Applicability of Vitrification Technology for Secondary Waste Generated from Contaminated Water Treatment Systems at Fukushima Daiichi Nuclear Power Station

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Various types of radioactive waste have been generated in Fukushima Daiichi Nuclear Power Station (NPS) site. The purpose of this review is to reduce and stabilize radioactive waste by vitrification technology using Cold Crucible Induction Melter (CCIM) — especially waste with a high level of radioactivity such as secondary waste generated from contaminated water treatment systems in which the development of vitrification process using CCIM was carried out. This paper describes approaches to completing development of treatment technology for such waste including IHI's activities.

1. Introduction

The waste produced by Fukushima Daiichi NPS (hereinafter referred to as "Fukushima accident waste") includes a wide variety of waste, such as rubble, cut trees, and secondary waste including sludge generated by contaminated water treatment and zeolite (used in adsorption towers that were employed for contaminated water treatment).

IHI started to research the treatment of Fukushima accident waste in FY2011 and began studying the applicability of highly stable, volume-reducible fused glass solidification technology (the technology to which the vitrification technology used in the stabilization of high-level liquid waste is applied; see **Section 3.1** for details) to the secondary waste generated from contaminated water treatment (hereinafter referred to as "secondary waste"), of which the radioactivity level is high among the Fukushima accident waste. Moreover, in FY2012, IHI concluded an agreement with Korea Hydro & Nuclear Power Co., Ltd. (KHNP), which has a track record in treating low-level radioactive waste in South Korea, and started to study the applicability of Cold Crucible Induction Melter (CCIM) to secondary waste[(1)]. In FY2017, IHI started the subsidy program for the "Project of Decommissioning and Contaminated Water Management (Research and Development of Processing and Disposal of Solid Waste (Research and development on preceding processing methods and analytical methods))," [(2)] which is a subsidized project of the Agency for Natural Resources and Energy of the Ministry of Economy, Trade, and Industry; IHI is now evaluating the applicability of fused glass solidification technology using CCIM to secondary waste.

In this paper, we introduce our efforts to study the applicability of fused glass solidification technology using CCIM to secondary waste alongside the status of development.

2. Characteristics of secondary waste from Fukushima Daiichi NPS

The secondary waste has the following characteristics.

- Because of the high radioactivity level of the waste, there are concerns about hydrogen caused by radiolysis if water is contained in the waste after treatment, which is called solidified waste.
- There is a wide variety of waste; it is possible for the composition of the waste to change.
- Some of the waste contains combustibles, which must be mineralized for disposal.
- As there is also high-level radioactive waste that has α nuclides, in some cases it is required that solidified waste be stable.
- Because there is a large amount of waste, the volume

must be reduced as much as possible from the viewpoint of reducing the area required for storage and disposal.

- As some of the waste was not generated during the operation of the nuclear power station, in some cases the technology to treat such waste must be developed.

In consideration of the aforementioned characteristics, it is necessary to reduce the amount of hydrogen to be generated, to implement measures to cope with a wide variety of waste, and to ensure volume-reducibility and stability of solidified waste in order to treat the secondary waste.

3. Concept to select technologies for volume reduction and stability

Because of the aforementioned characteristics of secondary waste, it is necessary to select technologies that are highly capable of reducing the amount of hydrogen generated as well as stabilizing and reducing the volume of solidified waste. Therefore, as described below, we decided to adopt fused glass solidification technology, which is considered to be more effective compared to cement solidification and other technologies to stabilize low-level radioactive waste with respect to the points indicated above.

The melting furnaces used for fused glass solidification technology of secondary waste are required to cope with a wide variety of waste and to be capable of producing highly volume-reducible, stable solidified waste. Therefore, we evaluated that CCIM, which can satisfy these requirements, is highly applicable as a melting furnace for treatment of secondary waste (see **Section 3.2**).

3.1 Characteristics of fused glass solidification technology

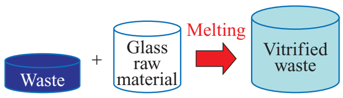
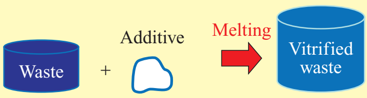
In this development, we used the technology to which the vitrification technology(3) (technology for achieving vitrification by adding glass raw materials such as borosilicate glass to waste) used to treat high-level radioactive liquid waste in Japan is applied, which we refer to herein as fused glass solidification technology. **Table 1** shows the characteristics of this technology. Fused glass solidification technology vitrifies waste with the minimum volume of additives by using the components (such as SiO_2) contained in the waste itself as glass-forming components. Depending on the requirements and disposal methods of vitrified waste, it is possible to adjust the volume reducibility, operability, and stability of solidified waste to meet needs of various cases. Moreover, it is also possible to stabilize solidified waste by combining different types of waste.

Secondary waste includes waste that contains many glass-forming components (e.g., zeolite), and application of fused glass solidification technology is expected to have an effect.

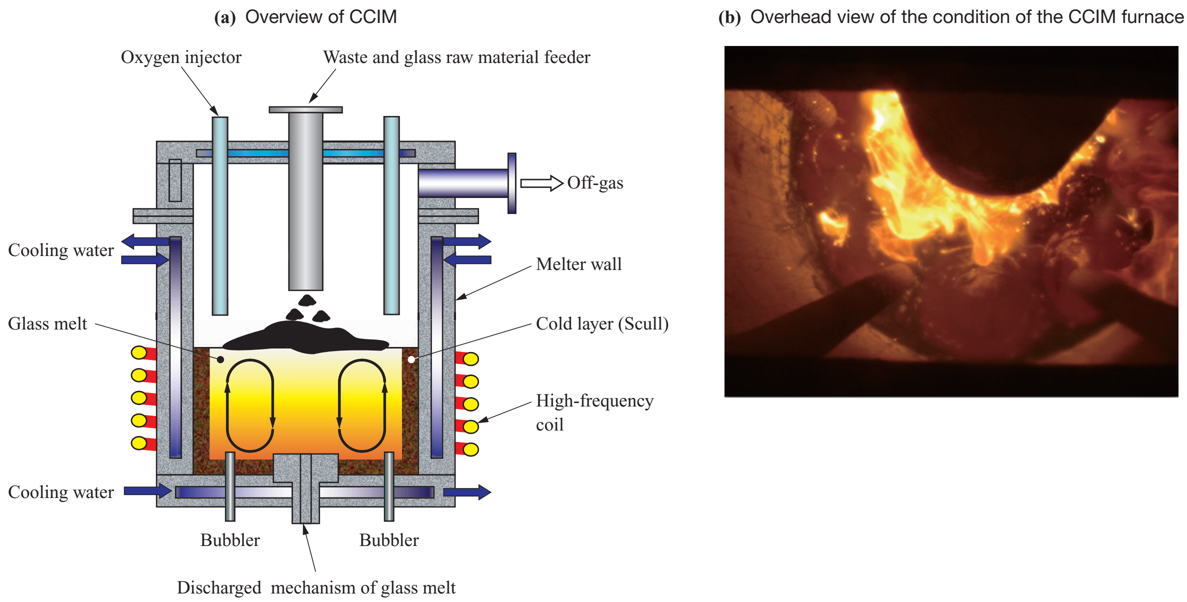
3.2 Characteristics of CCIM

IHI has CCIM technology and a CCIM practical-scale test unit; IHI is promoting the development described herein under a cooperative agreement concluded with KHNP, which has a track record in vitrification of low-level radioactive waste by employing this technology in South Korea. An overview of CCIM is shown in **Fig. 1** and as follows.

Table 1 Comparison of vitrification processes

Item	Vitrification technology		Melt solidification technology
	Vitrification (conventional)	Fused glass solidification technology	
Overview	Method of vitrification by adding prescribed glass raw materials (e.g., borosilicate glass) to waste	Method of vitrification with minimized additives by using components contained in the waste itself (e.g., SiO_2) as the glass-forming components	Method to melt waste and solidify it as slag
			
Volume reducibility	△	○	◎
	Volume reducibility is low because the waste loading rate is kept constant by the addition of glass raw materials.	Volume reducibility is relatively high because the volume of additives is reduced to the minimum within the range in which stability can be ensured. However, volume reducibility varies depending on the waste composition.	Volume reducibility is high because there are no additives.
Operability	◎	○	△
	Heating and pouring (tapping) conditions are always constant because the high-temperature physical properties of molten glass can be controlled within a certain range. However, in the case of high-level liquid waste, platinum group management affects operation.	As the high-temperature physical properties of molten glass can be controlled within the determined range, operation is possible within a range in which heating and pouring (tapping) conditions do not change greatly.	Because the high-temperature physical properties vary depending on waste composition, heating and pouring (tapping) conditions must be set each time.
Solidified waste stability	◎	○	△
	Superior in stability because the composition after vitrification is managed so as to always be within a certain range.	Relatively high stability is achieved by reducing the volume of additives to the minimum within the range in which stability can be ensured. However, stability varies depending on the waste composition.	Because the slag composition is determined by the waste composition, stability is not constant.

(Notes) 1. Characteristics of low-level waste
There are many types of waste that contain glass-forming components (e.g., SiO_2 and Al_2O_3).
2. Results of technology evaluation
◎ : Excellent, ○ : Good, △ : Fair



(Source : KHNP's brochure)

Fig. 1 Appearance of a Cold Crucible Induction Melter (CCIM)

- High-frequency heating is used as a heat source, and metal is applied to the part that comes into contact with molten glass.
- The corrosiveness of the glass is reduced by scull layers formed by water cooling of the furnace walls (also applicable to highly corrosive glass, and extends the service life).
- Startup and shutdown are both within 4 hours (the waste to be treated can be changed easily).
- It is possible to cope with various types of waste, such as waste that contains organic matter and liquid waste.

In addition, CCIM has the characteristics described in **Table 2**. Based on these characteristics, we determined that CCIM is appropriate for treatment of the secondary waste.

4. Development of fused glass solidification technology for secondary waste

How to proceed with applicability evaluation in this development is shown in **Fig. 2**. First, settings of glass compositions are made in accordance with the chemical compositions and characteristics of secondary waste, and glass compositions are selected by evaluating glass properties through laboratory-scale tests that employ crucibles. Next, using glass compositions that were favorable in the laboratory-scale tests, practical-scale tests are conducted with practical-scale CCIM equipment to confirm CCIM's

Table 2 Characteristics of CCIM

Item	Description
Applicable waste	It has high corrosion resistance and can be applied to various types of waste.
Stability	The melting and mixing properties in melting furnaces are good and stable vitrified waste can be produced.
Volume reducibility	As it is a pouring type, it can be charged to a high volume in a solidified waste container; its volume reducibility is high.
Processing capacity	It has high processing capacity because of continuous operation. Processing capacity can be improved by convection accelerated by bubbling.
Cost efficiency	Solidified waste containers can be produced inexpensively (the required heat resistance is relatively low because it is unnecessary to directly heat the containers).
Inventory evaluation	The inside of the furnace and vitrified waste can be evaluated by sampling and analyzing poured glass.
Operability	Pouring operation is necessary and operation is relatively complex. Because scull layer management is important, it is necessary to accumulate technologies by testing in the future.

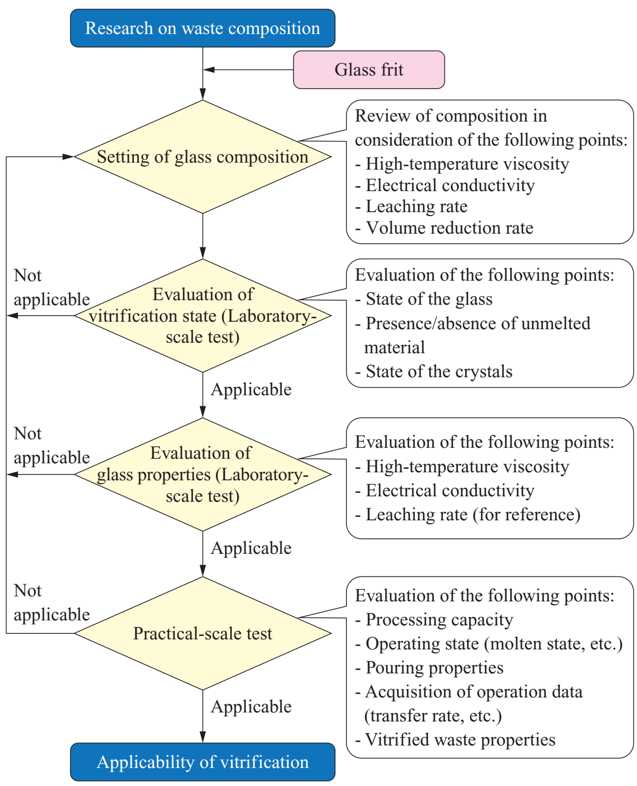


Fig. 2 Procedures for applicability evaluation

applicability.

Moreover, to clarify the image of the equipment, the concepts of pieces of equipment (e.g., equipment to supply waste and glass raw materials as well as waste gas treatment equipment) are reviewed. The results of items implemented are as follows.

4.1 Selection of glass compositions

(1) Settings of glass compositions

We set the compositions of the vitrified waste (hereinafter referred to as "glass compositions") to be eventually produced by reviewing the compositions of those additives that are added to the typical secondary waste in accordance with the compositions and characteristics of the waste. When setting glass compositions, we made use of glass databases, reduced the number of test objects, and efficiently reviewed the compositions. Moreover, we set the glass compositions by considering how to ensure that the high-temperature physical properties (high-temperature viscosity and electrical conductivity) that are necessary to operate melting furnaces satisfy the target values.

(2) Evaluation of vitrified state (laboratory-scale tests)

- It was confirmed that both the vitrified state and high-temperature physical properties are good by mixing zeolite and incinerated ash at a ratio of 75 wt% of zeolite and 25 wt% of incinerated ash.
- We set glass compositions in accordance with the waste compositions of five types of secondary waste by the multi-radionuclide removal system known as the Advanced Liquid Processing System (ALPS): carbonate slurry, iron coprecipitation slurry, zeolite, silico titanate, and ferrocyanide sludge. We reviewed these compositions by setting melting temperatures 1 200°C or lower, and we confirmed that waste can be vitrified in a satisfactory manner at a waste loading rate of the vitrified waste from 20 to 65 wt%. **Figure 3** shows examples from the results of the review of glass compositions. Among these, because zeolite contains highly concentrated volatile simulated nuclides (Cs), we reviewed it under conditions in which the melting temperature is lowered to about 1 050°C. Even in this case, because SiO_2, a glass-forming component, is the main component, we achieved a high waste loading rate of 62 wt%. **Table 3** shows the results of this review of glass compositions.
- To confirm the effect of volume reduction in the case of waste vitrification, we roughly estimated the volume reduction rates. We achieved high volume reduction rates, such as for zeolite, whose volume reduction rate was 0.4 (the volume of waste decreased to four-tenths). Thus, volume reduction effects can be expected through fused glass solidification technology (see **Table 3**).

(3) Evaluation of glass properties

We evaluated the glass properties of the five types of secondary waste described in paragraph (2) above. **Figure 4** shows examples from the results of measurement of high-temperature physical properties.

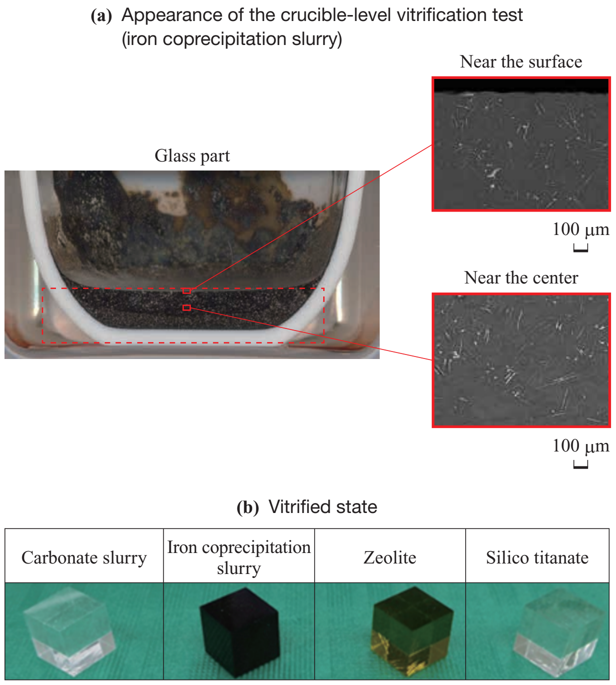
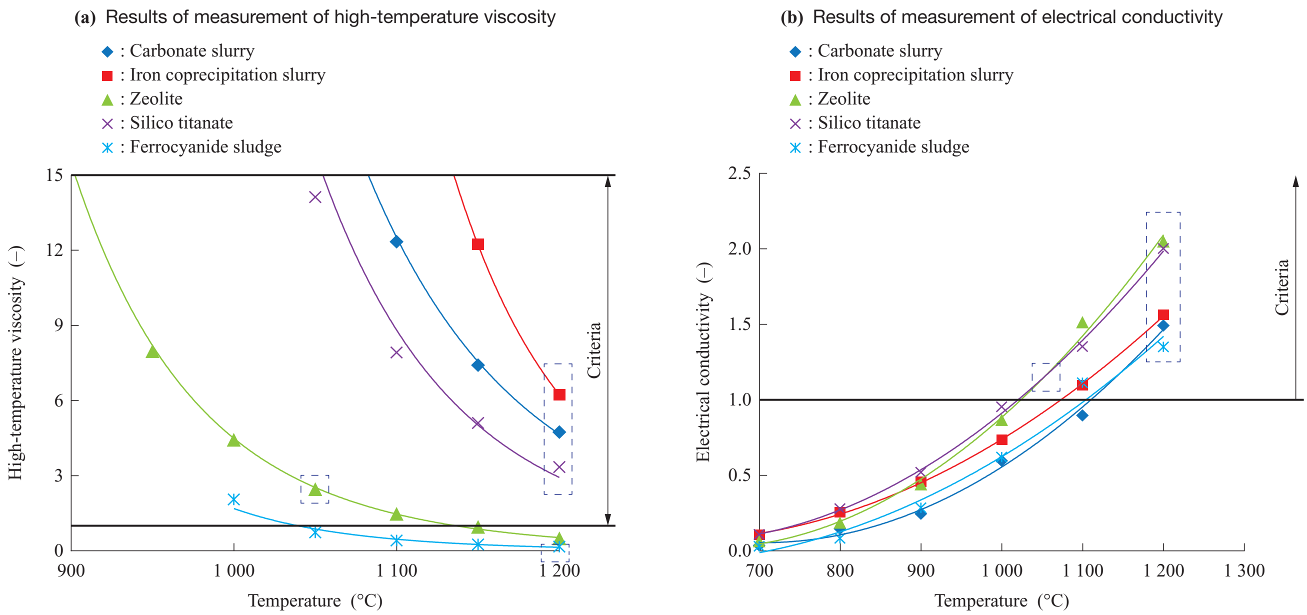


Fig. 3 Examples from the results of the review of glass compositions

Table 3 Results of this review of glass compositions

Applicable waste*1	Waste loading rate*2 (wt%)	Weight reduction rate*3	Volume reduction rate*4	Vitrified state	High-temperature viscosity	Electrical conductivity
Carbonate slurry	20	1.6	0.8	○	○	○
Iron coprecipitation slurry	35	1.1	0.7	○	○	○
Zeolite	62	0.7	0.4	○	○	○
Silico titanate	25	1.7	1.0	○	○	○
Ferrocyanide sludge	35	1.0	0.5	○	×	○

(Notes) *1 : In the case of 50 wt% water content.
*2 : The waste loading rates are the values obtained in this development.
*3 : Weight reduction rate = Weight of vitrified waste / Weight of waste. For this calculation, the density of the vitrified waste is the value obtained in this development. Bulk density is an assumed value.
*4 : Volume reduction rate = Volume of the vitrified waste / Volume of waste. For this calculation, the density of the vitrified waste is the value obtained in this development. Bulk density is an assumed value.



(Note) The blue-dashed portions of the figure indicate the temperatures (melting temperatures) of evaluated high-temperature physical properties.

Fig. 4 Result of evaluation of glass properties

Excluding ferrocyanide sludge, for four types of waste we were able to select glass properties that satisfy the standard values (see **Fig. 4**) of high-temperature physical properties that are necessary to operate CCIM. For ferrocyanide sludge, adjustment of physical properties is considered necessary.

To select the aforementioned glass compositions more efficiently, we are making efforts to develop models to estimate glass properties.

4.2 Practical-scale tests

We conducted practical-scale tests on the glass compositions obtained by the laboratory-scale tests, and we collected data on scale-up effects, CCIM operability, and practical-scale operation as well as confirmed the performance of vitrified waste. The details of the tests conducted to date are described below.

(1) From FY2013 to 2017

We conducted tests on mixtures of zeolite and incinerated ash as well as simulated wastes of liquid waste that contained high percentages of ferrocyanide sludge, carbonate slurry, and Na.

(2) In FY2018

We conducted tests on simulated wastes of carbonate slurry (we used simulated waste with a composition closer to that of actual waste in consideration of the latest analysis results).

The major results obtained from the aforementioned tests are described below.

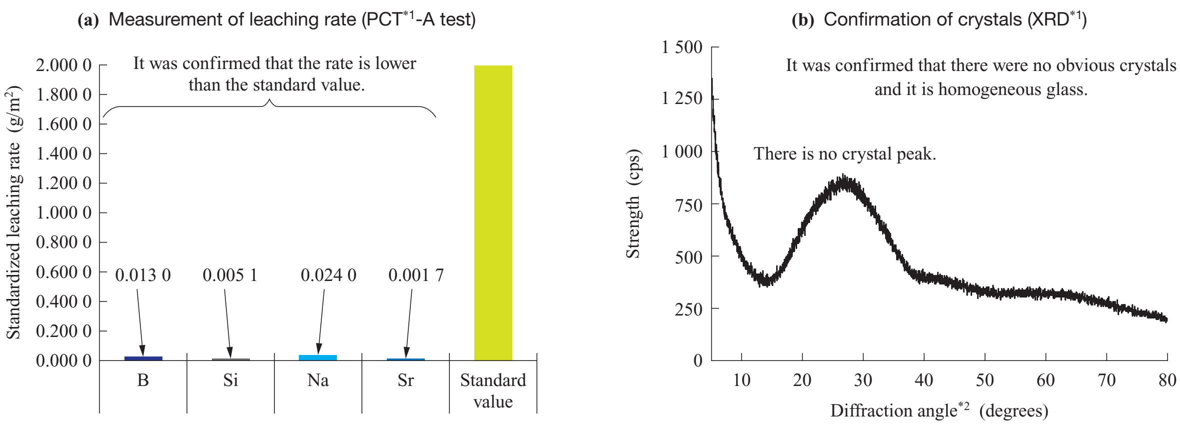
- For all reviewed simulated wastes of secondary waste, we achieved short-time startup and shutdown as well as high processing capacity by bubbling, and stable pouring and glass extraction were possible by performing adjustment of glass compositions.
- Regarding the simulated wastes of carbonate slurry, we supplied them at supply speeds of several patterns (40 *l*/h or higher) and maintained the cold cap (low-temperature layer formed on the melting furnace's upper surface) used as an indicator of stable operation of CCIM and bubbling holes (exits of bubbling air on the glass surface); by doing so, we were able to continue to operate practical-scale CCIM in a stable state. We confirmed that homogeneous glass can be produced because the produced vitrified wastes, whose leaching rates are kept low, have high chemical stability (water resistance), and no obvious crystals were seen to be generated in the glass. **Figure 5** shows example results from the practical-scale tests.
- Regarding the simulated wastes that consisted of a mixture of zeolite and incinerated ash, it was possible to maintain a stable state of operation. Moreover, as a result of obtaining the transfer rate of Cs, even though bubbling was conducted, we confirmed that the volatilization rate of cesium oxide (Cs_2O) could be kept as low as about 8%. While recovering Cs_2O with waste gas treatment equipment, we plan to consider further reduction by operation optimization in the future.
- As for the simulated wastes of ferrocyanide sludge, it was possible to maintain a stable state of operation. Moreover, at the time of solidification of highly corrosive iron-phosphate glass, we confirmed that there was no corrosion of the furnace walls as well as high corrosion resistance.

4.3 Review of the equipment concept

The equipment concept of the treatment system that uses CCIM for secondary waste is as follows.

(1) Process

We established a supply system, the basic process of the waste gas treatment system, and the configuration



(Notes) *1 : Pressure Cooker Test
B : Boron
Si : Silicon
Na : Sodium
Sr : Strontium

(Notes) *1 : X-Ray Diffraction
*2 : 2θ, angle between the incident beam and diffraction beam

Fig. 5 Result example of demonstration test

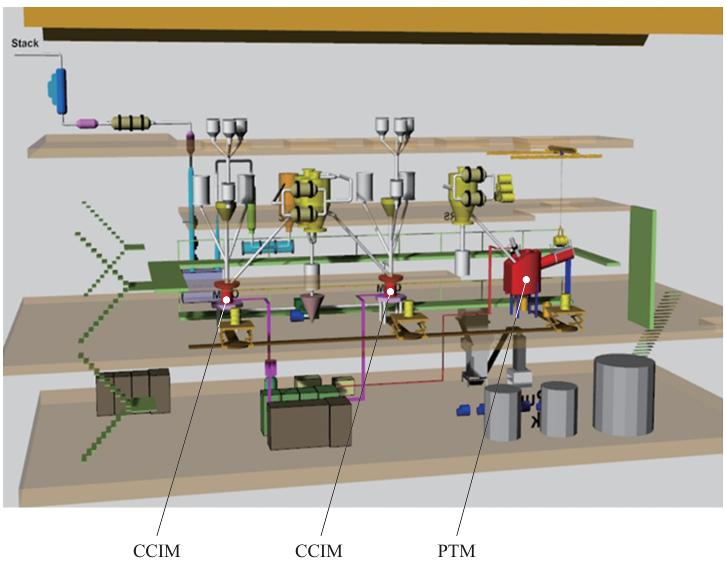
of major pieces of equipment, all of which are suitable for the secondary waste. The waste gas treatment system that we considered can trap 99.97% of the transferred nuclides within the system by circulating the liquid waste that has recovered nuclides transferred from melting furnaces to the waste gas treatment system, and the system can trap the remaining 0.03% with HEPA (High Efficiency Particulate Air) filters.

In our past research, we used expected values for the waste treatment rate and the quantity of waste materials to consider the planned layout for major pieces of equipment. Thus, we were able to clarify the images of the equipment. The layout plan is shown in **Fig. 6**.

(2) Conformity with Japan's regulations

In introducing the CCIM system that is already in practical use in South Korea to Japan, we compiled information on the relevant domestic laws and regulations as well as technical regulations, and we also reviewed the designing flow in conformity with laws and regulations as well as technical regulations from the perspectives of Japan's safety evaluation and procedures for acquiring permits and approval.

In consideration of the latest data on compositions and generation based on the results of analyses of secondary waste, we plan to study the operation conditions of CCIM under conditions in which the degrees of simulation of actual waste are increased. Also, by making use of glass fusion furnace technology, waste gas treatment (trapping) design technology, and remote techniques, which have been nurtured through high-level liquid waste treatment, we plan to realize equipment that is highly reliable from the perspectives of stable operation of the equipment including



(Notes) CCIM : Cold Crucible Induction Melter
PTM : Plasma Torch Melter

Fig. 6 Layout sketch of vitrification facility

CCIM as well as trapping and handling of radionuclides and so forth.

5. Conclusion

Fused glass solidification technology that uses CCIM for typical secondary waste can be evaluated to be highly applicable from the following perspectives.

- Through the study on glass compositions against the secondary waste, we were able to select the glass composition that satisfies high-temperature physical properties of glass required for the operation in CCIM. In addition, high efficiency in the volume reduction can be expected when each waste is vitrified.
- We conducted tests in a practical-scale CCIM with the selected glass composition. As a result, we confirmed that CCIM can be continuously and stably operated with a high processing capacity against the simulated secondary waste in various aspects including slurry and solid. At the same time, we also obtained the solidified glass with homogeneousness and high chemical stability. Moreover, we confirmed the applicability for highly corrosive glass because of the good corrosion resistance of CCIM.

We plan to review more detailed information about the quantities of waste materials and their storage conditions, the requirements to be set in the future (requirements for vitrified waste regarding intermediate storage and disposal, and restrictions on and requirements for treatment periods and the operation method of waste and treatment facilities), and further operation. After that, we intend to proceed with consideration of the applicability of fused glass solidification technology, optimization of CCIM treatment conditions, and refinement of the equipment concepts.

Going forward, IHI will continue to make use of its technologies nurtured through the treatment of high-level radioactive liquid waste, and advance efforts toward the introduction of treatment equipment, including fused glass solidification processes that employ CCIM, for secondary waste.

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