# DEVELOPMENT OF TRU SLUDGE VITRIFICATION PROCESS USING MICROWAVE HEATING

Y. Ishiyama, J. Yamaji, and T. Mizushima
EBARA Corporation
11-1 Haneda-asahicho Ohta-ku Tokyo, 144 Japan

T. Mimori and K. Miyajima
Japan Atomic Energy Research Institute
Tokai Research Establishment
2-4 Shirakata-aza-shirane Tokai-mura Naka-gun Ibaraki, 319-11 Japan

## ABSTRACT

Japan Atomic Energy Research Institute (JAERI) and EBARA Corporation jointly developed a process for treating TRU sludge waste solution by vitrification process using microwave for first time in Japan and installed the equipment in the Tokai Research Establishment of JAERI.

The TRU sludge is watery and fluid sludge, that has been derived from a coagulation/sedimentation process treating alpha-bearing liquid waste originated in reprocessing test (Purex process).

This process supplies TRU sludge and glass formation materials to a metal melting pot, repeats the evaporation and solidification by microwave and electric heating, finally melts all the solidified materials, and produces homogeneous vitrified products. This process can treat TRU sludge 5 liters/h maximum, and volume reduction factor is 1/25 maximum.

Unique characteristics of this process are the formation of homogeneous vitrified products by using an electric heater for compensating the shortcoming of the microwave heating, the simplification of the vitrification process by adopting the In-Can-Melt method, and the adopting laminated operating method. Since the melting furnace is housed in a glove box, zinc borate-based glass of a low melting pint was adopted as vitrified product. Glass formation materials are directly supplied in tablet form to the melting pot placed in the melting furnace. The completion of melting operation is detected by measuring NOx concentration as a product of decomposition of TRU sludge in the exhaust gas. It controls the fluctuation of the quality of vitrified product for each treatment.

During cold tests, vitrified products having the unconfined compressive strength and leaching rate satisfying the design conditions were obtained even for simulated solution under severe conditions for vitrification, and hot operation is being performed at present.

## INTRODUCTION

Japan Atomic Energy Research Institute (JAERI) and EBARA Cooperation jointly developed a process for vitrifying waste containing TRU sludge (hereinafter, "TRU sludge") by using microwave. This process is designed for forming vitrified products by placing TRU sludge and glass tablets in a melting pot made of metal, by heating and melting with microwave. The equipment was installed in JAERI in order to reduce TRU waste volume and to safely manage storage of the vitrified products.

The TRU sludge to be treated by this process is the sludge having a fluidity with a high water content produced during the coagulating sedimentation of the waste of low level of alpha-bearing generated in reprocessing tests (Purex process) of spent nuclear fuel at JAERI.

EBARA Corporation started the research on the treatment of various radioactive waste by microwave heating from 1981 and developed this new process through the joint research program with JAERI, in which TRU waste treatment technology of the institute was combined with the EBARA's technology.

The development of the process involved installation of an experimental pilot plant, establishment of operating method, and review of the composition of vitrified product. The measure to prevent microwave discharge were also substantiated to enhance the reliability of equipment and improve the quality of the vitrified products.

In this paper, the characteristics of the vitrification process of TRU sludge and the results of the cold tests will be reported.

## OUTLINE OF THE PROCESS

Process flow diagram is shown in Fig. 1. Basic specifications of this process and main equipment are shown in Table I and Table II respectively. The process comprises four system indicated below, and the main equipment was housed in the glove box.

- TRU sludge supply system
  - This system receives TRU sludge, adjusts the composition of TRU sludge, and then supplies it to the vitrifying system.
- Vitrifying system
  - This system receives TRU sludge into a melting pot, were glass tablets are later added. The mixture is evaporated, melted, vitrified and gradually cooled, to form stable vitrified products.
- Offgas treatment system
  - This system gives decontamination treatment by dry method to offgas generated from the melting furnace. The concentration of NOx gas is measured. Offgas is exhausted to a stack.
- Auxiliary facility system
  - This system supplies cooling water and heated air.

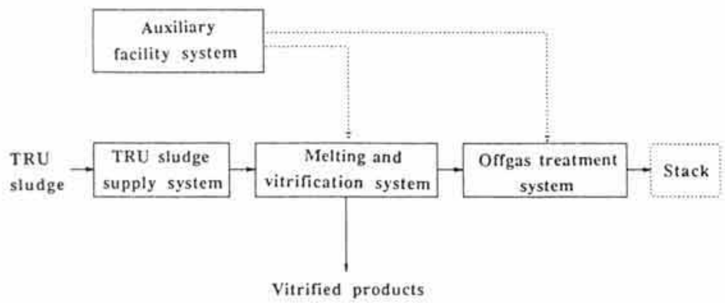


Fig. 1. Process flow diagram.

**TABLE I**
Basic Specifications for TRU Sludge Vitrification Process

| Item | Basic Conditions |
|---|---|
| Process Specification | Type: microwave heating, supplemented by electric heater, In-Can-Melt method vitrification process<br><br>Design capacity: 5 liters/h max<br>Design volume reduction : 1/25 max |
| Composition of the TRU Aludge | $NaNO_3$: 0.12 ~ 13.0 wt%<br>$Fe(OH)_3$: 0.02 ~ 0.4 wt%<br>Other suspended solution: 0.17 ~ 2.8 wt%<br>$H_2O$: All of the remainder |
| Concentration of Radioactivity of the TRU Sludge | alpha: 0.26 ~ 111 $kBq/cm^3$<br>beta: 0.08 ~ 3.70 $kBq/cm^3$<br>gamma: 0.04 ~ 1.85 $kBq/cm^3$ |

## FEATURES OF MELTING FURNACE

Structure of the melting furnace, which is the major equipment of the process, is shown in Fig. 2. The size is about 165 mm in diameter and about 1700 mm in height.

The melting furnace comprises upper and lower furnace bodies where the melting pot is housed. The lower furnace body can move vertically and horizontally. Upper and lower furnace bodies are equipped with nozzles for lighting fixtures, pressure gauges, thermometers for measuring melting pot and molten substances temperature as well as other nozzles shown in Fig. 2. A hopper is placed at the top of the glass tablet nozzle. Characteristics of the melting furnace will be described below.

### In-Can-Melt Method

The melting furnace is of batch type, and In-Can-Melt method was adopted. Reasons for adopting the In-Can-Melt method are:

**TABLE II**
Specifications for Major Equipment of TRU Sludge Vitrification Process

| Name of Equipment | Specifications for Equipment |
|---|---|
| Melting furnace | Type: microwave heating, supplemented by electric heater, In-Can-Melt method<br>Materials: austenite-based stainless steel, INCONEL 600<br>Electric heater capacity: 5 kW |
| Microwave generator | Type: Magnetron type<br>Output: 2,450 MHz, 0 ~ 5kW (variable type) |
| Melting pot | Type: cylindrical flange-fixed type<br>Materials: austenite-based stainless steel<br>Capacity: about 3 liters |

- The thermally affected melting pot is replaced for each vitrifying treatment, so that the main body of melting furnace is not deteriorated.
- The melting pot itself is a storage container, and handling after vitrifying treatment is easy.

### Microwave Heating

Microwave was adopted as the main heating source for the melting furnace considering the advantages of microwave heating as described below.

- A microwave generator can be installed outside the glove box, and thus the remote control of heating is

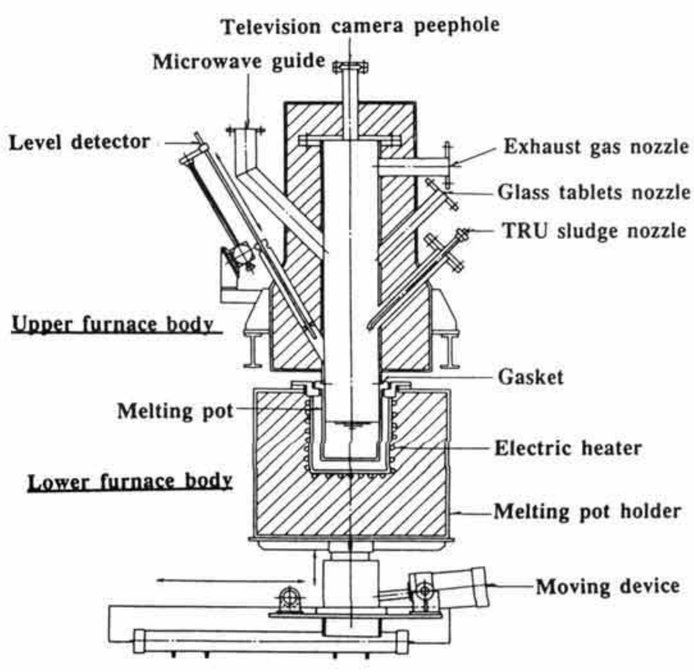


Fig. 2. Structure of the melting furnace.

easy. Furthermore the contamination of the main body of the microwave generator can be prevented.

- The substances in the melting pot are heated directly, and the energy loss is small.
- Since there is not contact between heating source and the substances to be heated, the structure inside the melting furnace can be simple.

On the other hand, the microwave heating has a shortcoming of poor heating efficiency near the metal surface. To heat up the portion with poor heating, electric heaters are installed in this furnace. It resulted in uniform heating of the substances, good convection state, consequently shorter vitrification time and more homogeneous vitrified product.

### Microwave Discharge Prevention Measures

Microwave discharge and leakage can be potential problems in microwave heating furnace. The following counter measure are, however, taken to cope with them:

- A lifting type level detector is used and microwave generation is stopped by the control system when inserting it to the melting furnace.
- By intermittent liquid supply method, sudden gas generation which triggers microwave discharge is suppressed.
- Special electrically conductive gaskets are adopted for the connecting portion between the melting pot and the upper furnace body.
- Installed are a television camera for monitoring molten matters and radiation thermometers for monitoring the temperature of molten matters outside the furnace, to monitor the conditions of the molten matters without contact.

These measures were verified during the experimental pilot plant tests. The optimum operating range was checked to suppress gas generation in terms of the amount and intervals of simulated sludge supply and heating temperature.

## OPERATION METHOD OF THIS PROCESS

### Laminated Operating Method

Agitation for molten matters is preferable to obtain a homogeneous vitrified product, but it may cause a complicated furnace structure. To cope with the problem, laminated operating method with no agitation was invented to provide the same effect as with agitation. In this new method, solidified matters are laminated within the melting pot after repeating TRU sludge supply, evaporation and solidification. All solidified laminae have uniform composition, and uniform vitrified matters can be obtained finally. Also, the solidified matters are completely melted by the convection effect created by using both microwave and electric heating, and thereby homogeneity of the vitrified product has been enhanced.

### Intermittent TRU Sludge Supply Method

In the laminated operating method, the TRU sludge supply is performed intermittently with a small volume. By adopting this method, it become possible to suppress overflow and forming. For preventing overflow during TRU sludge supply, the amount in the melting pot is checked with a level detector. The lifting type level detector with the detection mechanics by electric conductivity is inserted into the melting pot before TRU sludge supply. The TRU sludge supply line is rinsed with about 10 cc of water after TRU sludge supply, and rinse water is treated together with TRU sludge.

### Completion Detection Method

In this process, NOx gas was monitored to judge the completion of melting. The TRU sludge contains sodium nitrate, so NOx gas is generated by the thermal decomposition. Its concentration decreases as the melting comes close to the end. NOx gas is analyzed inline after offgas treatment by condenser and HEPA filter. In this way, the completion of melting treatment was detected precisely, by which the fluctuation of the quality of each vitrified product was minimized.

## VITRIFIED PRODUCTS

The vitrified products adopted in this equipment are zinc borate-based glass. In selecting the composition, we put the priority on the melting temperature that permits the treatment within glove box and to make vitrified products having leaching rate as low as possible.

### Composition of Vitrified Product

Conditions governing the composition of vitrified product are shown in Table III. In the review of the composition of vitrified product, an electric furnace was used. Out of various combinations, we performed solidification tests with the experimental pilot plant. Then, we reviewed the possible problems related to the physical properties of vitrified products and equipment. All the tests were conducted by adding glass formation materials to simulated sludge. It was found that the mixture of diboron trioxide ($B_2O_3$), zinc oxide ($ZnO$) and calcium oxide ($CaO$) is effective for the component of glass formation materials.

An example of the composition of vitrified product obtained from the above results is shown in Table IV. Since this vitrified product has a low melting point, the high leaching rate was expected. However the rise in the leaching rate was suppressed by adding calcium oxide ($CaO$) within the range where the low melting point was maintained. This value was used as target value for adjusting the composition of glass formation materials during operation.

### Shape of Glass Formation Materials

The shape of the glass formation materials was evaluated to enable stable supply via a hopper at a constant rate. During the experimental pilot plant tests, glass frits, beads and tablets were evaluated. Finally the tablets shape was selected because of the following reasons:

- The composition suitable for making glass beads is somewhat limited in range, and do not often meet the requirements for the vitrification process.
- Frit type glass has irregular shape, and poor fluidity, and therefore stable and constant supply is difficult.

The tablets are made from powder materials by tablets machine. The typical size is 8 mm in diameter, about 6 mm in thickness, and crush strength is 2 to 3 kgf/grain.

**TABLE III**
Selecting Condition for the Composition of Vitrified Product

| Selecting Conditions of Glass Formation Materials | Restricting Conditions for Equipment |
|---|---|
| • Low melting point.<br>• Large range of vitrification.<br>• Not to induce a microwave discharge. | • Melting temperature: Less than 1000°C |
| • Processability.<br>• Availability at low cost.<br>• Low toxicity and foaming. | • Treatment capacity: 5 liters/h possible |

**TABLE IV**
Composition of Representative Vitrified Product

| Components | Composition (wt%) |
|---|---|
| $Na_2O$ | 18.0 |
| $Fe_2O_3$ | 8.5 |
| $B_2O_3 + ZnO + CaO$ | 73.5 |

## RESULT OF COLD TESTS

### Treatment Condition of Cold Tests

Cold tests were performed using the equipment installed in JAERI. Composition of simulated sludge during the cold tests is shown in Table V. Also, the composition of glass tablets used in the test is shown in Table VI.

### Outline of the Operation

Operation time chart of the cold test is shown in Fig. 3. Operation was made in two steps. In the first step, the simulated sludge was supplied twice for one supply of glass tablets, and then evaporation and solidification are performed. These are considered as one cycle, and 7 cycles were repeated. Thereafter, solidified matters were all melted and formed to about 1-liter of molten vitrified matters.

In the second step, the operation was repeated on the vitrified matters of 1 liter of the first step. Finally 2 liters of the mixture were all melted. Molten vitrified matters were moved to annealing equipment for each melting pot and slowly cooled and then taken out as vitrified products.

**TABLE V**
Composition of Simulated Sludge in Cold Tests

| Components | Composition (wt%) |
|---|---|
| $NaNO_3$ | 13 |
| $Fe(OH)_3$ | 3 |
| $H_2O$ | 84 |
| ss-100 | 1 (ppm) |

**TABLE VI**
Composition of Glass Tablets

| Components | Composition (wt%) |
|---|---|
| $H_3BO_3$ | 59.0 |
| ZnO | 25.5 |
| $Ca(OH)_2$ | 9.5 |
| Binder | 5.0 |
| Lubricant | 1.0 |

Basic data in this operation are:

- Final temperature of molten vitrified matters :Approx. 890°C
- Concentration of $NO_x$ gas at the time to stop heating : 6 ppm
- Annealing temperature: 450°C
- Ratio of volume reduction: 1/10 (vitrified product/simulated sludge)

### Physical Properties of Vitrified Product

Composition of vitrified product obtained in the cold test is shown in Table VII. An example of the physical properties of the vitrified products is shown below.

- Unconfined compressive strength: 1200 kfg/cm$^2$
- Leaching rate: $1.3 \times 10^{-3}$ g-Na$^2$O/cm$^2$ day
- Density: 2.78 g/cm$^3$ (at 20°C)

Measurement of the leaching rate was performed in accordance with the method proposed by IAEA (1), and the mean value up to fourth day was used for $Na_2O$.

## CONCLUSIONS

Microwave directly heats substances at a high heating rate. It has, on the other hand, some disadvantages; when the substances to be heated are placed in a metal container, the portion near the metal surface is heated slowly; and if internal structure is complicated, then microwave discharge occurs easily.

In the equipment evaluated in this report, to solve said disadvantages, electric heaters are supplementary used for heating metal melting pots from the outer side, by which heating ability near the metal surface has been enhanced. The furnace structure and operating method capable of suppressing the occurrence of microwave discharge have been established. The laminated operating method is

**TABLE VII**
Composition of Vitrified Product in Cold Tests

| Components | Composition (wt%) |
|---|---|
| $Na_2O$ | 18.0 |
| $Fe_2O_3$ | 8.5 |
| $B_2O_3$ | 50.5 |
| ZnO | 18.0 |
| CaO | 5.0 |

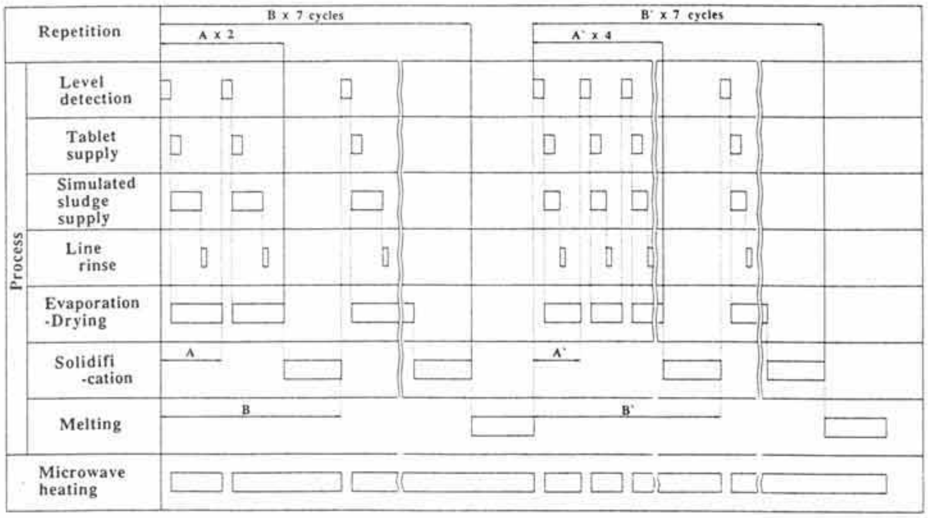


Fig. 3. Operation time chart of cold tests.

invented, which requires no agitation and provides the same effect as with agitation. In this way, respective disadvantages are canceled each other, and both the quality of vitrified products and the efficiency of the equipment have been improved.

The use of glass tablets was found to be advantageous in weighing management and also was fully usable even for the composition which could not be used for glass beads.

The composition of glass formation materials was determined to satisfy low melting point, high compressive strength and low leaching rate through the vitrification with the experimental pilot plant tests. The values were determined with full-scale tests. In the results of cold tests, the values of both the unconfined compressive strength and leaching rate were fully satisfactory. It indicates the applicability of this process to the TRU sludge, and the further hot tests are currently being carried out.

The present technology is very effective for TRU sludge treatment. This technology described in this report will be useful also for treating other kinds of wastes.

## REFERENCES

1. E.D. HESPE; "Leach Testing of Immobilized Radioactive Waste Solid" Atomic Energy Rev. 9 (1) 195-207 (1971)