratios as shown in Table II, taking account of fluctuations in the estimated annual waste quantities shown in Table I, and their physical properties were evaluated.

The specifications of the melter used are shown in Table III. As this melter is equipped with a program controller, conditions of temperature rising, maintaining and lowering can exactly be controlled.

TABLE II

Mixing Ratio of Simulated Wastes

Simulated Wastes	Mixing Ratio (wt%)
Simulated Calcination Product (Sodium Borate) <sup>a</sup>	30 ~ 90
Incineration Ash	0 ~ 60
Heat Insulations (Calcium Silicate Type)	0 ~ 60
Additive (Glass Frit)	0 ~ 40

a) Because the main components of calcination product of PWR liquid wastes are Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (approx. 85 wt%) and B<sub>2</sub>O<sub>3</sub> (approx. 15 wt%), sodium borate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) was used.

TABLE III

Specifications of Melter

Particulars	Specifications
Type	Resistance Heating External Furnace
Crucible Size (mm)	30 <sup>ID</sup> × 65 <sup>H</sup> (0.04 L)
Heater	Indirect, MoSi <sub>2</sub>
Electricity	3.3 kW
Temperature	Max. 1,650 °C

In this test, firstly, the applicable mixing range where the simulated surrogate wastes can be co-vitrified at a temperature of about 1000°C was determined using the composition of the surrogate as a parameter.

A substantial amount of incineration ash or heat insulations in the mixture impedes the melting and vitrification because of SiO<sub>2</sub> constituents having high melting points. However, mixing calcination product composed of Na<sub>2</sub>O and B<sub>2</sub>O<sub>3</sub> or glass frit containing Na<sub>2</sub>O lowers the melting temperature of the mixture, so that the vitrification can easily be achieved.

The following results of the evaluation test were obtained for physical properties of the vitrified product.

#### Density

The simulated waste mixtures each of 20g were placed in a small crucible and melted at the prescribed temperature. The densities of the products obtained were approximately 2.3g/cm<sup>3</sup> independent of the waste mixing ratio.

#### Leachability

Of the glass components, Na<sub>2</sub>O and B<sub>2</sub>O<sub>3</sub> have similar leaching rates. On the other hand, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> tend to have lower leachabilities.

In this evaluation, leachabilities were studied based on leaching rates for Na having a leachability similar to Cs which is commonly used in hot tests.

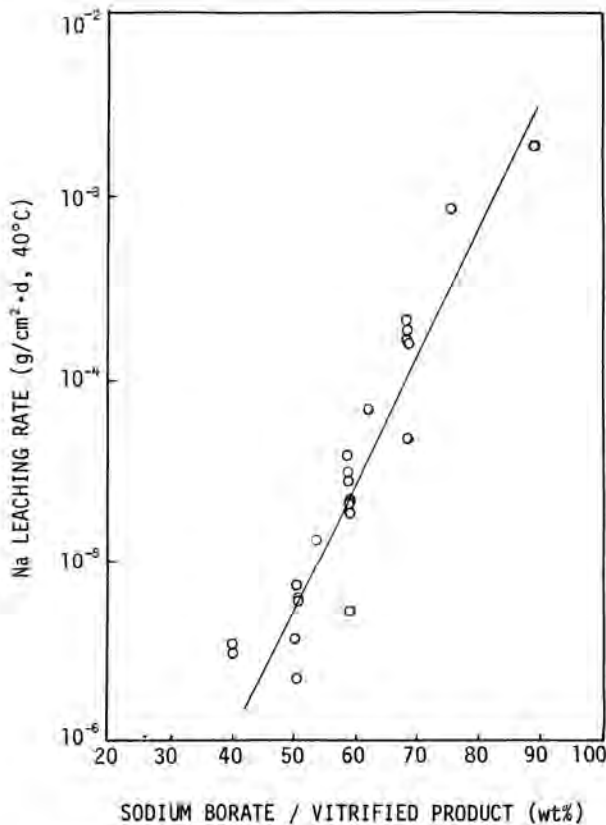


Fig. 2. Na Leachability of Vitrified Product

Figure 2 shows the leaching rates for Na of the vitrified products. The Na leaching rate decreases with decreasing wt% of sodium borate contained in the vitrified product.

#### Compressive Strength

Figure 3 shows the compressive strength of the vitrified product specimens prepared to have external sizes of 10φ × 20H.

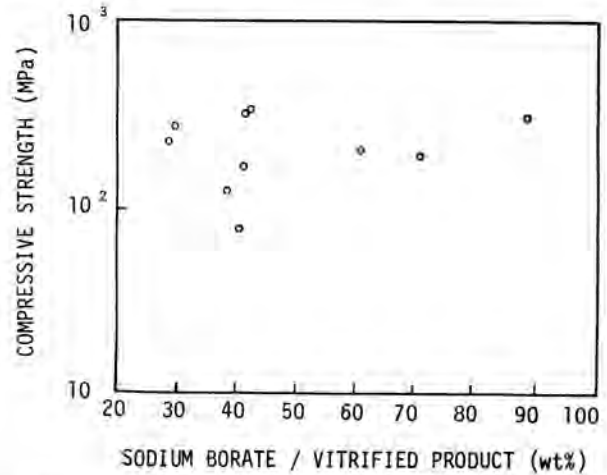


Fig. 3. Compressive Strength of Vitrified Product

All the product specimens indicated a compressive strength of 80 MPa or greater regardless of the product compositions, thus the waste materials were considered to be converted into vitreous forms.

#### Volume Reduction Effect

Improvements in the leachability can be attained by adding standard glass frit having a composition abundant in SiO<sub>2</sub> as shown in Table IV.

TABLE IV  
Glass Frit Composition

Composition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	Fe <sub>2</sub> O <sub>3</sub>	Others
wt%	71.4	1.1	14.8	0.6	8.7	0.1	3.3

Figure 4, which is calculated from Fig. 2, shows the relation between Na leaching rates and additive-to-waste ratios by weight which affect the volume reduction rates.

Figure 5 is to indicate expected volume reduction rates corresponding to the additive-to-waste ratios to be determined for the desired leaching rates based on Fig. 4.

Volume reduction effect is maximized when the product is vitrified only from the wastes without additive and decreases with increasing additive-to-waste ratios.

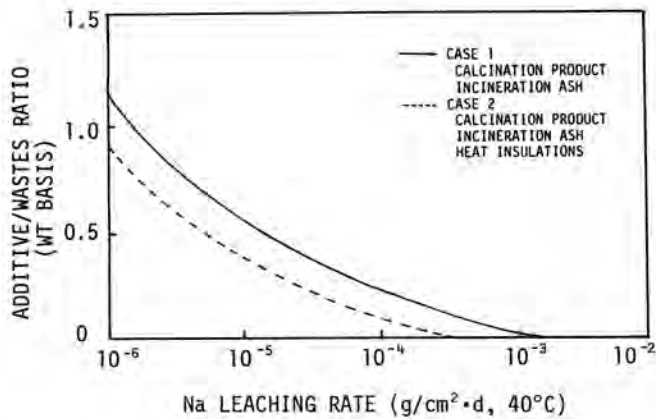
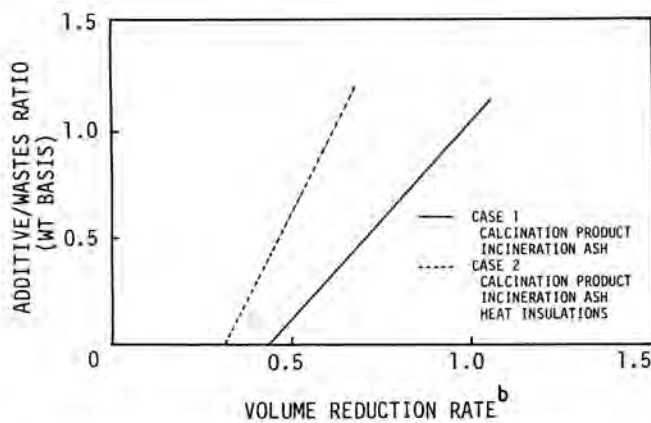


Fig. 4. Additive-to-Waste Ratio vs. Na Leaching Rate



b)  $\frac{\text{VOLUME OF VITRIFIED PRODUCT (WITH ADDITIVE)}}{\text{INITIAL WASTE VOLUME}}$

Fig. 5. Additive-to-Waste Ratio vs. Volume Reduction Rate

## STUDY OF PRACTICAL USE SYSTEM

### Scale-Enlarging Test

With a view to developing a practical use system, vitrification tests were performed using a medium-size in-can melter equipped with a 24 kW indirect SiC heater for temperatures up to 1400 °C, and various data including melting rate, required electricity, etc. were obtained for scale-enlarging.

Table V shows examples of the obtained data for a melting temperature of 1100 °C selected considering a flexibility in operation of the practical system.

### Outline of Practical Use System

The number of the vitrified products in 200-L drum size is calculated to be at most 100 or less for the annual waste quantity estimated in Table I, even if some amount of additive is added to improve the product leachability.

Therefore, it is reasonable to assume that the practical system will conservatively be designed to produce one vitrified product a day in 200-L size.

From the data shown in Table V, melting rates are calculated for 200-L size. A melting operation of six hours a day will be enough to process the wastes into

TABLE V  
The Results Using Medium-Size Melter

Particulars	Vessel 1	Vessel 2
Melting Vessel	138 <sup>ID</sup> × 460 <sup>H</sup> (6.8 L)	230 <sup>ID</sup> × 380 <sup>H</sup> (15.7 L)
Charge (kg)	8.0	27.4
Temperature (°C)	1100	1100
Melting Rate (kg/h)	6.9	16.1
Melting Time (h)	1.2	1.7
Electricity (kw·h/kg)	0.80	0.88

TABLE VI  
Calculated Melting Time for Practical Use Melter

Particulars	Heater Capacity (kW)		
	120	150	180
Charge (kg)	Abt. 430 (200-L Drum Size)		
Temperature (°C)	1100		
Melting Rate (kg/h)	54.0	73.2	91.9
Melting Time (h)	8.0	5.9	4.7

a 200-L size product as shown in Table VI, if a 150 kW heater is adopted.

Based on the above, a conceptual design of the practical use system was developed. Figure 6 shows a waste management flow including the developed vitrification system as marked by a chain line.

The vitrification system consists of processes for pretreatment, melting, off-gas treatment and product handling. The following outline these processes. Figure 7 shows a schematic view of the vitrification system.

### Pretreatment Process

In this process, calcination/incineration products and glass frit additive are mixed and supplied into the melter.

When heat insulations, compressed spent air filters, etc. are solidified as in Cases 2 and 3, they are firstly placed in a melting vessel, which is then set in the furnace and receives the above mixture for melting and solidifying.

### Melting Process

In this process, the wastes with pretreatments mentioned above are melted for vitrification.

Specifications of the practical use melter which can produce one vitrified product a day in 200-L size are shown in Table VII.

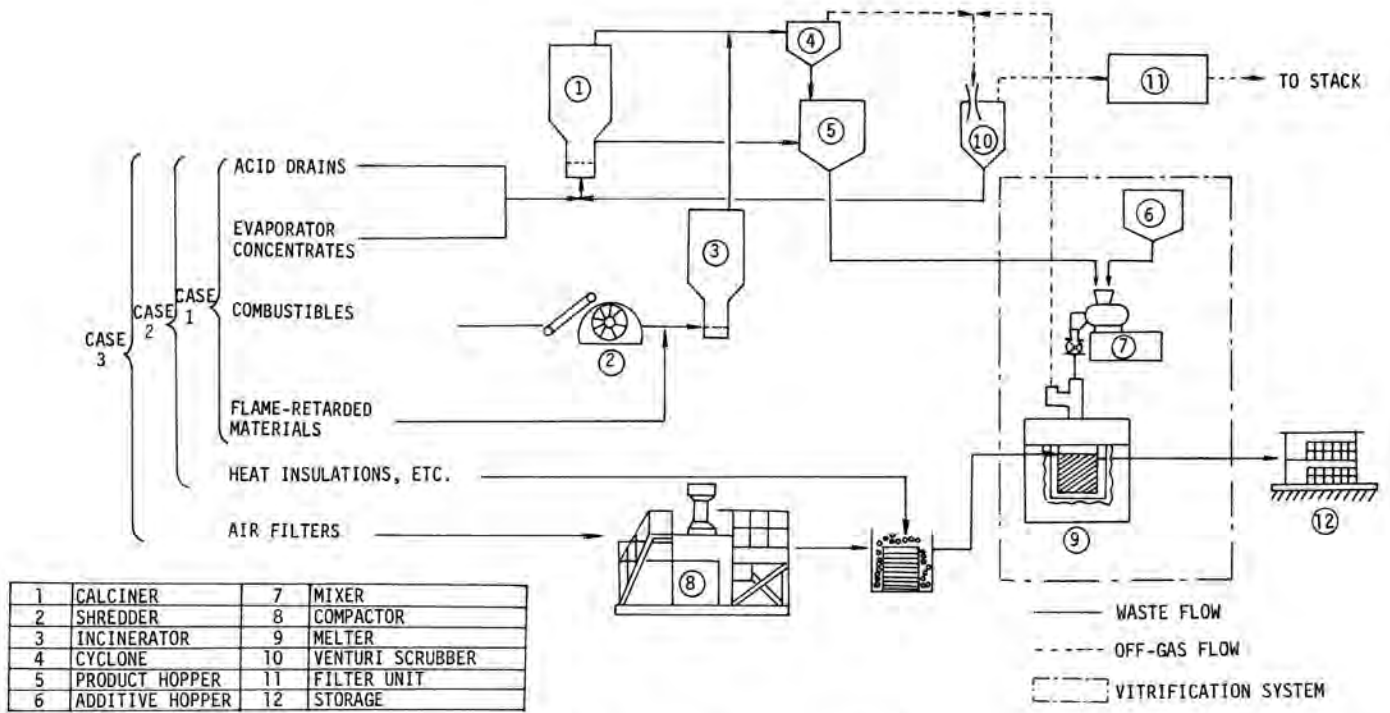


Fig. 6. Waste Management System Flow

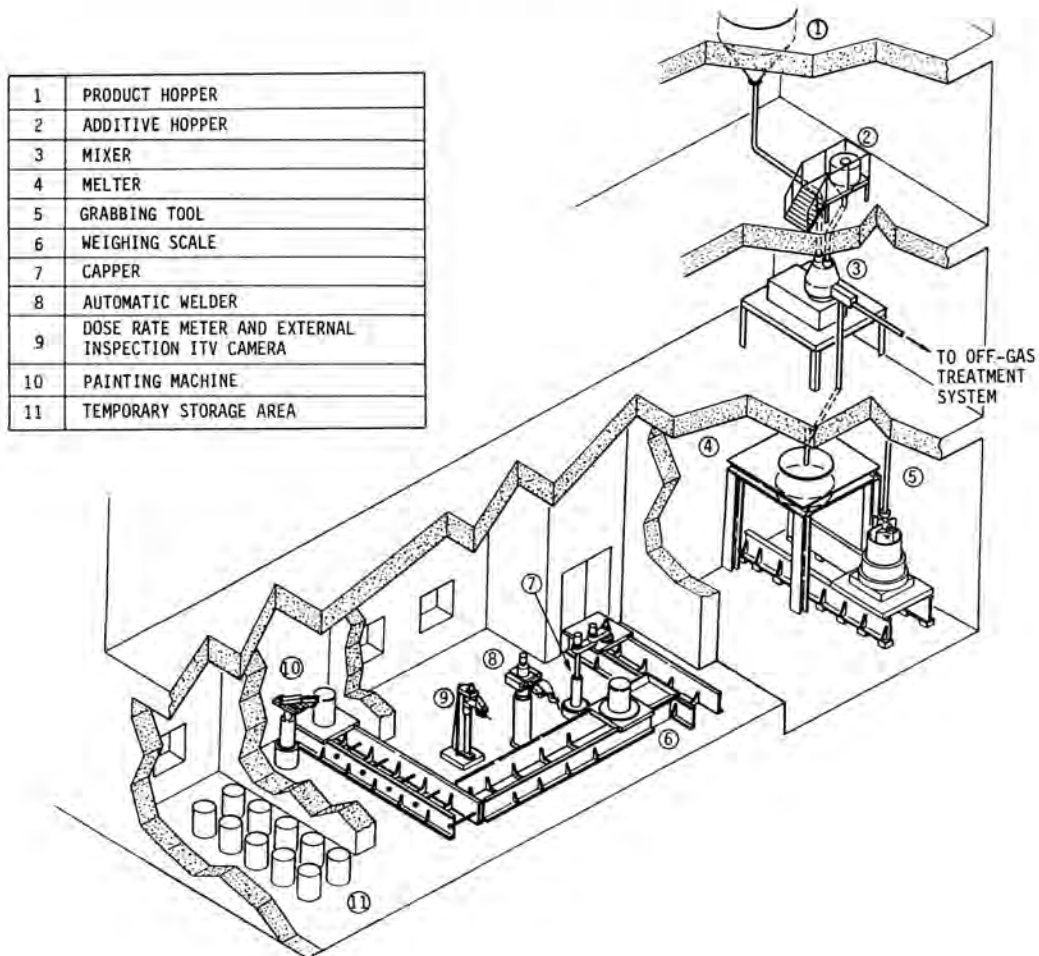


Fig. 7. Schematic View of the Vitrification System

TABLE VII

## Specifications of Practical Use Melter

Particulars	Specifications
Type	Resistance Heating External Furnace
Furnace Inner Dimensions	1000 <sup>ID</sup> × 900 <sup>H</sup>
Heater	Indirect, MoSi <sub>2</sub>
Temperature	1100 ± 20 °C (Max. 1200 °C)
Electricity	150 kW

Off Gas Treatment Process

The off-gas arising from the melting process is treated by a specially designed dust filter installed at the melter vent, and then sent to the off-gas treatment equipment separately installed for upstream facilities such as a calciner and a incinerator, and cleaned.

Product Handling Process

The vitrified product in a vessel is lifted off by a grabbing tool from the melter. Then, automatic weighing, cap seal welding and dose rate measurement as well as external inspection by ITV are applied and transferred to a temporary storage area for shipping.

## CONCLUSIONS

It has been confirmed that the vitrification process utilizing the components specific to PWR wastes is able to convert the wastes into a stable and rigid vitreous form having favourable physical properties for safe storage and disposal. Furthermore, desired leachability of the product can practically be achieved by using calcines and incineration ashes as basic feed materials and mixing a suitable amount of silica-containing wastes or glass frit as an additive.

Based on the results obtained, a pilot plant is subsequently planned with operations of the processes such as pretreatment, melting and off-gas treatment in view of actualization of the system promising for stabilizing solidification of low-level radioactive wastes.