Project of Decommissioning and Contaminated Water Management
(Research and Development of Processing and Disposal of Solid Waste)

The Holistic Evaluation of Applicability of GeoMelt® ICV™ for Treatment of 1F Water Treatment Secondary Waste
Fiscal Year 2021

December 5, 2022

Kurion Japan K.K.

VEOLIA NUCLEAR SOLUTIONS

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8. **Summary**

1. Purpose

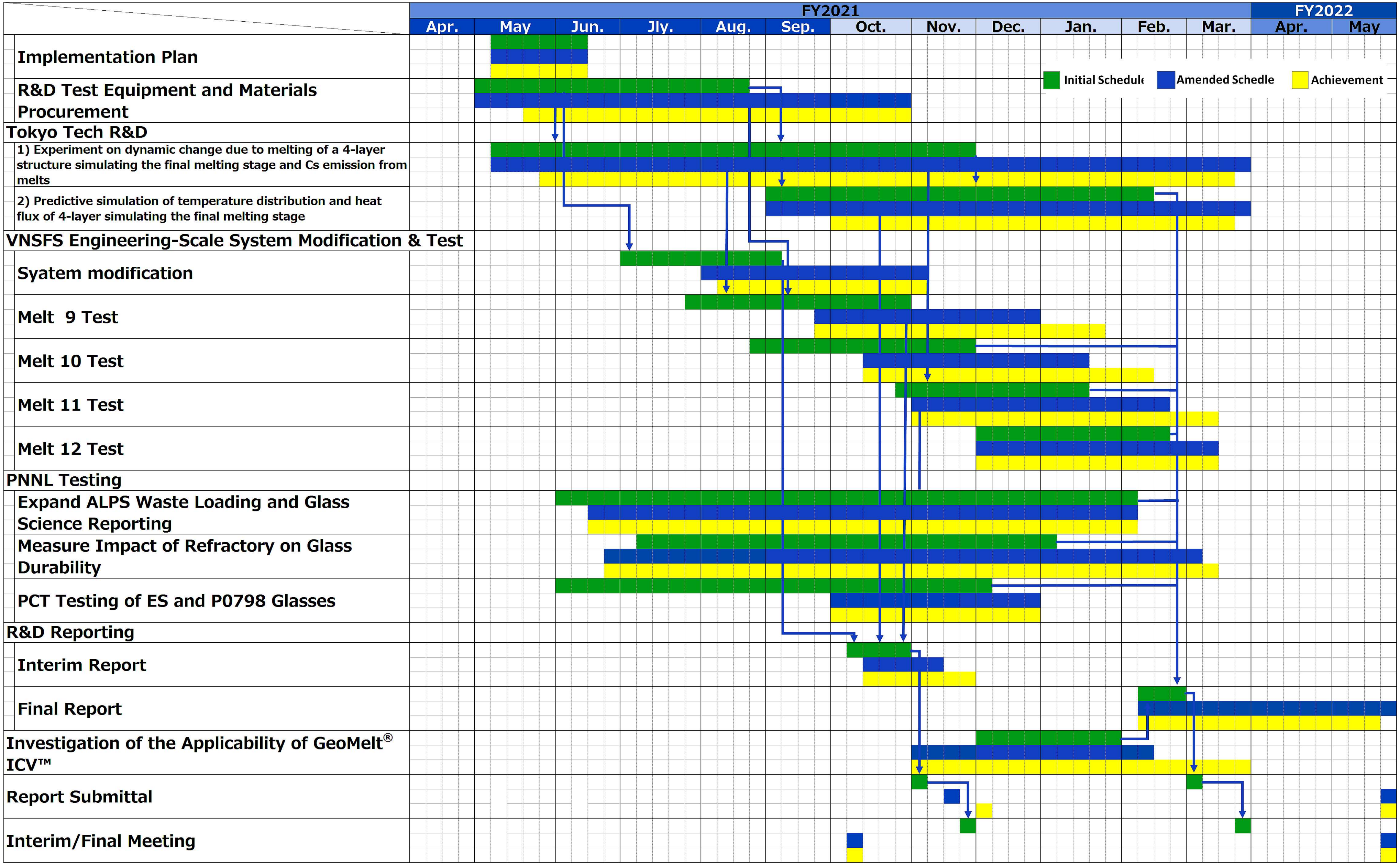
1) Holistic evaluation of applying GeoMelt®ICV™ technology as a method for stabilizing and immobilizing a huge amount of secondary water treatment waste (spent adsorbent [zeolite, etc.], slurry and sludge) generated at the Fukushima Daiichi Nuclear Power Station (hereinafter referred to as 1F) of Tokyo Electric Power Company Holdings, Inc. (TEPCO), has been continued from the subsidy project up to last year.

2) In the subsidized projects up to last year, engineering-scale melting tests, glass formulation / crucible tests, durability testing of manufactured glass, basic test on Cs volatilization suppression, pre-conceptual design of treatment plant, etc. were carried out. As a result, it was demonstrated that Cs emission during water treatment secondary waste treatment can be reduced (Cs retention rate in glass was 97.22% to 99.44%), and a vitrified waste form with excellent durability was obtained.

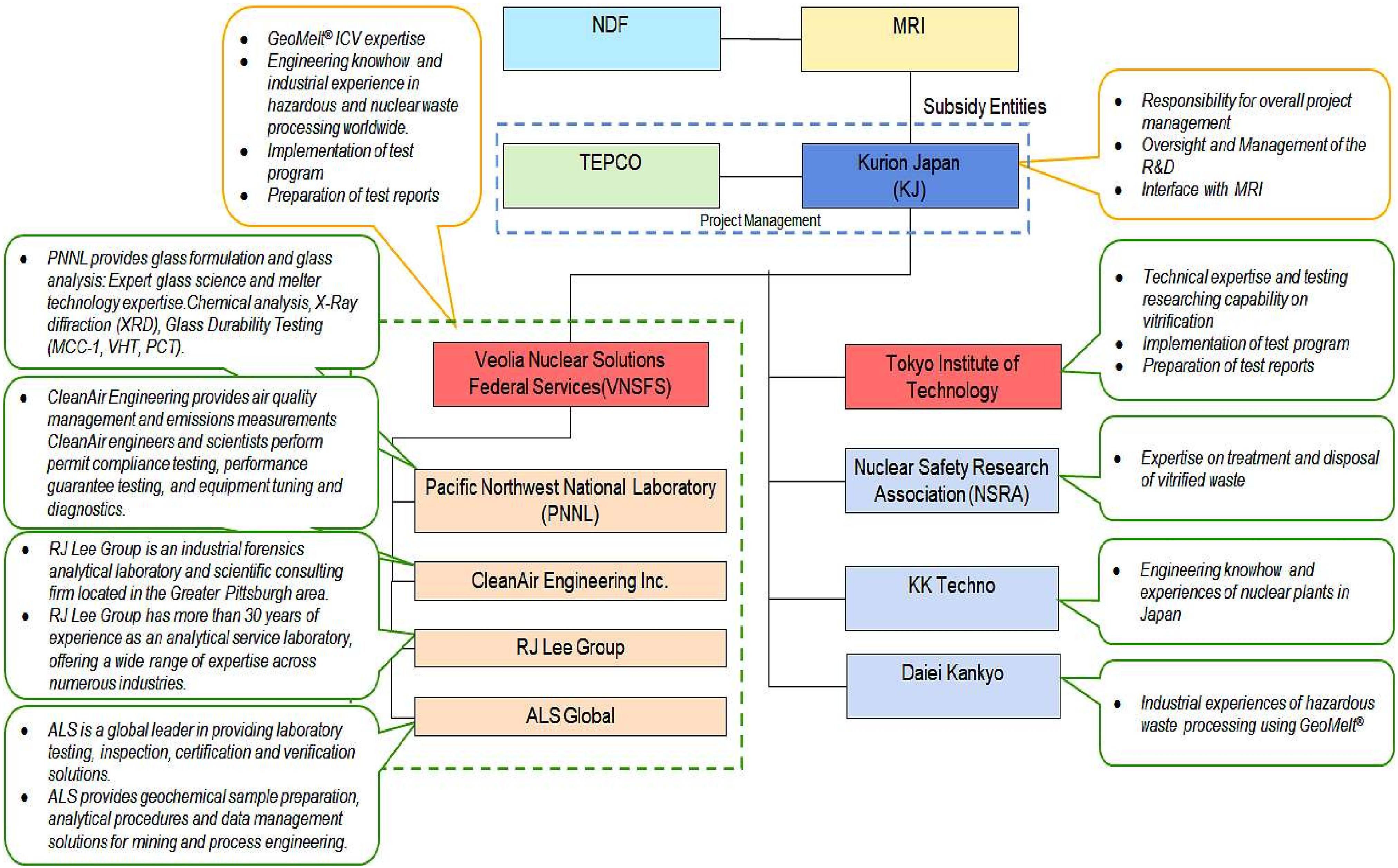
3) In the subsidy project in FY2021, as the purpose of responding to the remaining technical issues and improving the waste treatment process and gaining additional improvement in Cs retention, test on Cs volatilization suppression at the final stage end of melting and an engineering-scale melting test using a melting test equipment that a sintered metal filter is incorporated (including ALPS slurry dehydrate[1] as simulated waste), etc. is performed. Holistic evaluation of GeoMelt® ICV™ applicability is conducted, including the results of past subsidy projects.

1: ALPS carbonate Filtercake and iron coprecipitate Filtercake were obtained by dehydrating ALPS carbonate slurry and iron coprecipitate slurry by ATOX Co., Ltd., respectively.

2. Implementation Schedule



3. Implementation organization



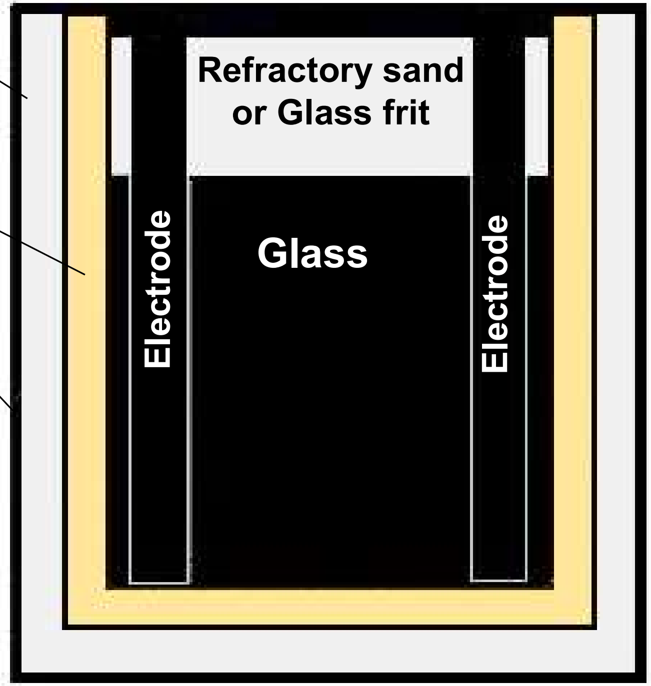
4. Features of GeoMelt® ICV™ (1/2)

① **Glass melt and vitrification in the container** (right)
- Supply and melt waste in the melting container.
- The molten glass is not needed to pour down from the bottom of the melting container. It is vitrified and kept in the melting/disposal container.

② **The melting container and waste form are the same.**
- The steel melting container used for melting treatment is part of the waste form. (replace the melting container for each batch)

③ **Structure of melting container**
- The refractory container to store glass, refractory sand on the outside and a steel container on the outermost side are installed.

④ **Reducing the effect of melting on the refractory container**
- Reduced heating time for refractory container due to batch processing.
- Less corrosion of ICV container even when melting at high temperatures.



GeoMelt® ICV™ Container structure

⑤ **High-loading waste can be melted due to high-temperature**
- Batch processing with GeoMelt® ICV™ can handle higher temperature operation (+1600℃), which allows higher waste loading because a higher fraction of silica-rich zeolite can be included.

⑥ **Co-treatment with zeolite or contaminated soil**
- The waste loading in glass can be further improved by treating it at the same time as other 1F waste.

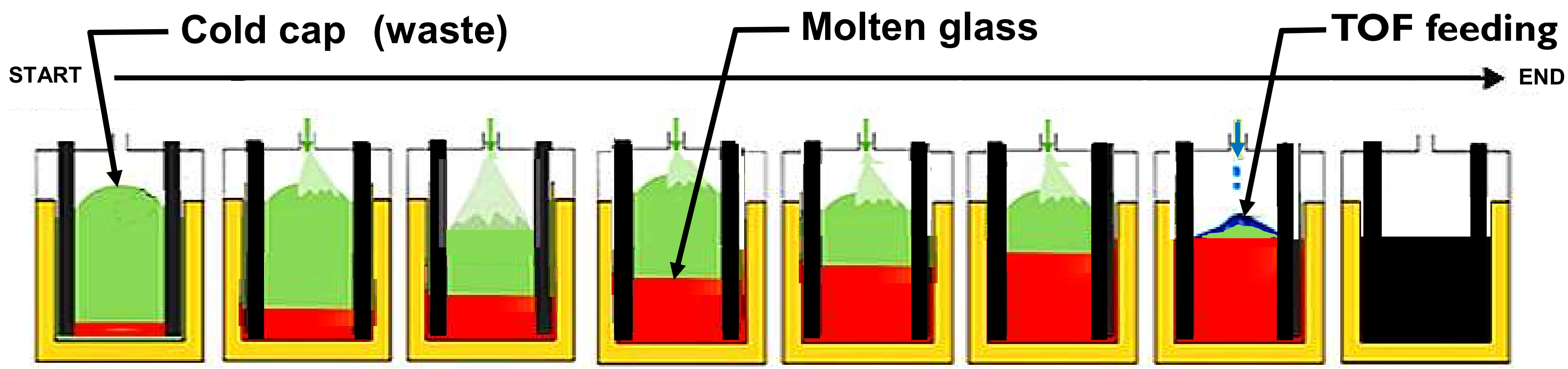
4. Features of GeoMelt®ICV™ (2/2)

⑦ **Suppression of volatile Cs emission by cold cap management (figure below)**

- Emission of volatile Cs is suppressed by maintaining and managing the appropriate thickness of the cold cap (waste) on the molten glass.
- The volatilized Cs condenses within the cold cap at the top, then reincorporates into the molten glass.
- Since the cold cap becomes thinner at the end of melting, top-off frit (TOF) is added, volatilizing Cs is condensed by the cold cap of TOF, and finally TOF helps further incorporate Cs.

⑧ **Various range of melting capacity**

- The ICV can be selected according to treatment needs, with a track record of melting capacity from -100 kg to up to 50 tons.



Operation Scheme of GeoMelt®ICV™ (cold cap management)

5. Tasks for applying GeoMelt®ICV™

Tasks to be examined for applying GeoMelt®ICV™, a vitrification technology, to secondary waste of 1F water treatment were extracted. Since FY2017, these have been examined and resolved in the subsidy project.

A. Glass formulation[1] ･Crucible test

① Setting the glass formation to make the glass durable according to each waste composition. (Ongoing)
② Setting of glass formation that enables increase of waste loading in glass of ALPS slurry. (New)

B. Demonstration of operation method of Melter

① Demonstration of good Cs emission suppression by the cold cap management. (Ongoing)
② Validation of suppression of Cs emission by TOF feeding at the final stage of melting. (Ongoing)
③ Demonstration of higher Cs retention by using a back-pulsing of sintered metal filter in the off-gas treatment system. (New)

C. Quantitative elucidation of the mechanism to suppress Cs volatilization

① Quantitative understanding of Cs volatilization behavior in the cold cap management. (Done)
② Test on suppression of Cs volatilization at the final stage of melting. (New)

D. Glass durability test

① Confirmation of long-term chemical durability of the glass obtained by the engineering-scale melting tests. (Ongoing)
② Confirmation of possible effects of the refractory to the glass durability in the disposal environment. (New)

E. Applicability evaluation

① Study and evaluation of facility concept including the melting container and its peripheral equipment (supply system, off-gas treatment system, etc.) . (Done)
② Investigation of applicability to actual treatment plant. (Ongoing)

1: Glass formulation is to combine wastes of various compositions and vitrify them, and the glass composition that satisfies the glass performance is set from the result of the glass formulation.

6. Relationship between the implementation contents / results of the previous subsidy projects and the FY2021 implementation items (1/3)

FY2017～2018 [1]	FY2019～2020	FY2021

A. Glass Formulation･Crucible Test

FY2017～2018

Glass formulation･crucible test

- Of 1F water treatment secondary wastes, 40 types of glass blends are available for major wastes.
- Understanding the glass characteristics in the crucible test.

→ Setting the glass formulation for Melts 1 to 3

FY2019～2020

Glass formulation･crucible test

- Of 1F water treatment secondary wastes, 12 types of glass blends are available for wastes with a relatively small amount.
- Understanding the glass characteristics in the crucible test.

→ Expanded the glass database for solidification of waste (Combined with the previous fiscal year's implementation).

Glass modeling analysis

- Evaluate the impact of changes in waste composition.
- Evaluate the effect of reducing glass produce amount when mixing different types of waste.
- Evaluate the effect of different melting treatment temperatures on glass produce amount,

→ Confirmed superiority of GeoMelt®ICV ™ (high temperature treatment).

FY2021

Glass formulation･crucible test

- Setting 10 types of glass blends corresponding to the increase in ALPS slurry content.
- Understanding the glass characteristics in the crucible test

→ Setting the glass formation for Melt 12

Note)

- Melting test: See the next page for the relationship between the glass composition of 4 to 10 and the glass composition of Melts 1, 2 and 3.
- The glass composition of Melt 11 was set by grasping the composition of the ALPS slurry dehydrate.

1: Kurion Japan K.K. received an order from ATOX Co., Ltd. for FY2017-2018 test as part of the IRID program.

6. Relationship between the implementation contents / results of the previous subsidy projects and the FY2021 implementation items (2/3)

FY2017～2018[1]

B. Demonstration of melt operation (Engineering-scale melting test)

4 Electrode Square Melter

Bottom-up

Melt 1
KUR-EH +ALPS carbonate･iron coprecipitate slurry

Melt 2
KUR-EH +KUR-TSG

Melt 3
KUR-EH +AREVA sludge

＜Results＞
- Cs retention rate 91.46 ～99.30%

＜Task＞
- Further improvement and stabilization of Cs retention rate (due to there was variation in it)

→ Test in a rectangular Melter with a small melting surface area.

Note) KUR-EH: Zeolite (glass former)
KUR-TSG: silicotitanate

1: Kurion Japan K.K. received an order from ATOX Co., Ltd. for the 2017-2018 test as part of the IRID program.

FY2019～2020

4 Electrode Square Melter Top-down

Melt 4
KUR-EH +KUR-TSG

＜Results＞･There is no difference in Cs retention rate between Top-down and Bottom-up.

2 Electrode Rectangular Melter

Bottom-up

Melt 5
KUR-EH +ALPS carbonate･iron coprecipitate slurry

Melt 6
KUR-EH +KUR-TSG

Melt 7
KUR-EH +AREVA sludge

＜Results＞
- Improved and stabilized Cs retention rate with good cold cap management（97.22%～99.44%）
- The superiority of the rectangular melter could not be confirmed.

＜Task＞
- Improvement of Cs retention rate during TOF supply process, optimization of operation

Melt 8
Soil +ALPS carbonate slurry

＜Results＞･ Demonstrated melting restart method when melting is stopped for long period
･ Demonstrated using soil as a glass–former to replace KUR-EH

FY2021

4 Electrode Square Melter

Bottom-up

SMF (sintered metal filter) installed in off-gas system.

Melt 9
KUR-EH +KUR-TSG

Melt 10
KUR-EH +KUR-TSG

Melt 11
KUR-EH +ALPS carbonate･iron coprecipitate Filtercake

Melt 12
KUR-EH+ALPS carbonate slurry (waste loading increased)

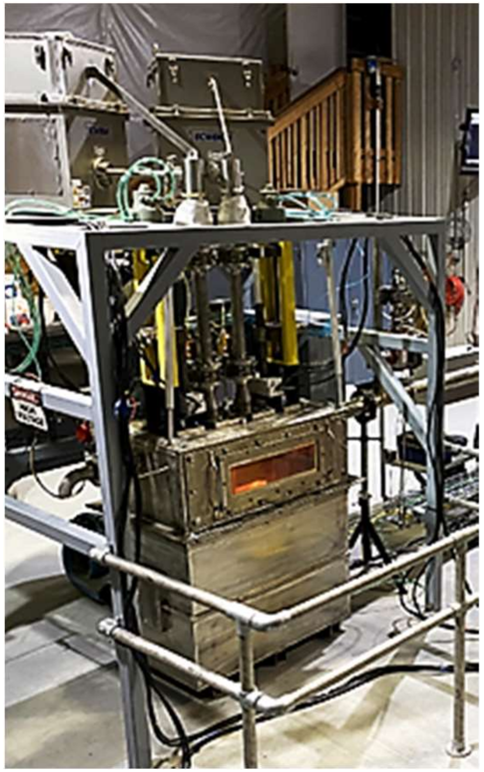
＜Action items＞
- Operation optimization of TOF supply
- Check the function of SMF
- Treatment of ALPS carbonate･iron coprecipitate Filtercake
- Treatment of ALPS carbonate slurry with high waste loading

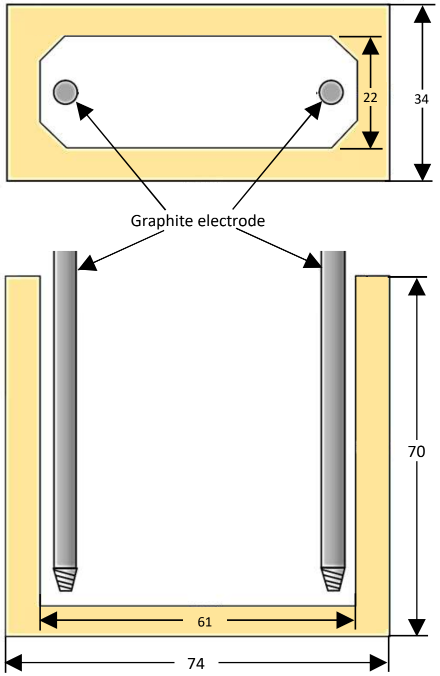
＜Results＞
- Demonstrated the recycling of SMF captured fine particles and the improvement of their Cs retention rate (99.98-100.00%)
- Demonstrated mixing, supply and treatment of ALPS carbonate･iron coprecipitate Filtercake
- Increased waste loading rate from 19.49% to 29.46% of ALPS carbonate slurry

(Ref.) Comparison of 2-electrode and 4-electrode melter

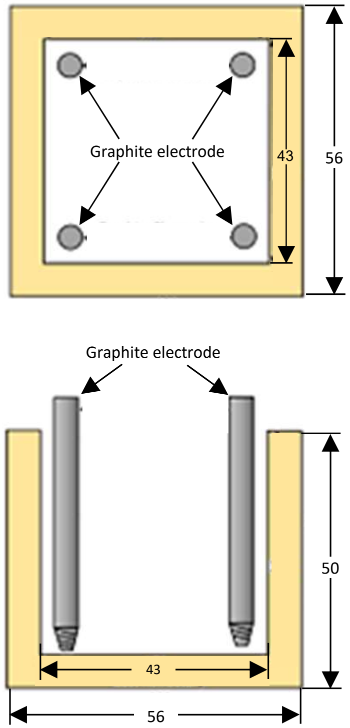
<u>2-electrode melter</u>
Inside dimensions:
61.0cm(L)×21.6cm(W)×63.5cm(H)
Melt surface area: 1266 cm^2 (surface area minus the area of the four corners)

<u>4-electrode melter</u>
Inside dimensions:
43.2cm(L)×43.2cm(W)×43.2cm(H)
Melt surface area: 1865 cm^2





（Unit：cm）



2-electrodes melter
(Melts 5, 6, 7, 8)

4-electrodes melter
(Melts 1, 2, 3, 4, 9, 10, 11, 12)

6. Relationship between the implementation contents / results of the previous subsidy projects and the FY2021 implementation items (3/3)

FY2017～2018 [1]	FY2019～2020	FY2021

C. Basic test / analysis on suppression of Cs emission at the end of melting

FY2019～2020:
- Quantitative understanding of Cs volatilization behavior in cold cap management: Test and analysis the inside of the melter as a 3-layer structure
→ Understand the mechanism

FY2021:
- Cs volatilization suppression research at the end of melting: Test and analysis the inside of the melter as a 4-layer structure
→ Reflect in the final stage of melting operation after Melt 9

D. Glass durability test

FY2017～2018:
- Glass MCC-1 test[2] for Melts1-3
→ Check durability.

FY2019～2020:
- Long-term MCC-1 tests (365 days) for Melts 4 -8 glass. (Melts 4, 5 were completed. Melts 6-8 got the data for 28days)
→ Check durability.

FY2021:
- MCC-1 tests for Melts 6 -8 glass (365days)
- MCC-1 test for glass in the presence of refractory (28 days)
- PCT tests for Melts 5-7 glass

E. Applicability evaluation

FY2019～2020:
- Pre-conceptual design, various evaluation reports
↓
- Present the overall features of the facility where two 10-ton scale melters are installed.
- Evaluate economic efficiency, maintainability, etc.

<see previous page>
- Results of engineering-scale melting tests / basic tests up to FY2020

FY2021:
- Applicability evaluation to actual treatment plant

< see previous page >
- Results of engineering-scale melting tests / basic tests in FY2021

1: Kurion Japan K.K. received an order from ATOX Co., Ltd. for the 2017-2018 test as part of the IRID program.
2: Example of MCC-1 Test
- Teflon® transformation vessel
- Surface Area and Solution Volume ASTM Standard No. C1220
- The specimen is about 14mm x 14mm x 1.5mm thick
- The test vessel is Savillex (S/V) with a ratio of 10 m^{-1}
- ASTM type 1 water (DIW water, > 18.0 MΩ cm)
- Tested at 90℃
- Sample water was taken at 7, 14 and 28 days and analyzed for major elements (Na, B, etc.) in the glass

7. Implementation items and contents of the subsidy project in FY2021

7.1 Study on suppression of Cs volatilization in the final stage of melting

① Investigation on the relationship between heating conditions and Cs volatilization at the end of melting including top-off frit (TOF).
② Analysis of the relationship between the temperature distribution of the 4-layer structure (TOF/waste mixture/calcined layer/molten glass) and the heat flux from the bottom

7.2 Engineering-Scale System Modifications and Result of Checkout Melt
7.3 Engineering-Scale Testing

① Test equipment modification: confirmation of specifications for directly backpulsable and washable sintered metal filter (SMF) installation in the first stage of the Melter off-gas treatment system.
② Evaluation of physical properties of simulated ALPS carbonate･iron coprecipitate Filtercake. Confirmation test on transfer and supply method.
③ Engineering-scale melting tests 9-12
- Validation of operations at the TOF supply processing stage (Reflecting the results of 7.1 ①)
- Capturing 99.98% of Cs in particulates released into off-gas by SMF and then recycling to the Melter.

  This improves the Cs retention rate in glass to almost 100%.
- Melting test with test materials simulating the following wastes.

  KUR-EH and KUR-TSG（Melt 9, 10）,
  KUR-EH and ALPS carbonate ･iron co-precipitate Filtercake（Melt 11）
  KUR-EH and ALPS carbonate slurry with increased waste loading（Melt 12）

7.4 Glass formulation･durability test

Glass formulation･crucible test

① Glass composition model update based on evaluation data such as glass formation, crucible test, viscosity, durability, etc.
Glass composition setting to increase the content of ALPS carbonate slurry.

Glass durability test

① Product Consistency Test (PCT) tests for Melts 5 - 7 glass samples
② Effect confirmation test on glass by the refractory constituting GeoMelt®ICV™ waste form under disposal environmental conditions
③ Long-term MCC -1 tests for Melts 6 - 8 glass samples

7.5 Investigation of GeoMelt®ICV™ applicability

Holistic investigation of the applicability of GeoMelt®ICV™ to solid wastes in actual treatment plant from a technical point of view

7.1 Study on suppression of Cs volatilization in the final stage of melting

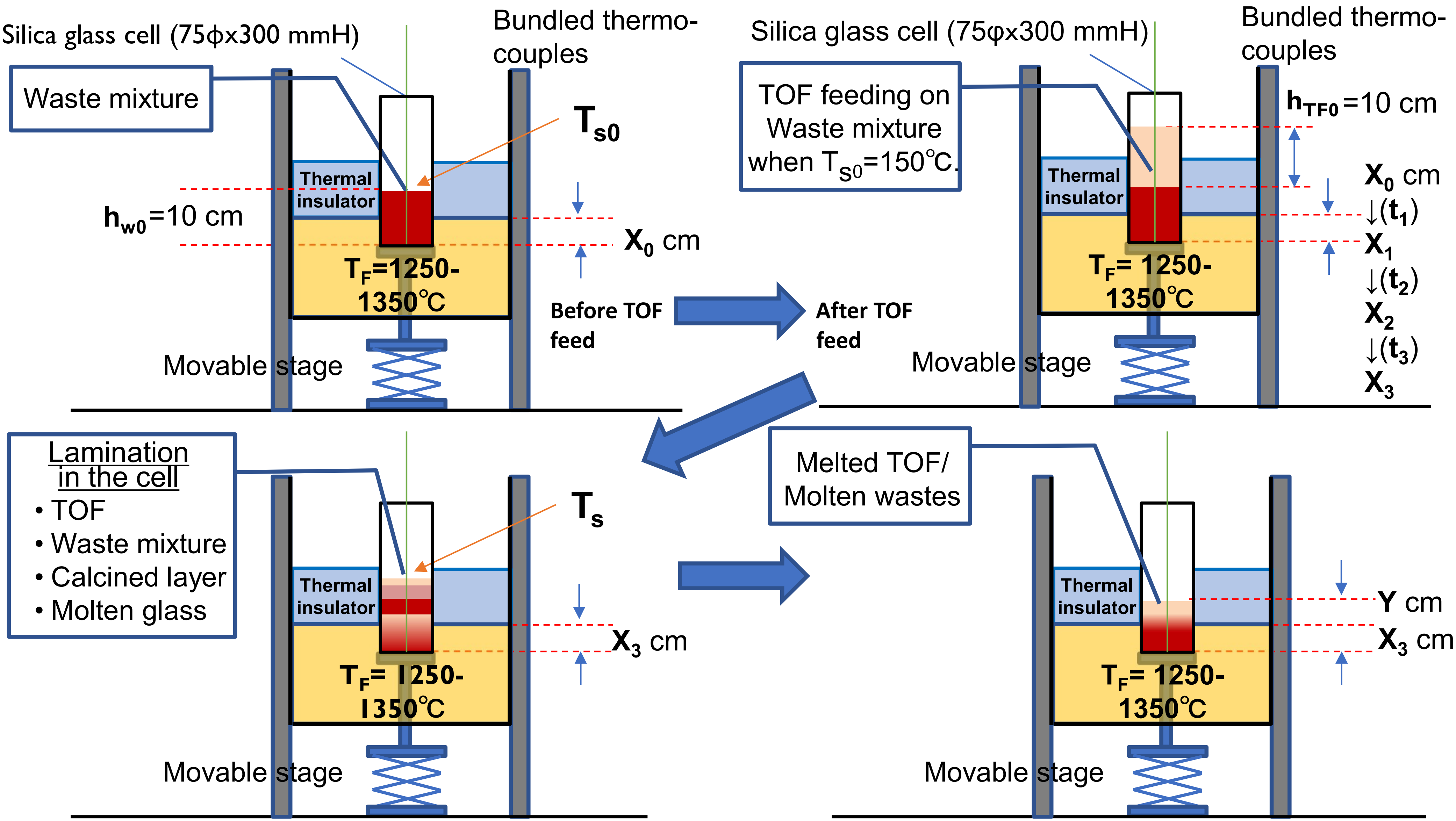
Test on the relationship between heating conditions and Cs volatilization at the end of melting, including top-off frit (TOF)

- **Test purpose:**
  - Since the amount of Cs volatilization at the TOF supply / treatment stage is relatively large and the fluctuation in batch is not constant (unstable), the relationship of melting between the waste mixture and TOF is grasped in order to suppress the Cs volatilization at the TOF stage.
- **Test contents:**
  - The tests to understand the relationship between heating conditions and Cs loss at the final stage of GeoMelt® melting including TOF, and the role of TOF in suppressing Cs volatilization are conducted.
  - The waste mixture used in the tests:

    KUR-EH＋ALPS carbonate･iron coprecipitate slurry

    KUR-EH＋KUR-TSG
  - Regarding the accuracy of recovery of volatile Cs that evaluates Cs loss, recovery of volatile Cs and estimation of the state by TOF（Time Of Flight）-SIMS（Secondary Ion Mass Spectrometry）are carried out.
  - A computer simulation is conducted by performing a calculation (Ansys®) by the finite element method (FEM) on the relationship between the temperature distribution and heat flux of a 4-layer structure including the TOF that simulates the final stage of melting.

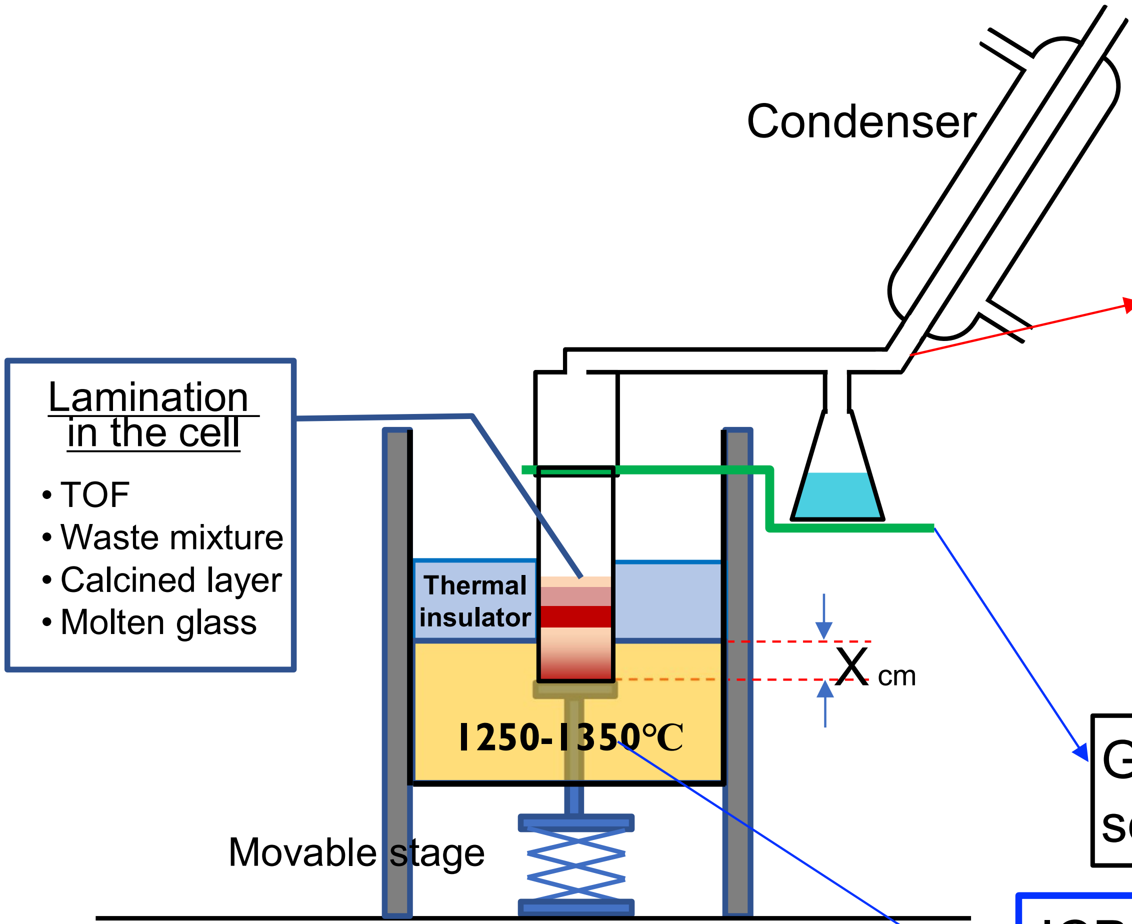
7.1.1 Relationship between Cs volatilization amount and TOF input amount
(1) Melting of TOF/waste mixture in long silica glass cell



(2) List of melting parameters

Parameters	Definition	Typical values
h_{W0} (cm)	Initial height of waste mixture filled in the cell	10
h_{TF0} (cm)	Height of ASG-FRIT (TOF) fed on waste	10
T_F (℃)	Operating temperature of furnace	1250~1350
T_{S0} (℃)	Temperature of waste mixture surface at which TOF is started to fed on wastes	150
T_S (℃)	Surface temperature of TOF monitored by TC	
X_i (cm)	Cell length projected into furnace. *i* =0; the initial value. *i* =3; final	2 (*i*=0), 4 (*i*=1), 6 (*i*=2), 8 (*i*=3)
Y (cm)	Estimated surface level from the furnace ceiling;	1 (when h_{W0}=10, h_{TF0}=10)
t_i (min)	Duration time for each *i*	2 (*i*=1), 2 (*i*=2), 2 (*i*=3)

(3) Off-gas analysis



- The off-gas generated during melting in the temperature gradient electric furnace is condensed by a water-cooled condenser.
- After finishing the experiment, clean the glass equipment.
- Condensed water and wash water are analyzed by ICP-MS to determine the total amount of Cs from molten waste.

Glass equipment for trapping Cs (A set of glassware above the green line)

ICP-MS analyses of melted glass samples are also carried out to evaluate Cs concentration inside.

(4) Protocol of Monitoring of surface temperature and Trap of Cs from materials

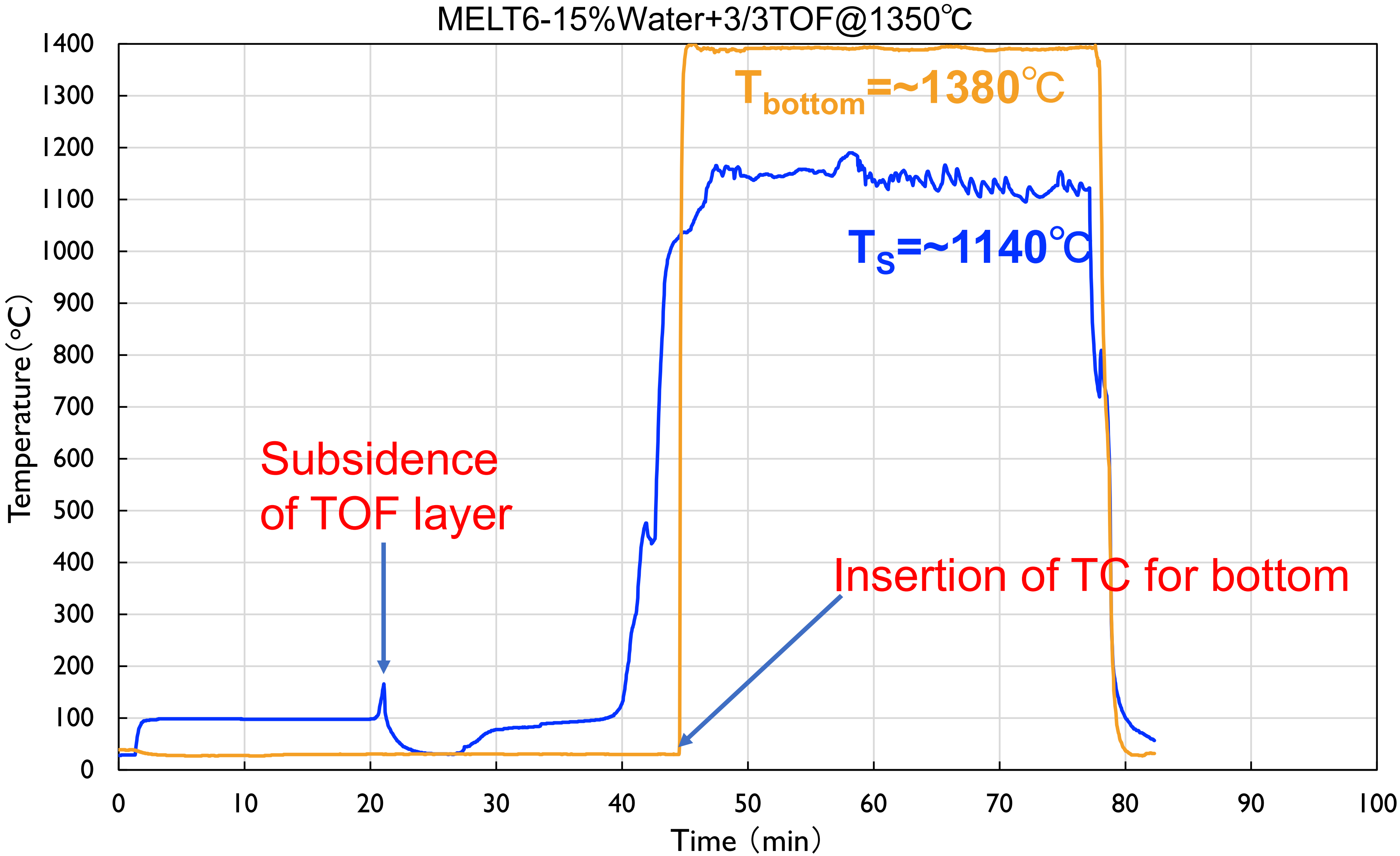
➢ Monitoring of Ts

MELT6-15%, -20%Water,	weight : 330-350 g for h_{W0}=10 cm
MELT5-10%Water,	weight : 285-305 g for h_{W0}=10 cm
T_F=1250℃, 1300℃, 1350℃	
TOF	weight : 520 g for h_{TF0}=10 cm
T_F=1350℃	
TOF	weight : ~520 g for h_{TF0}=10(3/3), 6.7(2/3), 3.3(1/3), 0(0/3) cm

➢ Trap of Cs from materials

- Test condition and protocol was same as in the experiments for monitoring Ts
- Glass equipment for trap of Cs was settled on the silica glass cell just after TOF was fed on MELT6-15%, -20%Water, MELT5-10%Water at Ts>150℃.
- Stage(silica glass cell) was moved downward, X=2cm→8cm by 2cm step every 2 min, and kept for 1 h after T_S shows const.
- Glass equipment was washed by pure water, and Cs in water was analyzed by ICP-MS.

(5) Waste mixture and TOF melting test



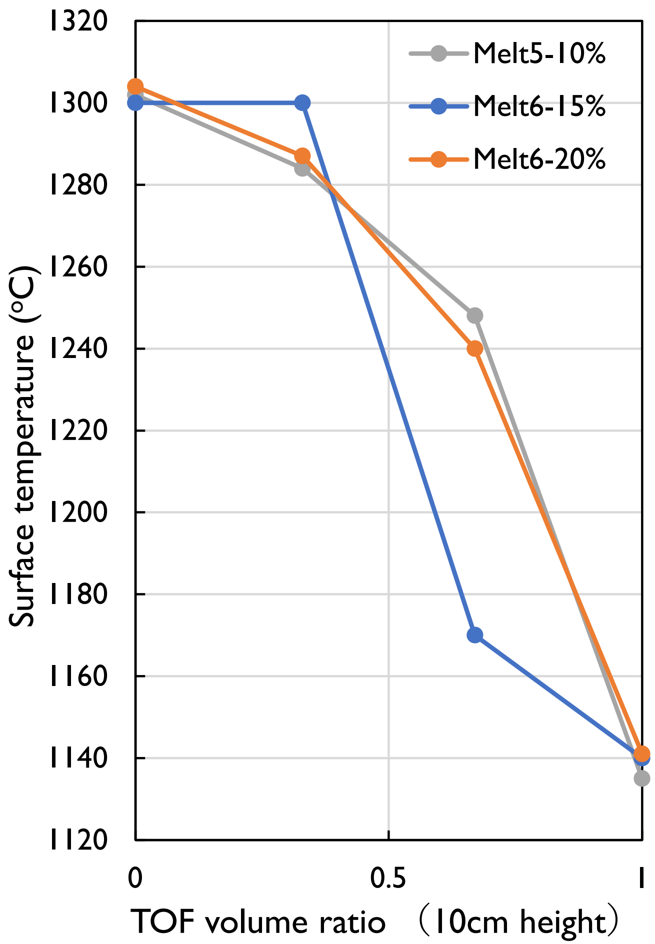
Waste mixture and TOF melting test

(6) List of data related to Cs loss generated and trapped from waste mixture

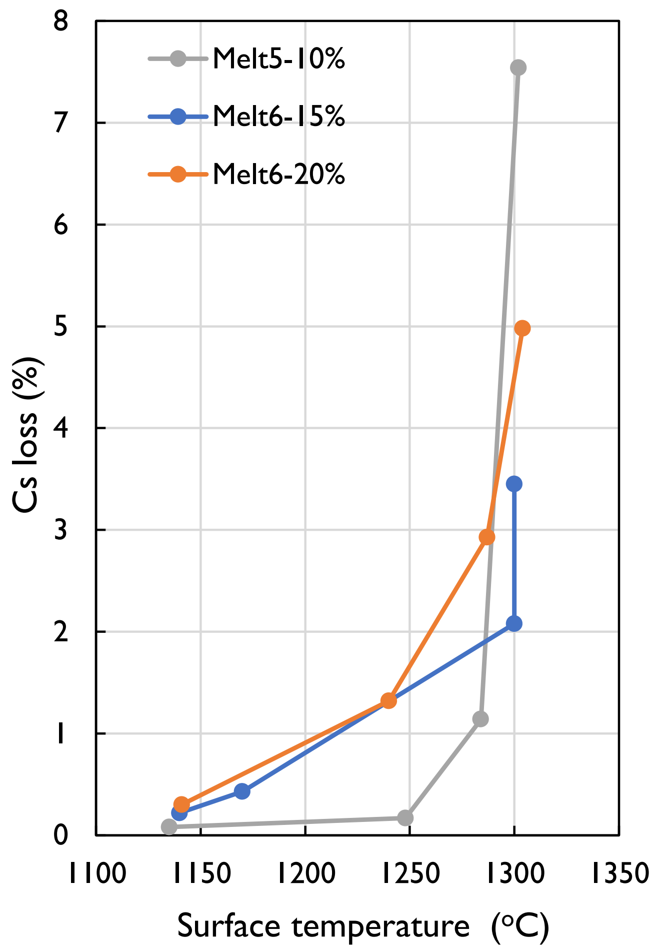
Experiment	T_F (℃)	T_S (℃)	T_{bottom} (℃)	Cs from waste (%)
MELT6-15%Water+3/3TOF	1350	1140	1390	0.08
MELT6-15%Water+2/3TOF	1350	1170	-	0.63
MELT6-15%Water+1/3TOF	1350	1300	-	2.08
MELT6-15%Water+0/3TOF	1350	1300	-	3.59
MELT6-15%Water+3/3TOF_2nd	1350	-	-	0.22
MELT6-15%Water+2/3TOF_2nd	1350	-	-	0.43
MELT6-15%Water+1/3TOF_2nd	1350	-	-	2.08
MELT6-15%Water+0/3TOF_2nd	1350	-	-	3.45
MELT6-20%Water+3/3TOF	1350	1141	1363	0.30
MELT6-20%Water+2/3TOF	1350	1240	-	1.32
MELT6-20%Water+1/3TOF	1350	1287	-	2.93
MELT6-20%Water+0/3TOF	1350	1304	-	4.98
MELT5-10%Water+3/3TOF	1350	1135	1352	0.08
MELT5-10%Water+2/3TOF	1350	1248	-	0.17
MELT5-10%Water+1/3TOF	1350	1284	-	1.14
MELT5-10%Water+0/3TOF	1350	1302	-	7.54
MELT5-10%Water+3/3TOF_2nd	1350	-	-	0.10

"-": Indicates that each temperature was not measured

(7) Relationship between Cs loss and surface temperature Ts



Relationship between TOF volume ratio and surface temperature

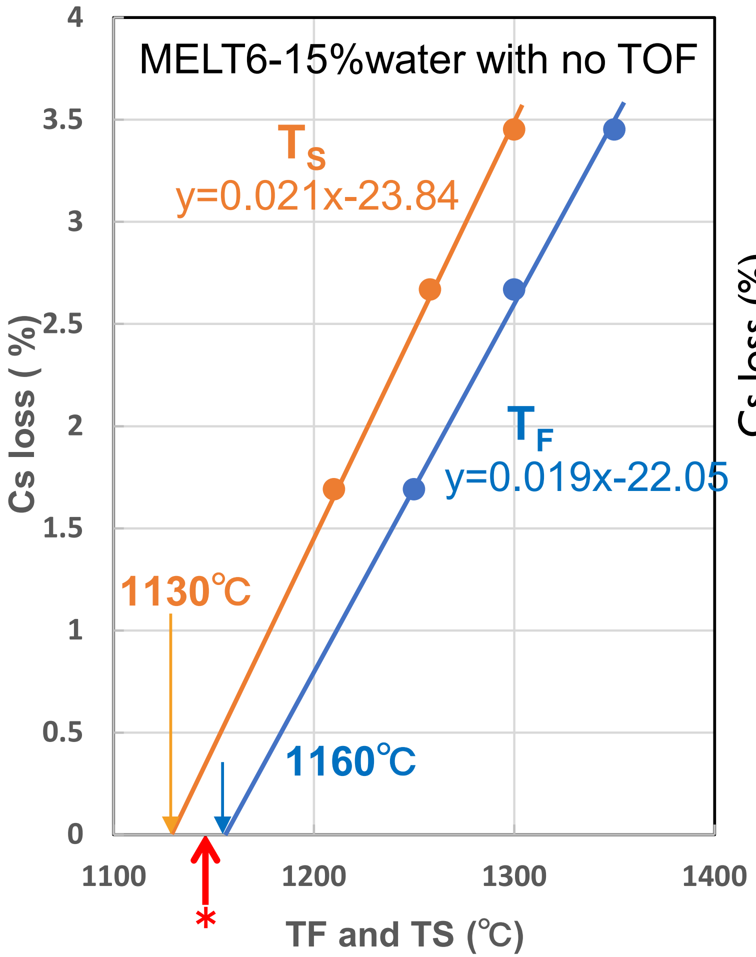


Relationship between surface temperature and Cs loss%

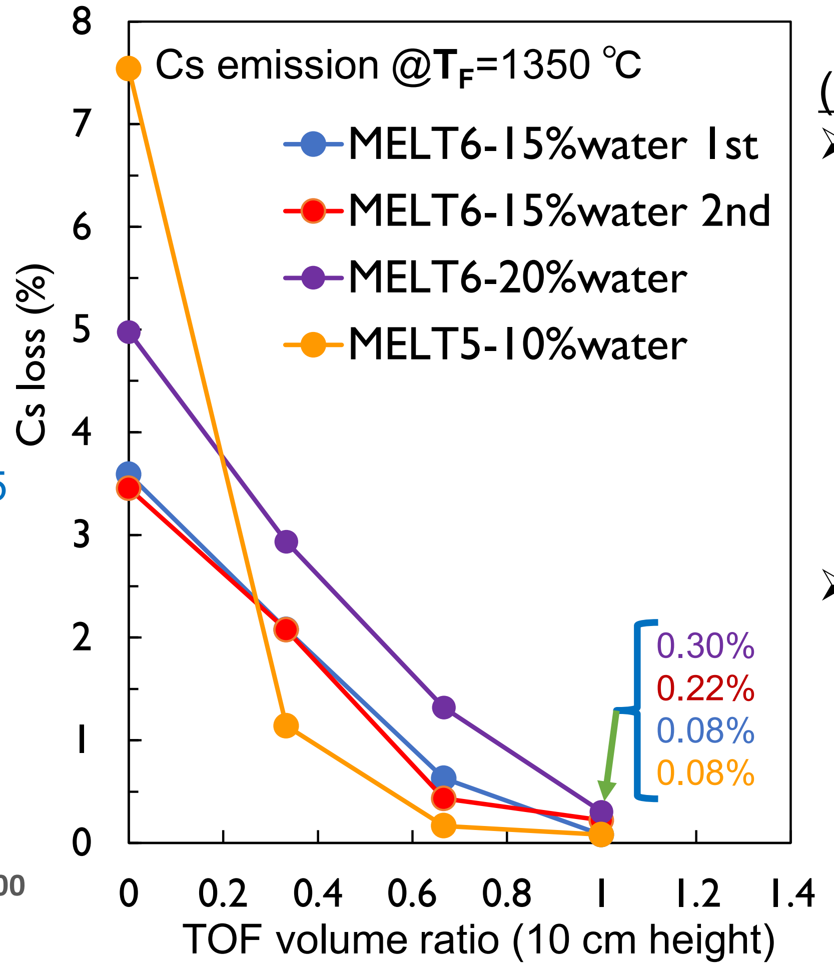
(Left)
When the amount of TOF decreases, the heat transfer increases and the surface temperature rises. The way the surface temperature rises differs depending on the chemical composition including the water content of the waste.

(Right)
Regardless of the water content, Melt 6 gradually increases the volatilization amount of Cs as the surface temperature rises, but Melt 5 behaves so that the volatilization amount increases significantly when the temperature exceeds 1250℃.

(8) Relationship between Cs loss% and T_F, Ts and TOF volume ratios



Relationship between Cs loss% and TF and TS



Relationship between Cs loss% and TOF volume ratio

(Right)

- Cs emission from MLET5-10%Water melting process was reduced to the same low level as that of MELT6 mixtures by covering with 10cm TOF.
- However, the thinner TOF of melt test 5 showed higher Cs volatilization than melt test 6, probably due to the difference in melt properties (composition, melt properties, etc.).

Zero Cs loss* when there is no TOF layer is achieved at a furnace operating temperature T_F of about 1150℃ or less or a waste mixture surface temperature Ts of 1130℃ or less, but when T_F is heated to 1150℃ or more or Ts is 1130℃ or more, volatilization of Cs is accelerated.

(9) Summary
Relationship between of Cs volatilization and TOF feed amount (1/2)

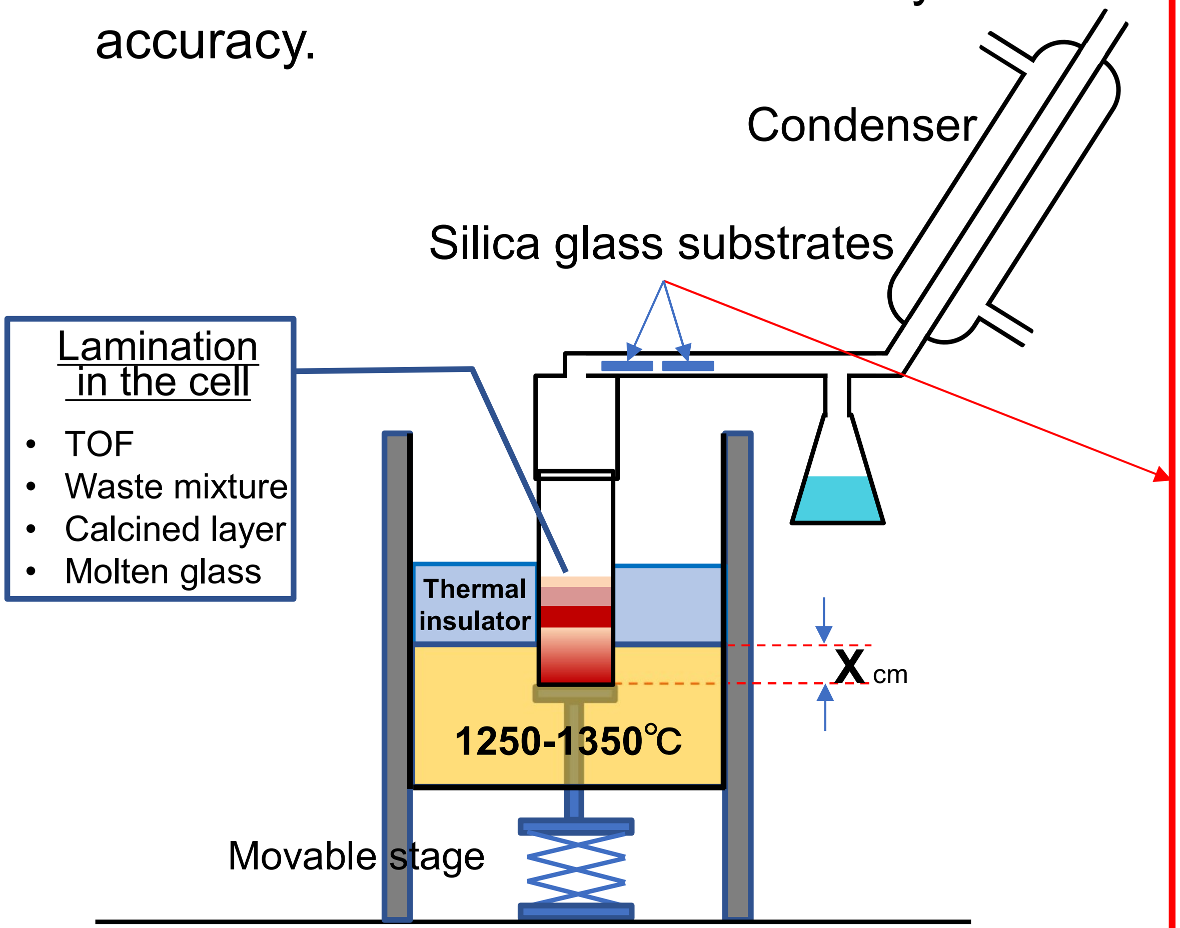
- Melting of the TOF involves the downward ' subsidence ' of the TOF layer on the waste mixture due to large void formation (60-70% volumetric shrinkage) caused by the melting of the waste mixture.
- Subsidence of the TOF layer causes the release of the gas phase contained in the voids. This could be a route for discharging Cs from waste.
- From the relationship between the measurement result of the surface temperature TS and the subsidence of the surface layer, it is necessary to add TOF before the evaporation of the water on the surface layer is completed.
- This allows TOF to sequentially fill the voids formed during melting of the waste mixture, allowing the process of melting the waste mixture at high temperatures to proceed at the bottom of the TOF rather than at the surface.
- Insufficient TOF coverage presumes that waste will melt on the free surface and induce Cs volatilization above 1130 ℃.

(9) Summary
Relationship between of Cs volatilization and TOF feed amount (2/2)

- T_S>1100 °C is necessary to complete melting of TOF and mixing with melted wastes. As a result, smooth glass surfaces were formed after cooling to RT.
- Cs volatilization from wastes under TOF(h_{TF0}=10cm) was ~0.3% of total Cs in wastes using maximum T_F(=1350°C).
  Thinner TOF layer on wastes increased Cs volatilization.
  Trend of Cs volatilization as a function of TOF volume depended on the wastes powder (probably, water content and the chemical composition of constituents).
- From the viewpoint of the viscosity of the melt, the mixing of the molten waste mixture and TOF is accelerated when the liquid properties (viscosities) are at the same level, so it is desirable to keep them at T>1100 °C with the same viscosities. At the same time, if mixing proceeds by convection, the ideal operation is to satisfy the surface temperature TS < 1130 °C to suppress Cs volatilization.

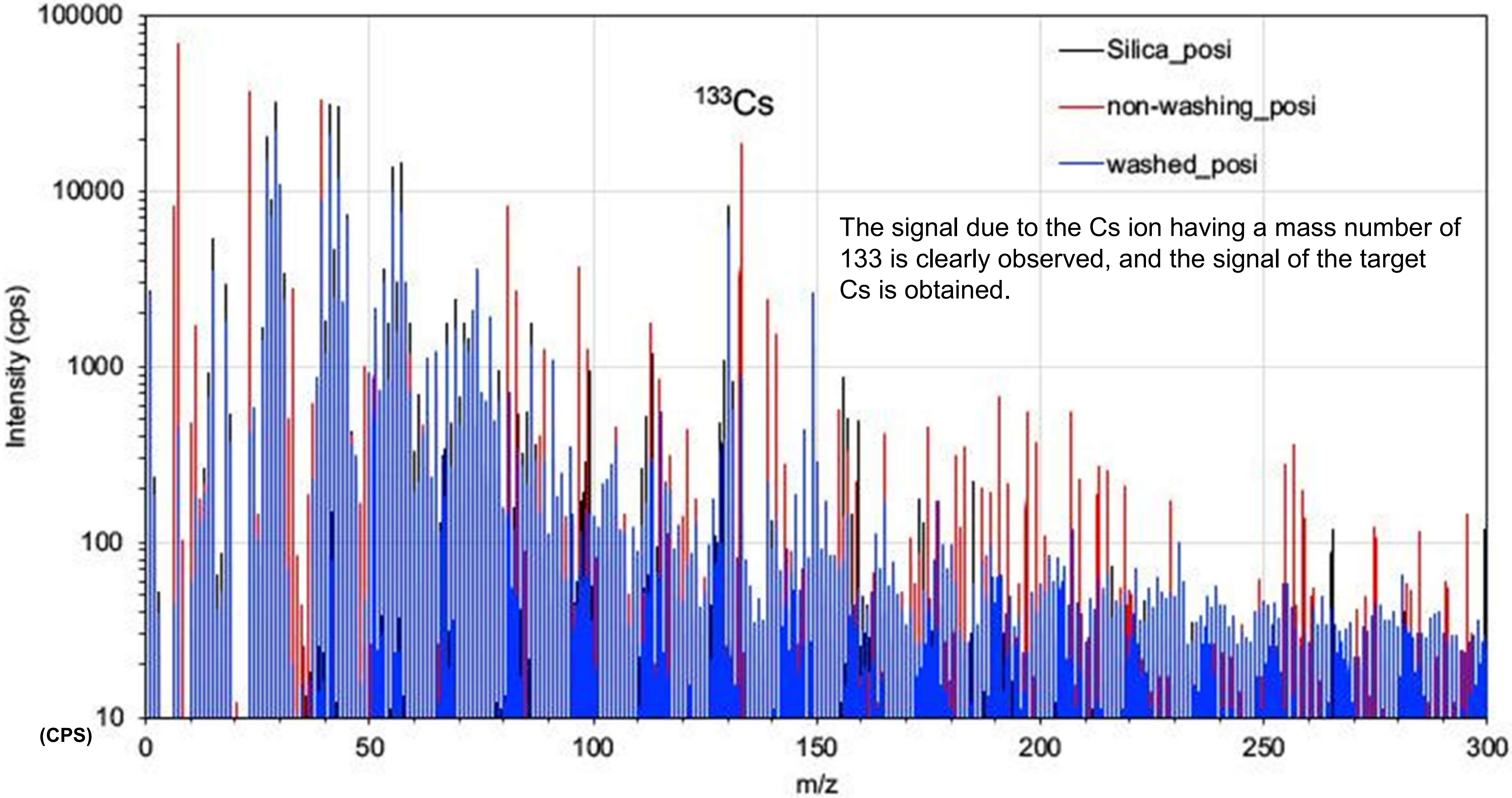
7.1.2 Recovery accuracy of volatilized Cs and assumption of substance (1) Off-gas analysis (Cs trap and analysis)

- Measured by inserting a silica glass substrates to check the Cs recovery accuracy.



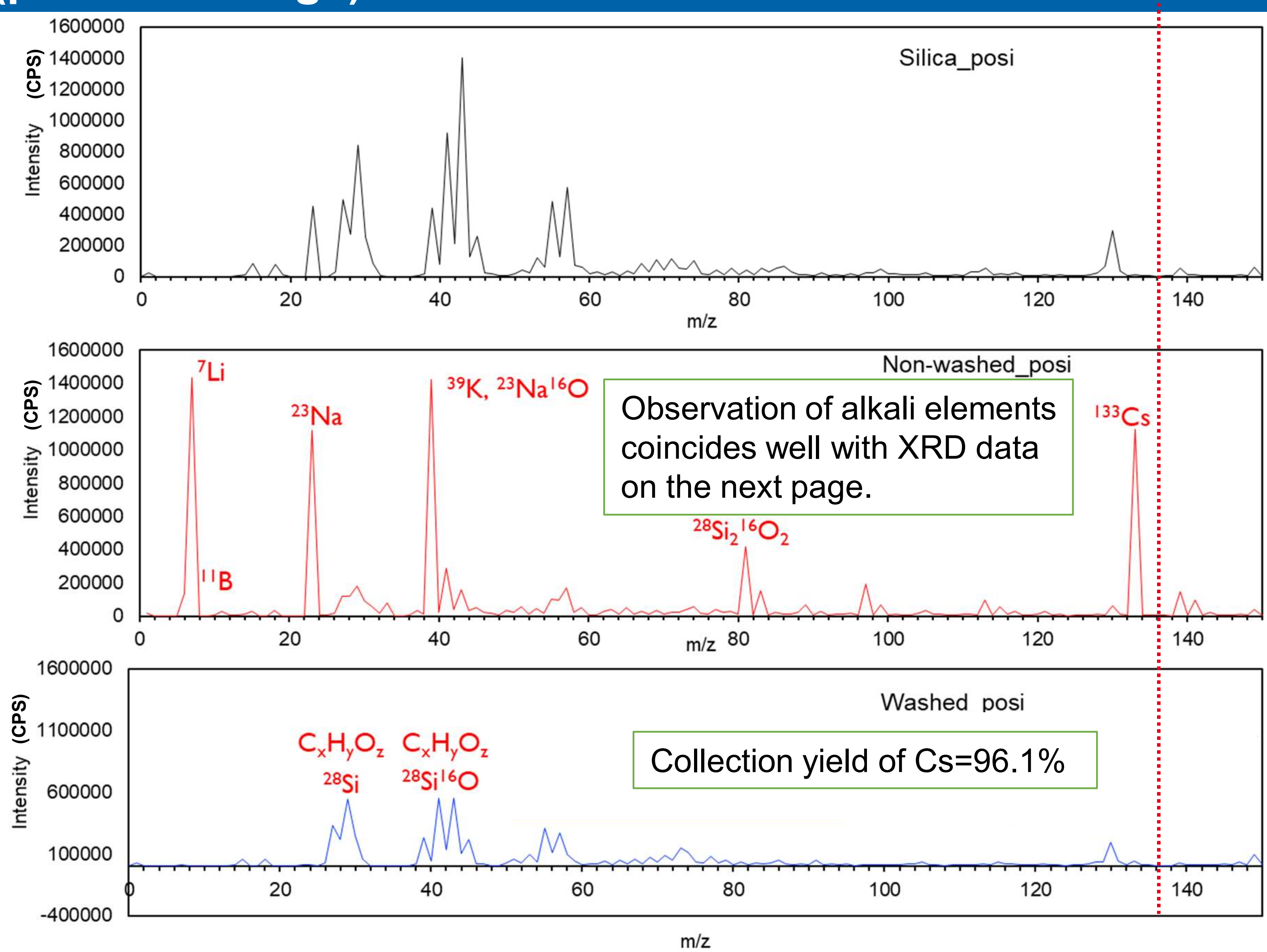
- Off-gas generated during melting in a temperature gradient electric furnace is condensed in a water-cooled condenser.
- A couple of clean silica glass substrates are placed in the trapping glass tube, and collected after finishing the experiment.
- The background measurement substrate is cleaned by performing the same treatment as the Cs trap test.
- Both substrates will be analyzed using TOF-SIMS, which analyzes the elements on surface with high sensitivity.

(2) TOF-SIMS spectrum of substances trapped on silica glass substrate surface (positive charge)



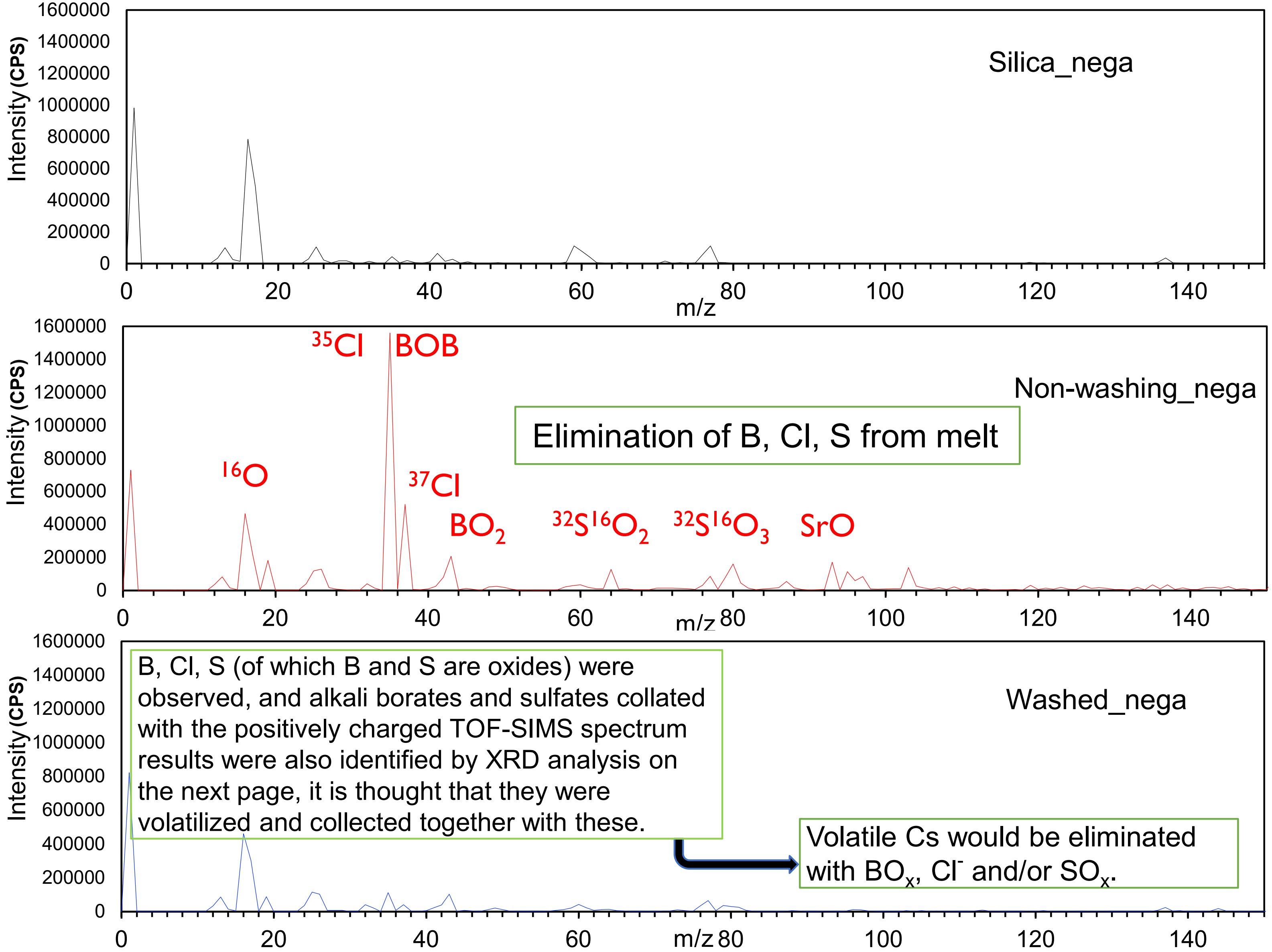
TOF-SIMS spectrum collected from silica glass substrate

(3) TOF-SIMS spectrum collected from the substrate (positive charge)



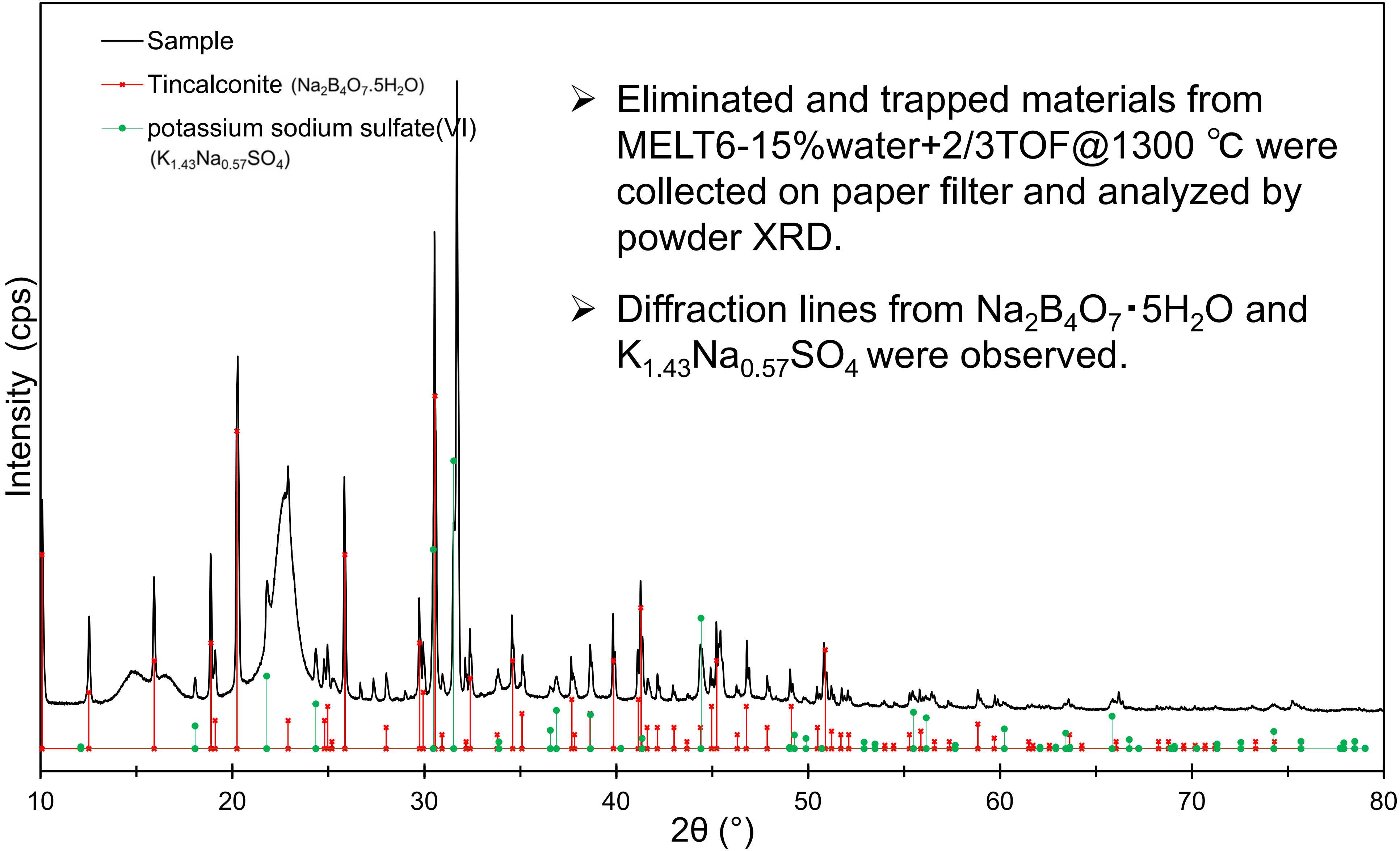
(Top) Unused substrate, (Center) Substrate before washing, (Bottom) TOF-SIMS spectrum (positive charge) collected from the substrate after pure water cleaning

(4) TOF-SIMS spectrum collected from the substrate (negative charge)



(Top) Unused substrate, (Center) Substrate before washing, (Bottom) TOF-SIMS spectrum (negative charge) collected from the substrate after pure water cleaning

(5) Powder X-ray diffraction pattern of the sample collected from the inner wall of a silica glass cell



- Eliminated and trapped materials from MELT6-15%water+2/3TOF@1300 ℃ were collected on paper filter and analyzed by powder XRD.
- Diffraction lines from $Na_2B_4O_7 \cdot 5H_2O$ and $K_{1.43}Na_{0.57}SO_4$ were observed.

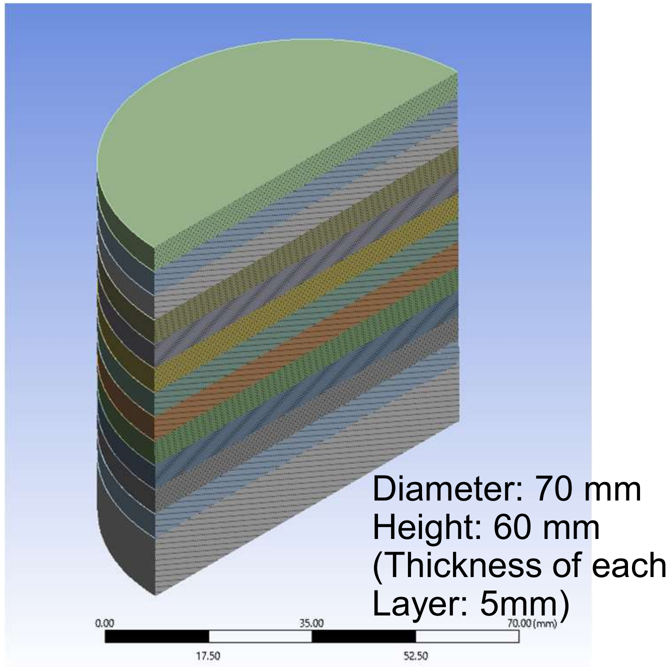
Powder X-ray diffraction pattern of the sample collected from the inner wall of a silica glass cell

(6) Summary
Recovery accuracy of volatilized Cs and assumption of substance

- Since more than 96% of Cs trapped on the inner wall of the glass instruments can be washed into the collected water for ICP-MS, it can be measured with sufficient reliability as a measurement of the amount of Cs volatilization.
- TOF-SIMS data revealed that Cs was emitted from the waste on heating with alkali metal, B, S and Cl.
  Although the volatile form of Cs is unknown, it is conceivable that alkali volatilize as boric acid, sulfuric acid or hydroxide and are flown together.
- This TOF-SIMS analysis technique would be used for stacking of emitted materials as function of time qualitatively, but not applied for qualitative measurement at the present due to a large vapor pressure of H_2O.
- Possible forms are borates, sulphates, chlorides, hydroxides, or metal vapors.

7.1.3 Analysis of the relationship between the temperature gradient of the melt and the heat flux by simulation using FEM
(1) FEM simulation model of melting process of TOF/ Waste mixture

Boundary conditions and thermal conductivity are given to the hierarchical structure in the container formed by the mesh, and the temperature profile is reproduced.

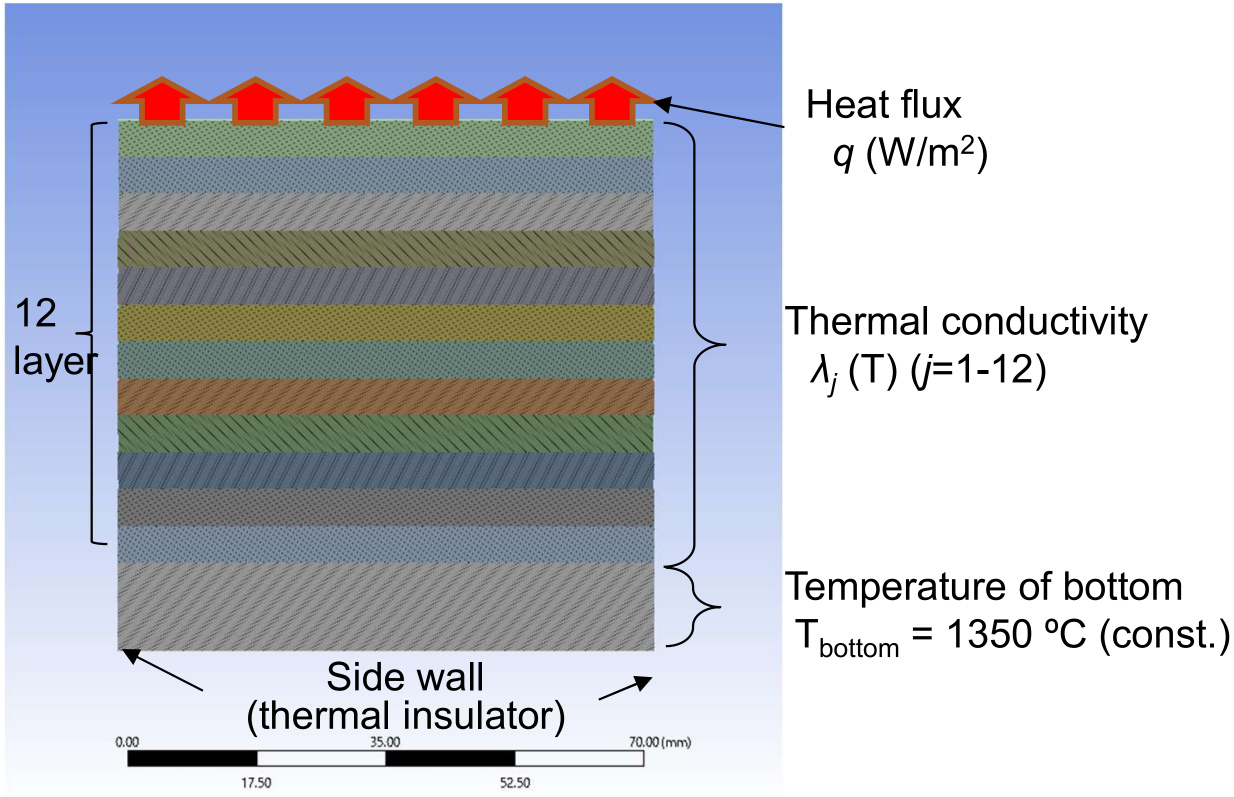


The calculation consists of 12 layers (Layer 0-11).

Layer 0: Assuming a constant temperature in the lower molten layer.

Layer 11: The layer in contact with the air at the top.

FEM simulation model composed of 12 layers



Parameters given to the each component and basic condition for thermal conduction in the model

Parameters, λ_j and q, are set up to simulate temperature profile and compare with experimental results.

(2) Model of thermal conductivity
- Maxwell-Eucken model -

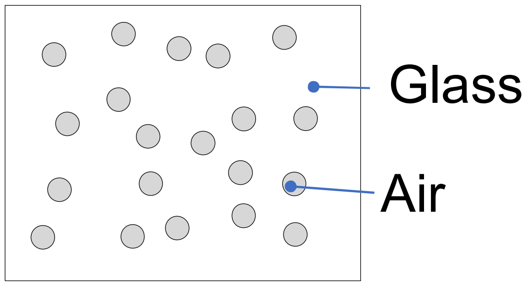
The Maxwell-Eucken model is applied because it is a structural model that can best reflect the actual aspect from the observation of the cross-sectional structure of the melt by the melting test.

$$\lambda_{\text{Eucken}} = \lambda_c \frac{1 + 2\,\varepsilon_p \left(1 - \frac{\lambda_c}{\lambda_d}\right) / \left(2\,\frac{\lambda_c}{\lambda_d} + 1\right)}{1 - \varepsilon_p \left(1 - \frac{\lambda_c}{\lambda_d}\right) / \left(\frac{\lambda_c}{\lambda_d} + 1\right)}$$

λ_c: Thermal conductivity of continuous phase
λ_d: Thermal conductivity of the dispersed phase
ε_p: Volume fraction of gas phase

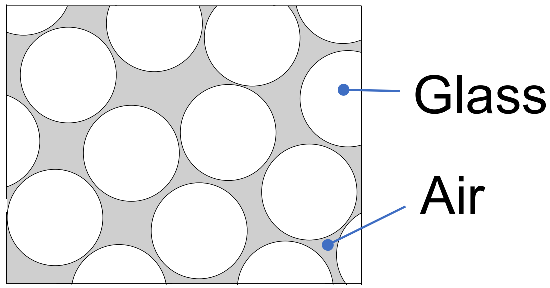
Bulk

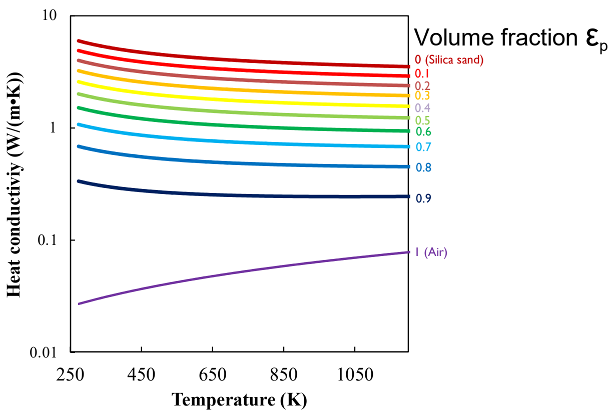
Bubble dispersion model Continuous phase: solid

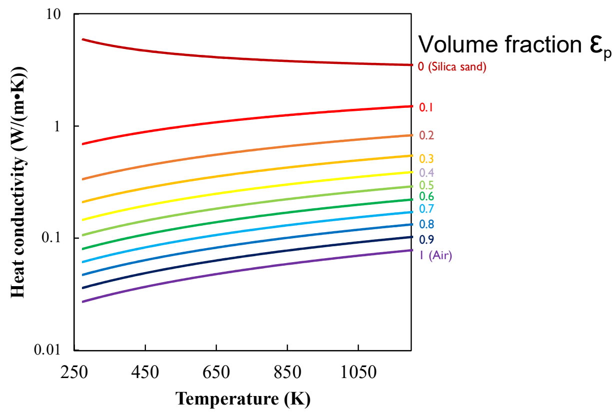


Powder

Glass particle filling model Continuous phase: air





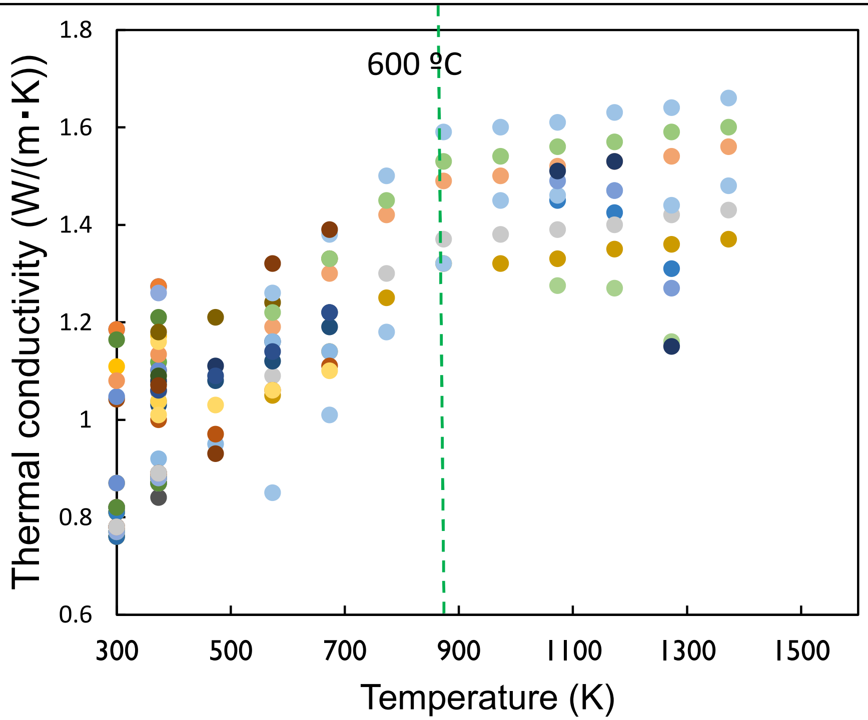


Temperature dependence of λ_{Eucken} and ε_p for each model

(3) Thermal conductivity value of various borosilicate glass melts for modeling

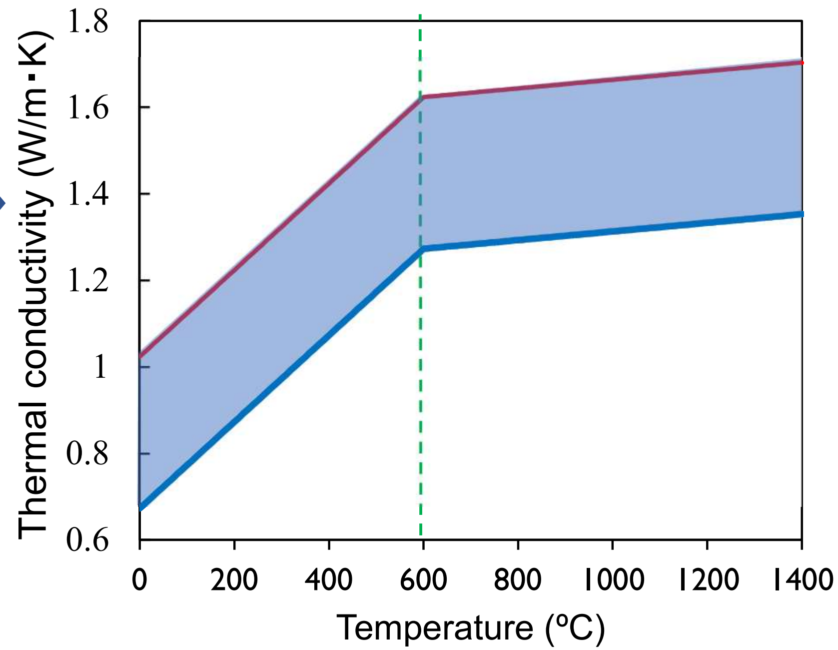
The temperature dependence of thermal conductivity differs between the low and the high temperature region, and the boundary is the glass transition temperature Tg. In the temperature range of T <Tg, it shows a large temperature dependence, changes linearly, and the higher the temperature, the higher the thermal conductivity. In the temperature range of T> Tg, the temperature dependence is very small and is almost constant.

In the modeled temperature dependence, Tg is set to 600ºC, and it is expressed as a function (a × TºC + b) that thermal conductivity changes linearly with respect to T before and after that.



Thermal conductivity data collected from the glass database InterGrad®

Thermal conductivity of borosilicate glasses
(Ref.: from glass database, InterrGrad ver.8.0)
Note: Plots are color-coded according to differences in glass composition in the database

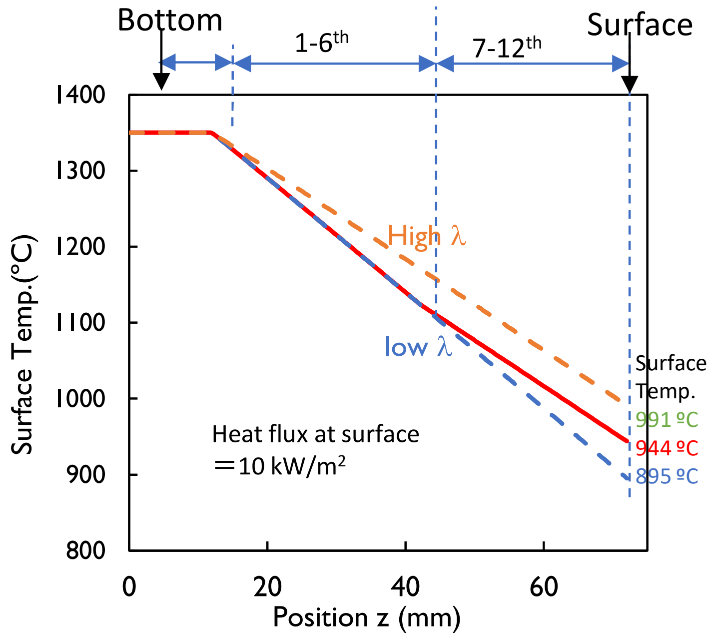


Simplified temperature dependence of thermal conductivity of borosilicate glass melt

λ will be set up in this experimental data region to fit the measured temperature profiles

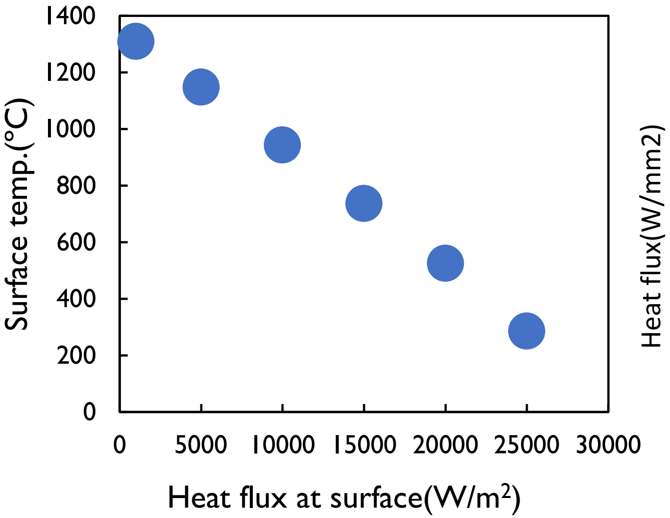
(4) Model calculation using conductivity data of glass melt (1/2)

The effects of each factor of thermal conductivity, void ratio, and heat flux on the simulation by FEM are confirmed, and the measured temperature gradient is reproduced based on the calculation results. The results of confirming the effects of each factor are shown in ① to ③ below, and ④ to ⑥ are shown on the next page.



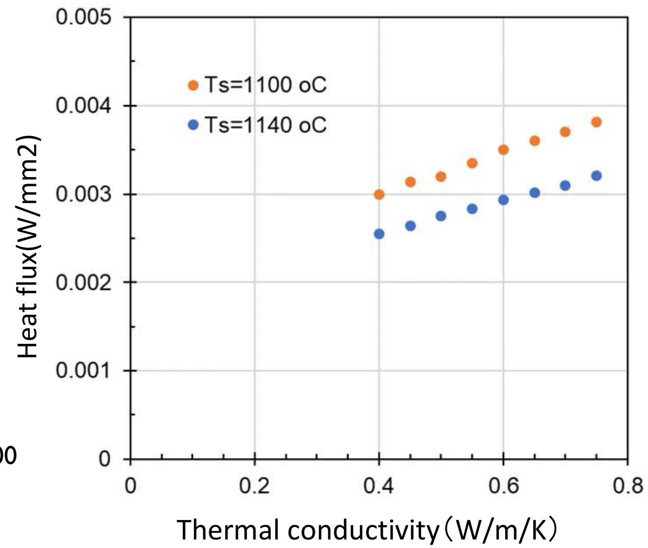
①

- Temperature gradient obtained assuming two types of glass (thermal conductivity: high λ, low λ)
- The higher the thermal conductivity, the higher the surface temperature.



②

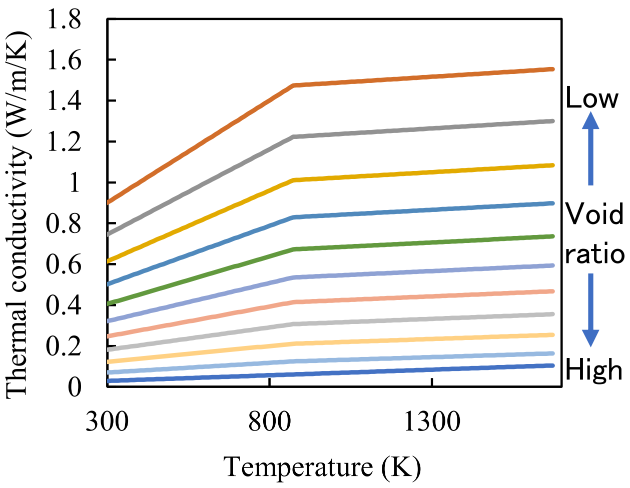
- Ts changes by changing the heat flux in a system in which two different glasses are laminated.
- Since the measured Ts is 1150ºC or higher, it is estimated that the heat flux is in the range of about 5 kW/m^2.



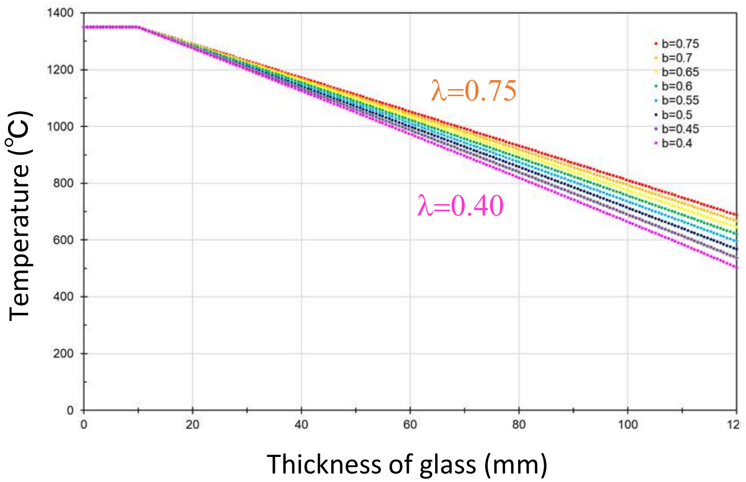
③

- Since the actual thermal conductivity data of glass is b> 0.65, the condition that the surface temperature is close to the actual measurement is predicted to be heat flux q> 3.0kW/m^2 (0.003W/mm^2).

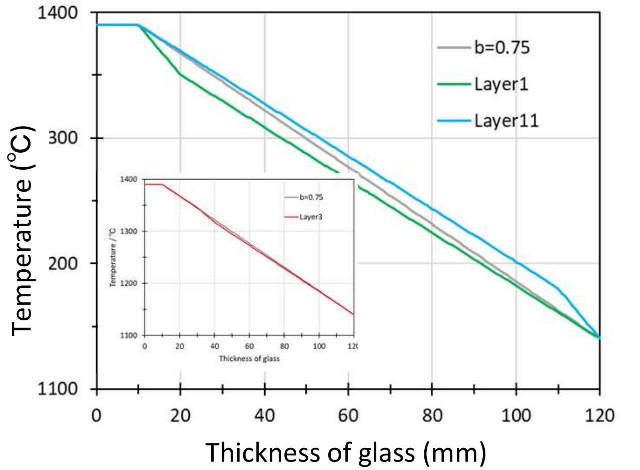
(4) Model calculation using conductivity data of glass melt (2/2)



④



⑤



⑥

- The temperature change of Eucken when the porosity εp is changed is shown.
- It can be seen that when εp is large, the conductivity decreases and it becomes adiabatic. The calculation uses the apparent thermal conductivity of each layer, the interpretation of which must reflect the actual structure of the material.

- A linear profile is obtained by changing λ from 0.4 to 0.75 in increments of 0.05, and Ts is 503 to 688ºC. The heat flux is fixed at 0.01 W / mm^2.
- In order to adjust Ts to the measured 1100 to 1140ºC, it is necessary to reduce the heat flux q to about 0.003 W/mm^2.

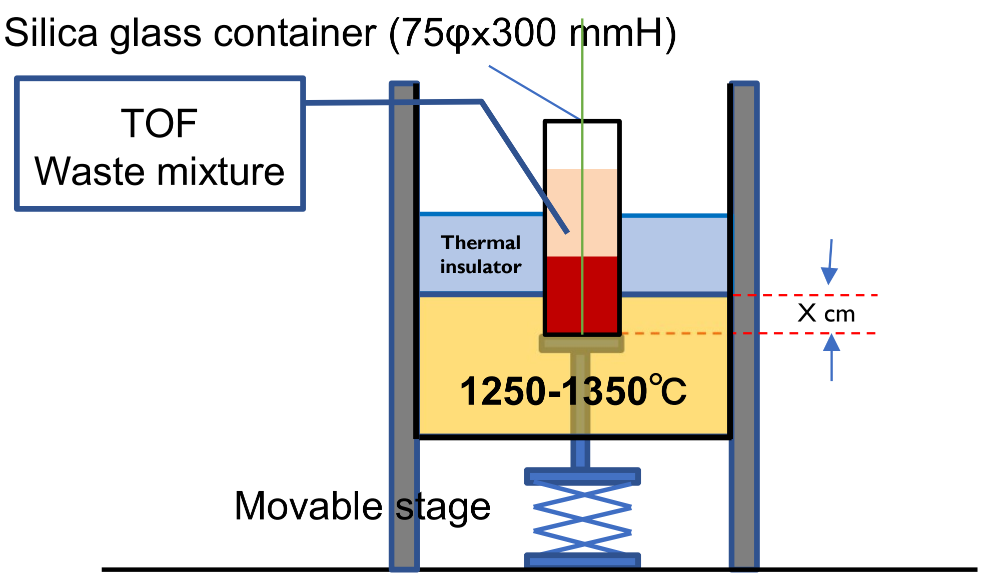
- When one layer containing bubbles is inserted, bending appears in the temperature distribution.
- When the insertion of layers containing bubbles is gradually increased, the temperature gradient becomes steeper as the number of insertions increases.
- When everything contains a foam layer, there is no difference, but this is because Ts is constant.

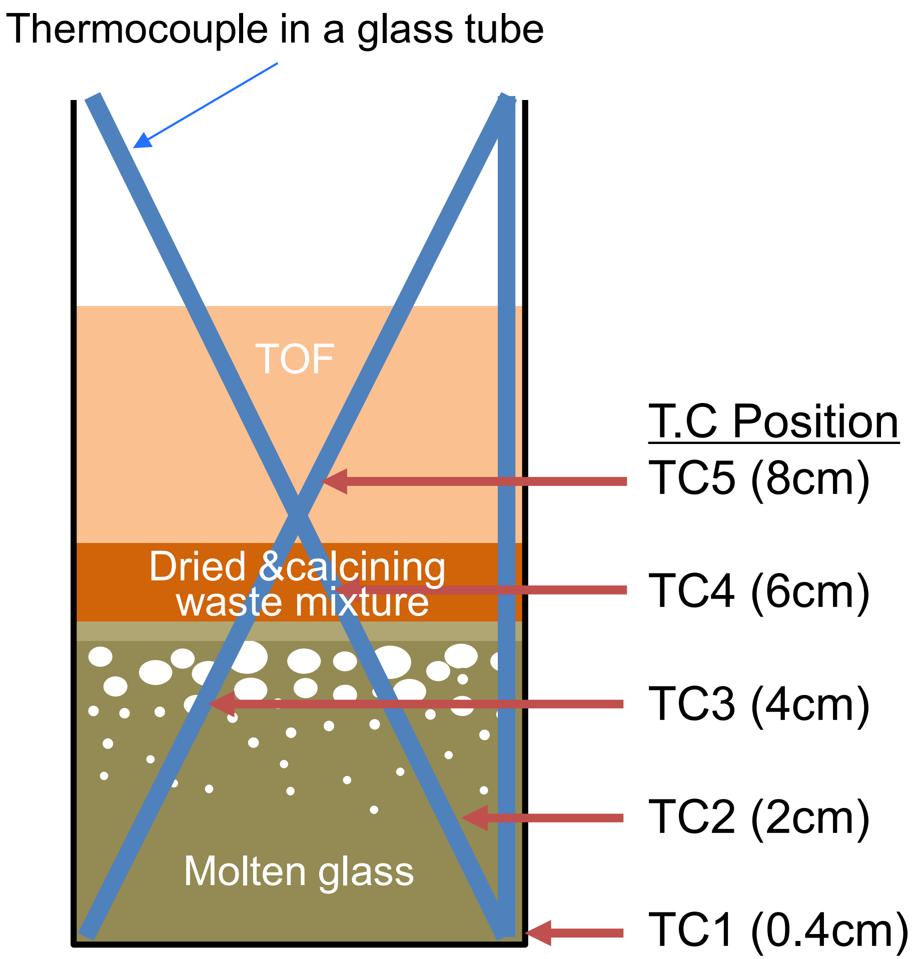
(5) Measurement method of the temperature gradient

- Measurement of temperature gradients of melting MELT6-20%Water/TOF (3/3) at T_F=1350℃

- Measurement method

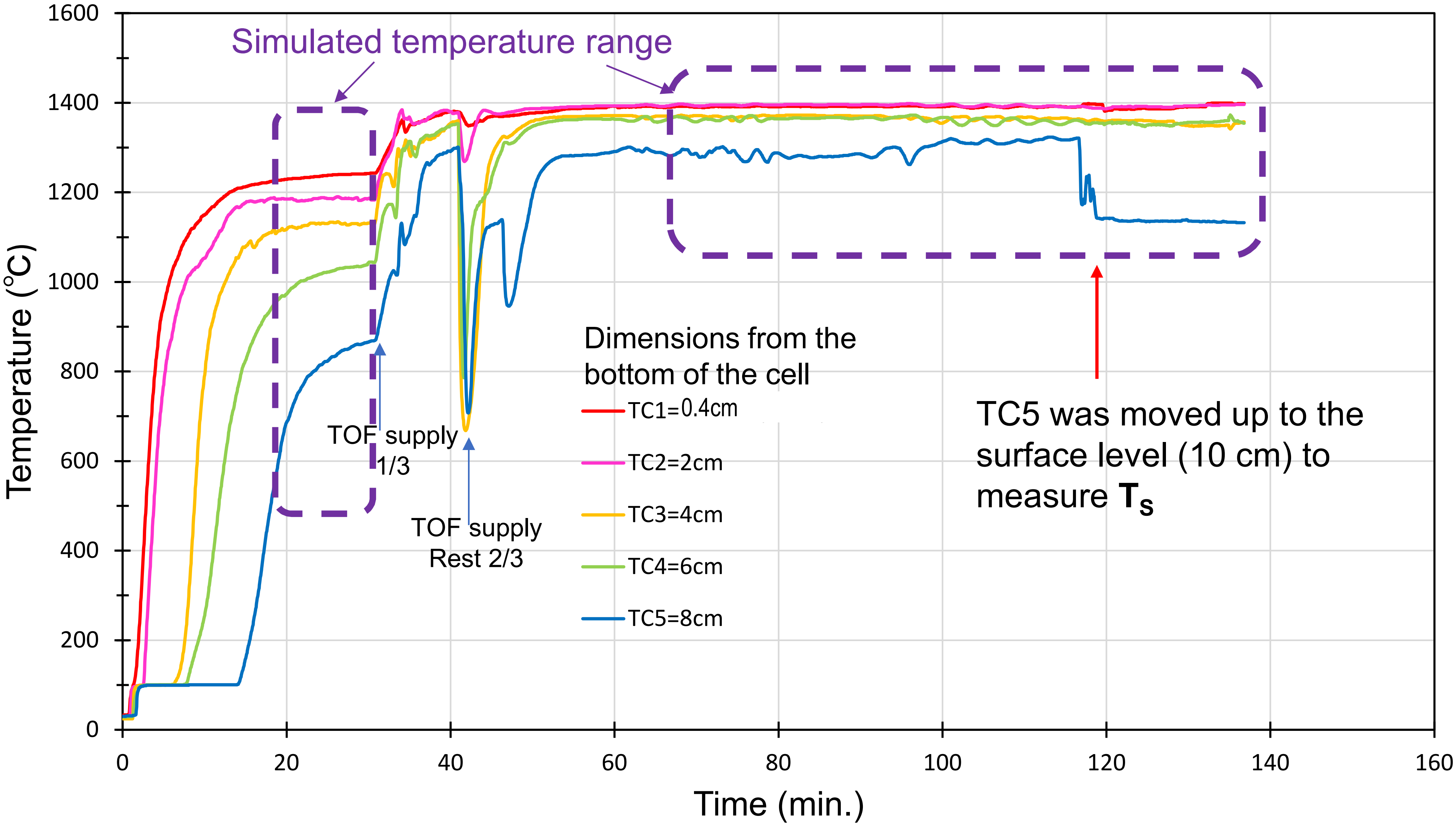
  Thermocouples (5 in total) are placed in each layer of TOF / waste mixture in MELT6 and heated in an electric furnace in the same manner as in the Cs emission experiment.





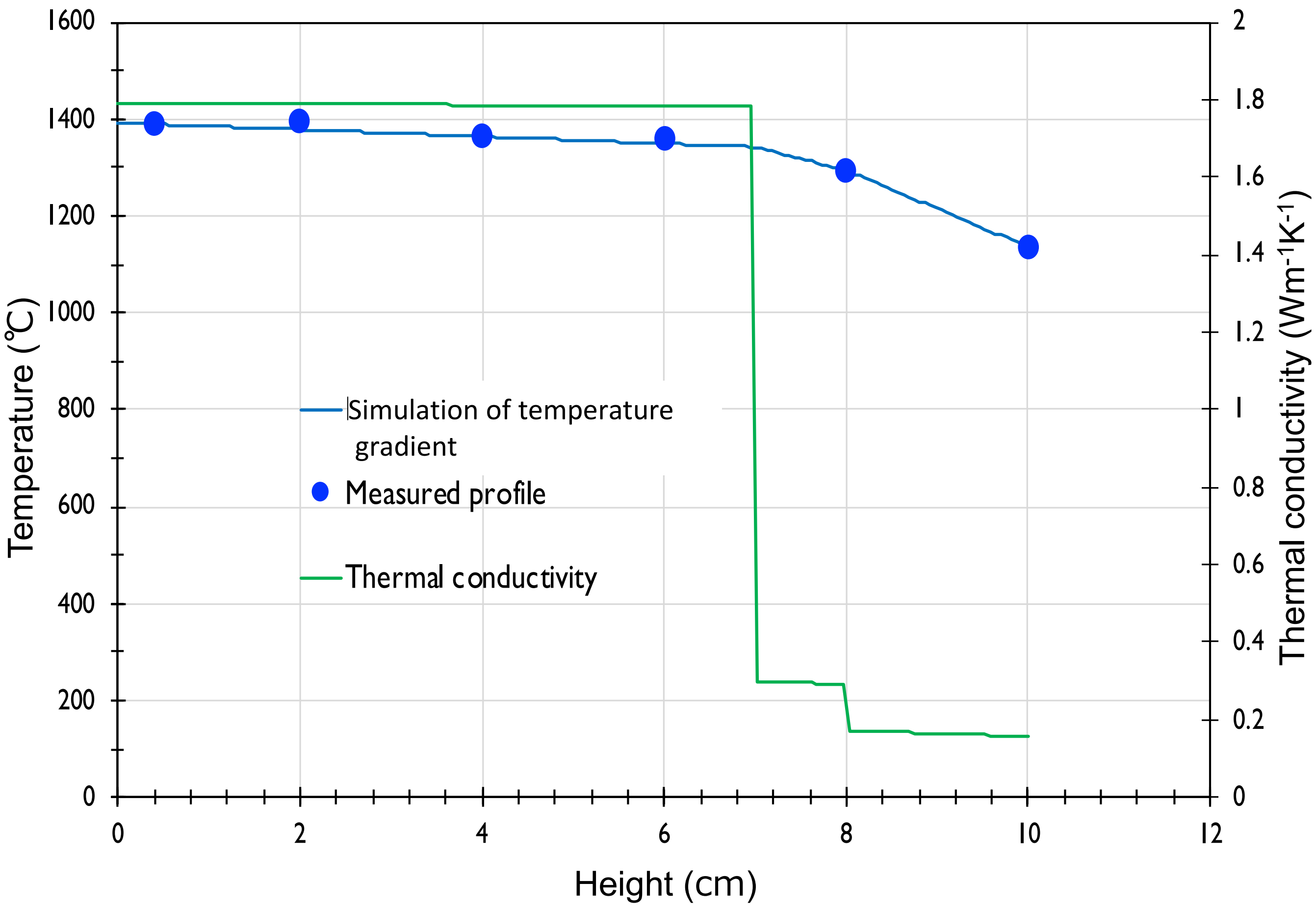
Temperature measurement in glass tube

(6) Measured temperature data



Measured temperature trace for temperature profiling of the material in the cell

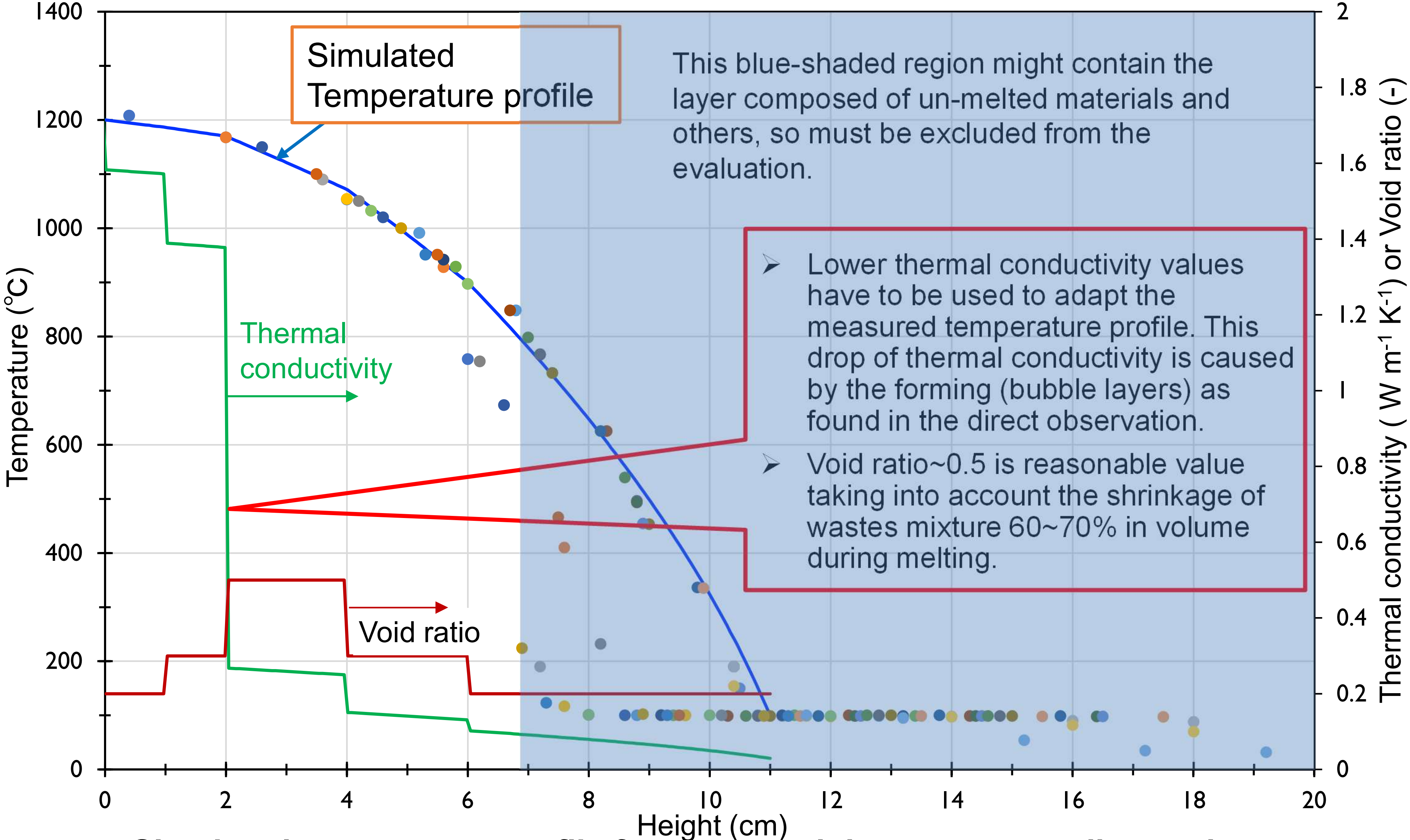
(7) Temperature simulation at final stage of melting using FEM



Simulated temperature profile for height from the bottom of the cell

- Thermal conductivity dropped sharply at a height of 7 cm from the bottom. This corresponded to the level of the interface between the molten waste mixture and the TOF.
- The molten TOF above this level is highly transparent and has a large effect of radiant heat transfer. Therefore, it is considered that the heat energy is dissipated by the radiant heat transfer, so that the heat energy transferred by the conduction heat transfer is lowered and the actual surface temperature is lowered.
- Therefore, even if the molten waste mixture (opaque) is higher than 1300℃ in the lower region about 3-4 cm below the top surface, the transparency of the molten TOF keeps the top surface temperature at Ts < 1150 ℃. This satisfies the surface temperature condition (Ts<1130 ℃) that ℃ suppresses Cs volatilization.
- When sufficient TOF is not filled, its heat conduction is conduction heat transfer, and the surface temperature has to be high in order to maintain the heat flux, forming a state in which Cs volatilization is likely to occur.

(8) Temperature profile in melting waste layers at early stage



Simulated temperature profile for measured data corresponding to the height above the bottom of the cell

(9) Summary - Analysis of the relationship between melt temperature gradient and heat flux by simulation using the finite element method (FEM)

- The temperature gradient around the surface of the molten glass depends on the heat conduction mechanism due to the balance between heat diffusion (conduction heat transfer) and heat radiation (radiation heat transfer). This gradient changes depending on the thickness of the TOF. The thinner the TOF, the gradually decreases and the higher the T_S.
- In lab-scale experiments, the convection of the melt during melting was very weak compared to the engineering scale tests. The transparent TOF covers the opaque waste mixture, and convection and mixing of these must occur after their melting is complete and viscous flow occurs.
- A 12-layer model was formulated for FEM simulation of steady-state heat transfer to obtain the final molten temperature profile of the molten TOF layer/waste mixture layer. The FEM simulations show good agreement with the measured temperature profiles using appropriate thermal conductivity values.
- Melted TOF layer on molten waste mixtures might have lower apparent thermal conductivity because of its high optical transparency (high ratio of radiant heat transfer to conduction heat transfer).
- The Maxwell-Eucken model incorporates a void factor and is therefore suitable for simulation of layers containing foam layers (early stage).

7. 2 Engineering-Scale System Modification and Checkout Melt
(1) Purpose and Method

- Purpose and method of Engineering Scale System Modifications

  Purpose:
  - Added a Sintered Metal Filter (SMF) for Cs recovery.
  - Improved IR Camera for monitoring melting conditions and Viewing Window.

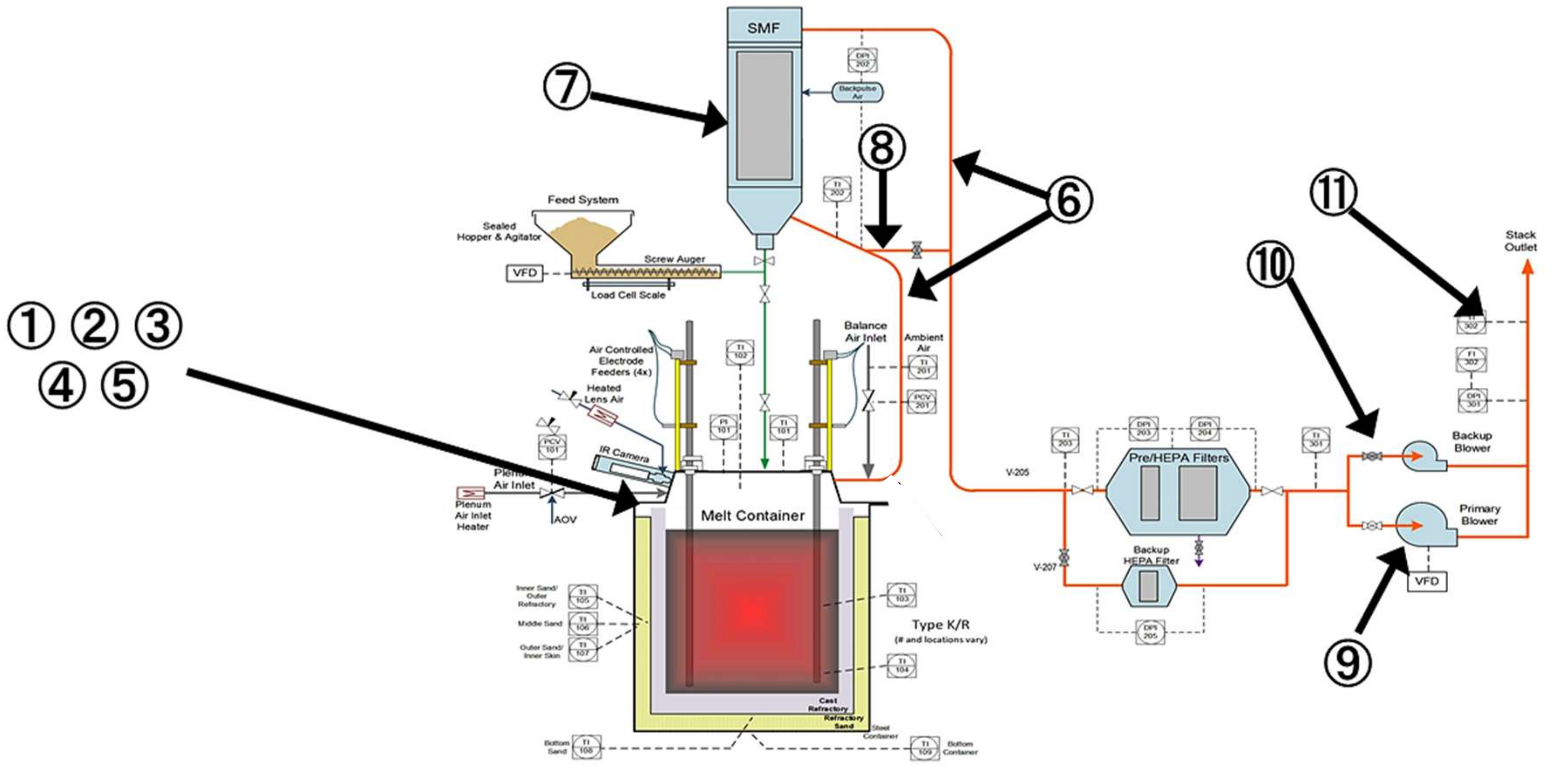
  Method:
  - Increased strength by enlarging the dimensions of the outer steel vessel of the melter to support the weight of the SMF.
  - Installed heat tracing and insulation to prevent condensation of moisture in the off-gas due to temperature drops in the SMF and off-gas piping and equipment.
  - Prevented the sticking of supply test materials (waste + glass frit) with dew in supply equipment and piping due to the temperature rise by heat tracing etc.

- Purpose and method of checkout melt

  Purpose:
  - Check the operation of the equipment modified parts. Perform checkout melting to confirm optimal implementation of SMF back-pulse. Confirmation of modified melt test preparation methods, training of test operators.

  Method (Check out the new melt processing test procedure):
  - In preparation of melt, load base frit and install starter path.
  - Transfer melter to melting position, set off-gas hood, then install electrodes remotely and connect them with starter path (Corresponding to the procedure assumed in the actual treatment plant.).

(2) Modification part of Engineering-Scale System



#	Component	Items Changed	Reason
①	Hood	Feed pipe – Increased size from 3” to 4” Diameter	To prevent feed sticking and match larger SMF filter inlet pipe
②	Hood	Outlet Pipe – Increased size from 3” to 4”	To minimize particulate carryover and to match larger SMF filter inlet
③	Hood	Front Hatch/Window – Increased size by 10%	To aid in melter system preparation and setup
④	Hood	Modification of Mount and windows for new IR camera	To better match new IR Camera matching surface
⑤	Melting Container	Melt Box perimeter flange dimensions increased	To match new larger hood dimensions
⑥	Off-gas Pipe	Melter to SMF increased size 3” to 4”	To match larger SMF filter inlet
⑦	First Stage Filter	Cloth Bag House filter replaced by SMF	Change to SMF make off-gas system more efficient and compatible with PCD
⑧	First Stage Filter Bypass	Bypass line diameter increase to 2” to 4”	To match new off-gas pipe size
⑨	Primary Blower	Replaced off-gas fan with new larger fan	Larger VNSFS fan installed to better match SMF requirements
⑩	Backup Blower	Replaced off-gas backup fan with larger fan	Larger VNSFS fan installed to better match off-gas system
⑪	Stack Off-gas Pipe	Increased fan outlet pipe from 2” to 4”	Allows increased flows of new off-gas system

With the removal of the cloth baghouse filter and the change in the flow rate due to the installation of the SMF, mainly the dimensions of the off-gas piping and the blower capacity were changed.

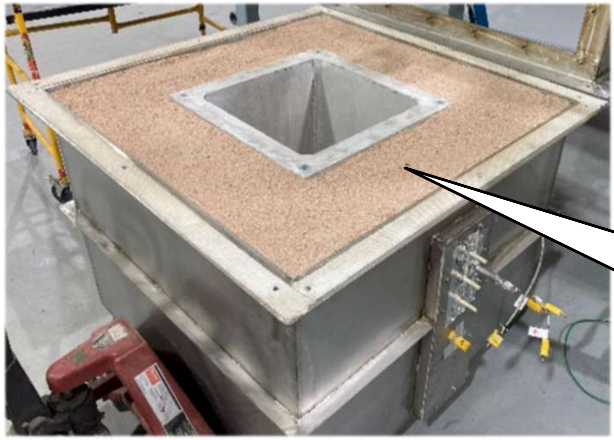
(3) Configuration of modified Engineering-Scale Melting Test Apparatus

Before Off-gas System was Insulated

Heat tracing applied to the off-gas system and SMF filter to ensure condensation does not occur on pipe walls

Final configuration of ES System during Checkout Melt with SMF and the off-gas piping insulation applied

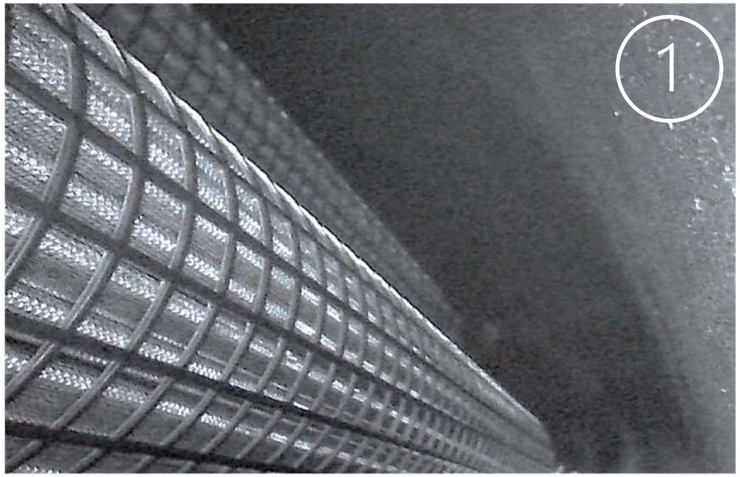
System during Checkout Melt



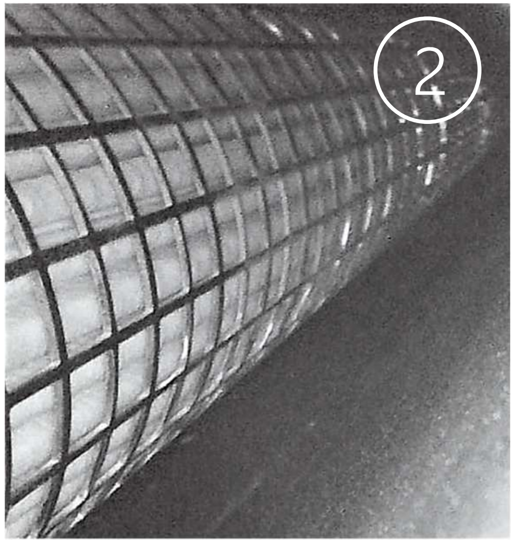
Melter Preparation

The new melter configuration placing under the off-gas hood (Adopts a steel container with dimensions that allow expansion of the refractory container)

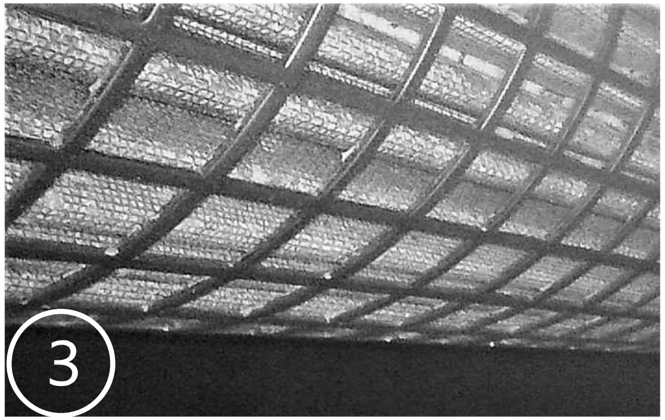
(4) Checkout melting results (SMF operating status)



SMF Clean Interior with New Cartridges
(Clean cartridge differential pressure before test start: 1.5)



SMF Cartridge with DE Coating before Checkout Melt
(Differential pressure when coating cartridge: 4.0)



SMF Clean Cartridge after Back-Pulsing, after Melt
(Differential pressure when filtering cartridge by the back pulse: 1.5 (return))

SMF Clean Wall after Checkout Melt

Purpose:

- ✓ Confirm that the clogging of cartridge (filter element) is removed and cleaned by the back-pulse.

Results:

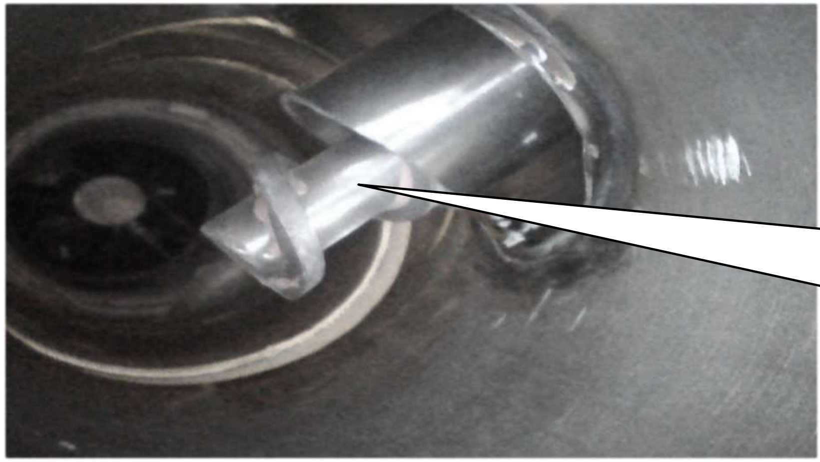
- ✓ It was confirmed by recovery of the differential pressure and good cleanliness inside the SMF that the simulated clogging (coating) could be removed by the back-pulse.

Filter Test Condition	Differential Pressure (Inches H_2O)
①	1.5 (=3.73 mbar)
②	4.0 (=9.95 mbar)
③	1.5 (=3.73 mbar)

Differential pressure before and after operation (Confirmed that the differential pressure can be returned to the reference pressure by the back-pulse.)

Conclusion: The SMF operated as designed during the Checkout Melt proving it was ready for Melt Tests.

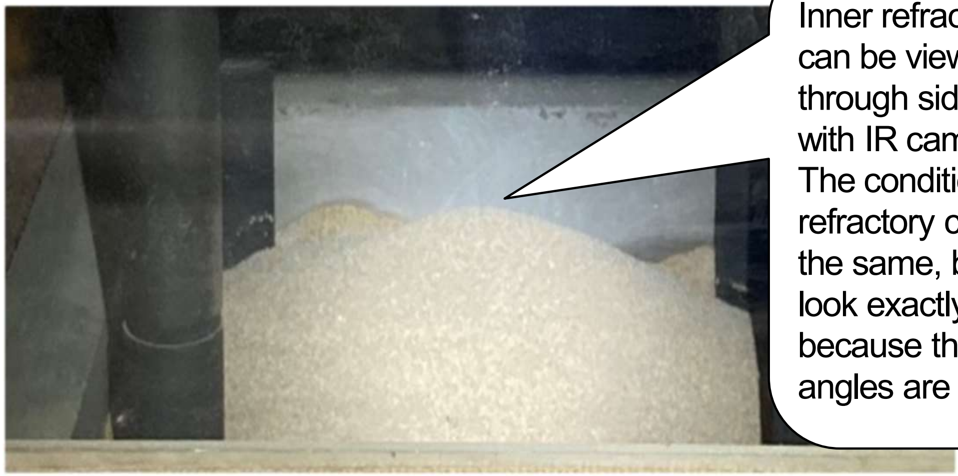
(5) Checkout melting results (screw auger, IR camera/sight glass operating status)



Inside feed pipe and auger outlet after Checkout Melt (downward view from upper)

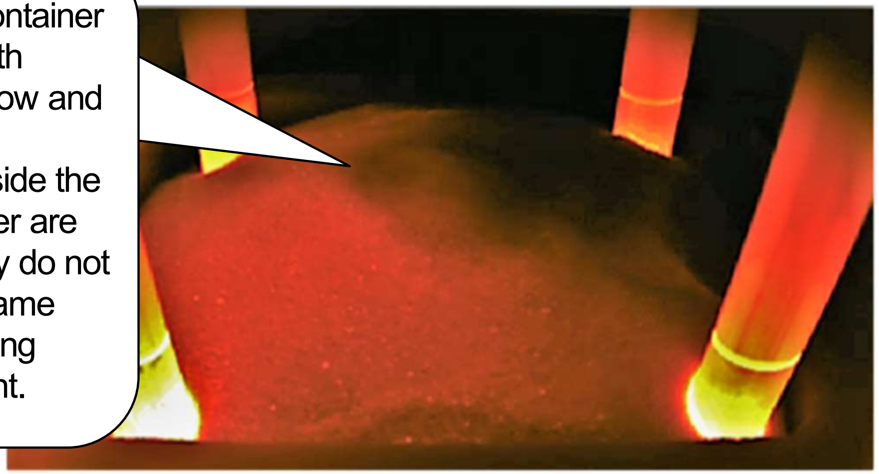
No feed material buildup on auger tube or feed pipe walls.

Feed pipe outlet inside the refractory container after checkout melting (upward view from the bottom side)



Inner refractory container can be viewed both through side window and with IR camera.
The conditions inside the refractory container are the same, but they do not look exactly the same because the viewing angles are different.

2 hours after the start of melting viewing through hood window



2 hours after the start of melting viewing through IR camera

Conclusion: Feed piping stayed clean and the ability to view the melt was proven during Checkout.

(6) Summary of modification of Engineering-Scale System and results of checkout melt

Confirmation Item	Result
1. **Verify operation of Sintered Metal Filter**	① SMF's monitoring and operation system works as designed. Specifically, the set temperature of the SMF was 100℃ or more (design limit of 300℃), the same as the off-gas piping, and the design limit of the differential pressure is 20inH$_2$O, which was monitored by the SMF monitoring and operation system. The duration of the back-pulse was measured by the control system and was 0.3 seconds. In addition, the back-pulse frequency is automatically set by the monitoring and operation system. ② It is confirmed that the differential pressure was returned to the reference pressure by the back-pulse. (Refer to page 44: Differential pressure change by test) ③ Good cleanliness of the filter element (SMF cartridge) was confirmed by observing the inside of the filter housing after melting. (See page 44: State of SMF internals and cartridges for each test)
2. **Prevention of condensation in SMF and off-gas**	① Heat tracing with insulation worked as designed, maintaining off-gas piping and filter assemblies at or above 100 ℃ at all times, ensuring no condensation in the off-gas system throughout the test ② Inlet heater maintained the melter plenum above condensation point at all times as verified by visual and electronic (local and SCADA) indications.
3. **Prevention of sticking in feed device for test materials (waste + glass frit) and pipes, etc.**	① The temperature of the plenum of the melting container can be maintained above the dew point by means of an inlet heater that heats the air supplied to the melting container, which also contributes to the prevention of condensation in the off-gas piping. ② It is confirmed that the occurrence of condensation in the off-gas system could be prevented throughout the test.
4. **Verification of Improvement of process viewing (IR Camera, window)**	① The IR camera works without problems in the entire process temperature range from the start of melting to the end of melting. Process operation monitoring is improved with the increased resolution and improved viewing window. ② By calibrating using a melt thermocouple, it is possible to calibrate the emissivity value for more accurate temperature display.
5. **Verify the revised procedure of melt preparation procedure**	① In preparation of melt, load base frit and install starter path. ② Transfer melter to melting position, set off-gas hood, then install electrodes remotely and connect them with starter path. Successful melt processing preparatory work according to the new procedure.

Conclusion: The new Engineering-Scale System checked out and was proven "ready for use" for the Melt tests.

7.3 Engineering Scale Melting Test
(1) Purpose and Method

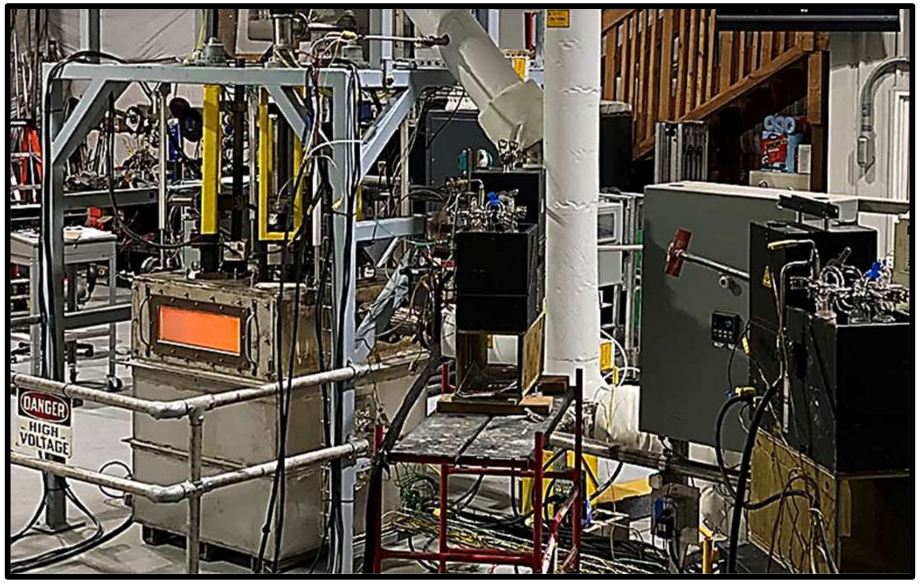
- Engineering scale Melts 9-12 performed in FY2021 following engineering scale melts 1-8 done by FY2020.
- Common purpose / method among 4 engineering scale melt tests
  - Demonstrate melt treatment with engineering scale (waste 180 kg treated in each melt test)
  - Verify and evaluate the operability and performance of Sintered Metal Filter (SMF) installed by test system modification.
  - Measure quantitatively and evaluate the release of Cs and Sr by stack sampling.
  - Apply and evaluate the findings obtained from Tokyo Tech study for operation at the final stage of melting.
  - Grasp the homogeneity of Cs distribution in glass by sampling glass after melt.
- Specific purpose/method for each melt test.
  - Melt 9： Treated waste is KUR-EH+KUR-TSG. Particulate captured by SMF is not recycled to melter but recovered to measure the amount of particulate and Cs concentration.
  - Melt 10： Treated waste is KUR-EH+KUR-TSG, same with melt test 9, but with higher water content (15→20%) to demonstrate treatment with high water content.[1]
    Particulate captured by SMF is recycled to melter during melting operation.
  - Melt 11： Treated waste is KUR-EH+ALPS carbonate･iron coprecipitate Filtercake. This dehydrate product is a simulated ATOX product. Transportability and feeding of the waste is verified by fundamental test prior to melt test. Particulate captured by SMF is recycled to melter during melting operation.
  - Melt 12： Treated waste is KUR-EH+ALPS carbonate slurry. Melt test 1, 5 are ALPS carbonate･iron coprecipitate slurry, but this test is with higher loading rate of carbonate slurry (content of MgO in waste) formulation. Particulate captured by SMF is recycled to melter during melting operation.

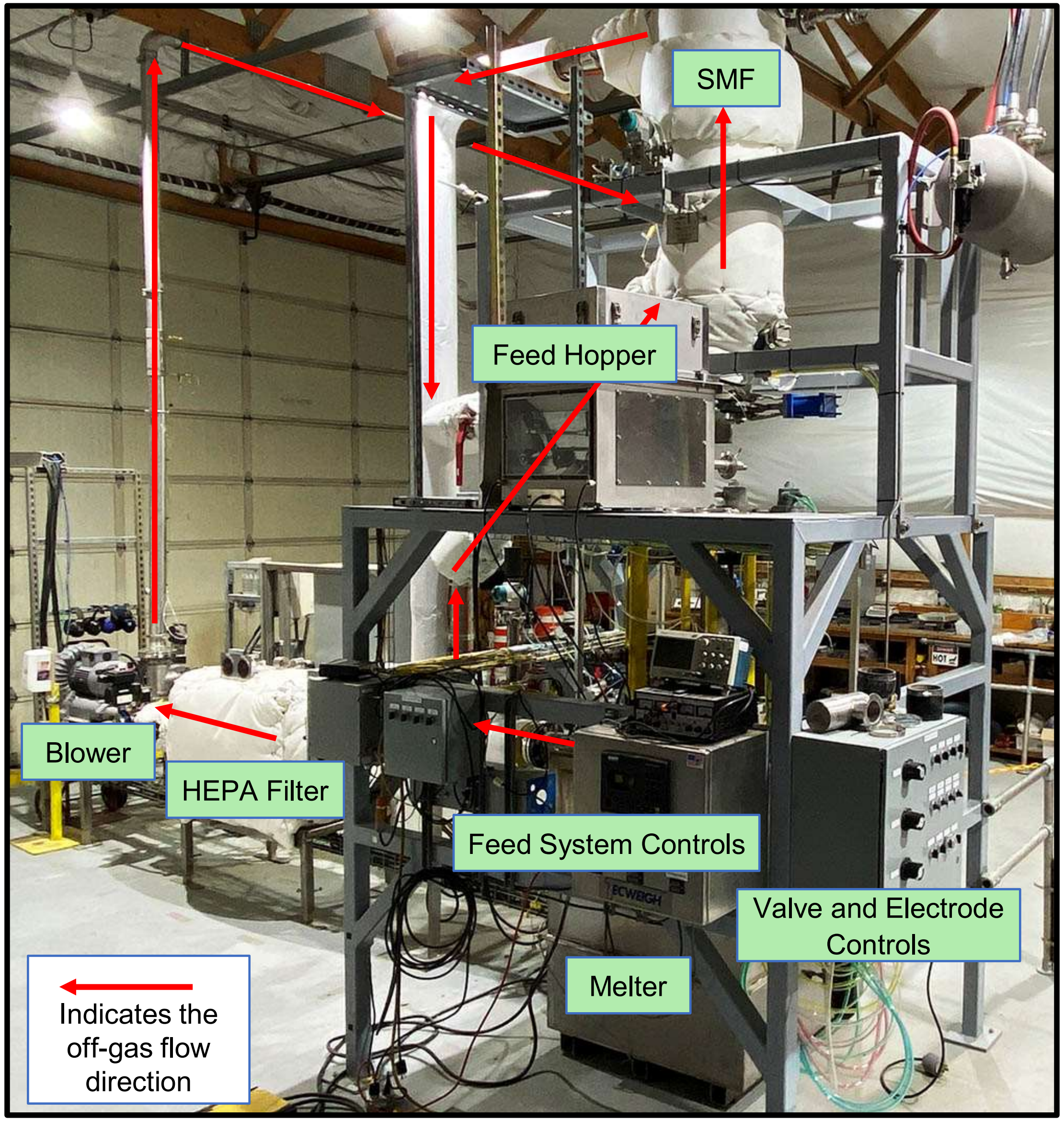
1: Purpose of demonstration of melting waste with high water content:
Various waste formulation (combination) can be treated by GeoMelt®ICV™ and water content can be adjusted in waste combination process. No problem for melting itself even for waste with a high water content but some issues could potentially occur in handling process for feeding (plugging etc.). From this point of view, demonstrate the handling and treatment of waste with high water content. The adjusting process of waste composition at the actual plant can be verified by the demonstration.

(2) Overview of test system

(Right)
Engineering scale melt test system modified
Used for 4 melt tests FY2021.
Installed waste feeding hopper and Sintered Metal Filter (SMF) above melter.

(Below)
Test system from opposite side
The orange part of the 4-electrodes melter is the observation window (orange because the melting test is in progress)





(3) Test Materials (waste + glass additives) Blending

- The Cs was adsorbed onto the KUR-EH before mixing.
- According to the PNNL glass formulation, water was added to the waste (including KUR-EH which also is glass former) and glass additive while mixing to adjust the water content, and the test material was used.
- The test material containing KUR-EH was mixed with adsorbed Cs tracer (CsCl) and the Sr tracer ($SrCO_3$) to adjust the final test material.
- The test material blended was weighed and sampled for lab analysis.

Test Waste Blend with Sample Vials

Recipe for Melt tests

Components	Melt 9		Melt 10		Melt 11		Melt 12	
	Mass (kg)	wt%	Mass (kg)	Wt%	Mass (kg)	Wt%	Mass (kg)	Wt%
KUR-EH	93.62	61.19	88.11	61.19	75.60	50.21	65.62	45.57
KUR-TSG	32.97	21.55	31.03	21.55				
ALPS Carbonate Filtercake					42.02	27.91		
ALPS Iron Filtercake					15.84	10.52		
ALPS Carbonate Slurry							42.42	29.46
SiO_2	1.61	1.05	1.51	1.05	5.04	3.35	10.92	7.59
B_2O_3	7.13	4.66	6.71	4.66	5.40	3.59	4.75	3.30
Li_2CO_3	12.09	7.90	11.38	7.90	2.52	1.67	8.35	5.58
Na_2CO_3	5.58	3.65	5.26	3.65				
ZrO_2					3.06	2.03	11.67	8.10
ZnO					1.08	0.72	0.27	0.19
Subtotal	153.00	100.00	144.00	100.00	150.56	100.00	144.00	100.00
Water	27.00	15[1]	36.00	20[1]	29.44	16.3[1,2]	36.00	20[1]
Base frit	5.00		5.00		5.00		5.00	
TOF	15.00		15.00		15.00		15.00	
Total	200.00		200.00		200.00		200.00	
Tracers:								
CsCl	83.59 g		78.67 g		67.50 g		58.59 g	
$SrCO_3$	156.32 g		156.32 g		156.32 g		156.32 g	

[1] water % of total test materials feed, not including BF and TOF.
[2] Water content due only to the water contained in the ALPS carbonate･iron coprecipitate Filtercake.

(4) Testing of transportability and feedability of ALPS carbonate･iron coprecipitate Filtercake

- Composition of ALPS carbonate･iron coprecipitate Filtercake (henceforth called ALPS Filtercake) were analyzed → The result shown in the table right below.
- ALPS Filtercake with glass formers and glass additives were tested for mixability, transportability and feedability before Melt 11.
- The elemental testing: a blending test using a spiral mixing arm ("bucket test"). → The ALPS Filtercake blended well with the glass former, additives.
- Transfer/feed testing: the blended material was fed through an engineering-scale screw auger. → no problems (no sticking or clogging).
- Blending of Melt 11 test material: blended in a 500-L vertical ribbon mixer. Blending was for 2 hours
- Particulate transferred to off-gas increased during melting (described later) : ← It was excessively pulverized as blending time was too long.
- Blending of Melt 12 test material: Using the same mixer with less time (20 minutes)

ALPS Filtercake appearance

ALPS Filtercake Anions

	ALPS Carbonate Filtercake (%)	ALPS Iron Filtercake (%)
Sulfate	0.0646	0.111
Chloride	3.11	11.8
Nitrate	ND	ND

Bucket Test with Spiral Mixing Arm

Feeding Test

500-L Ribbon Mixer

ALPS Filtercake Bulk Chemistry

Oxide	ALPS Carbonate Filtercake (%)	ALPS Iron Filtercake (%)
SiO_2	1.09	0.79
Al_2O_3	0.14	0.15
Fe_2O_3	0.29	55.9
CaO	15.85	0.56
MgO	17.6	1.15
Na_2O	17.5	10.2
K_2O	0.08	0.05
LOI [1]	42.5	31.6
Total	95.05	101.04

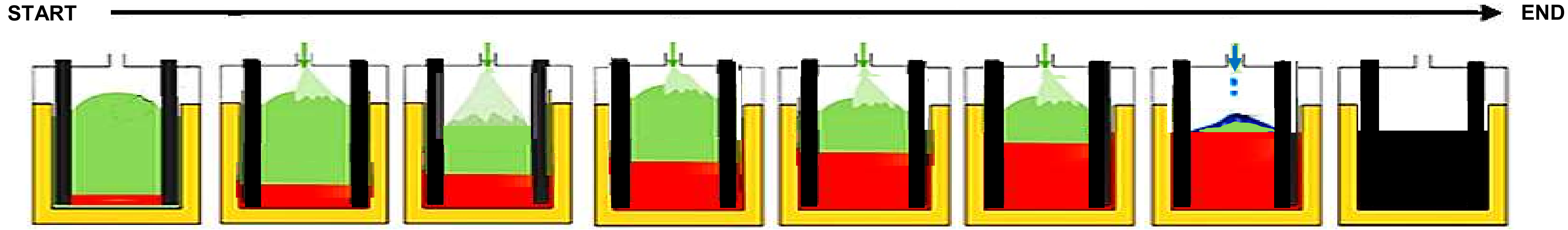
1 Represents the proportion of water and carbon dioxide present in some minerals lost during analysis.

(5) Melt preparation and melt test procedure

Melt preparation

- ➢ Installation of base frit, and starter path inside refractory container.
- ➢ Attach the off-gas hood on the melter.
- ➢ Install electrodes remotely and connect to the starter path.
- ➢ Supply the initial test material into the refractory container, cover the starter path.

Status inside the refractory container before melting in Melt 12

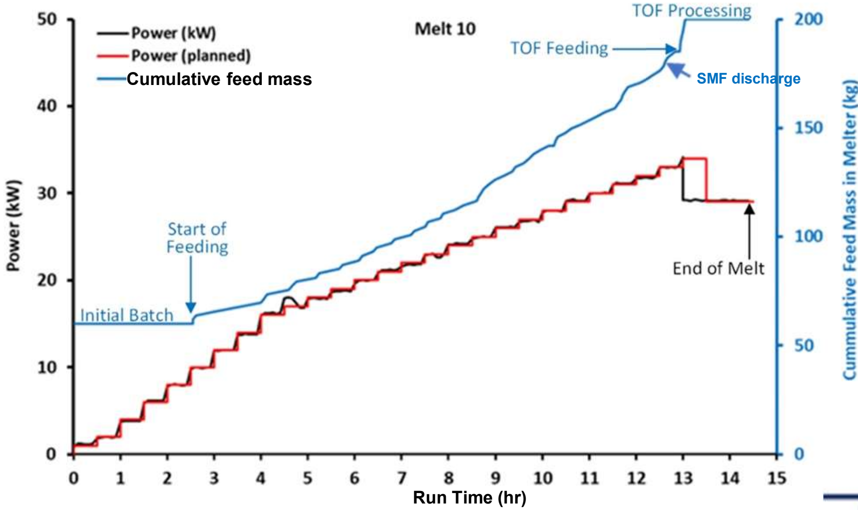


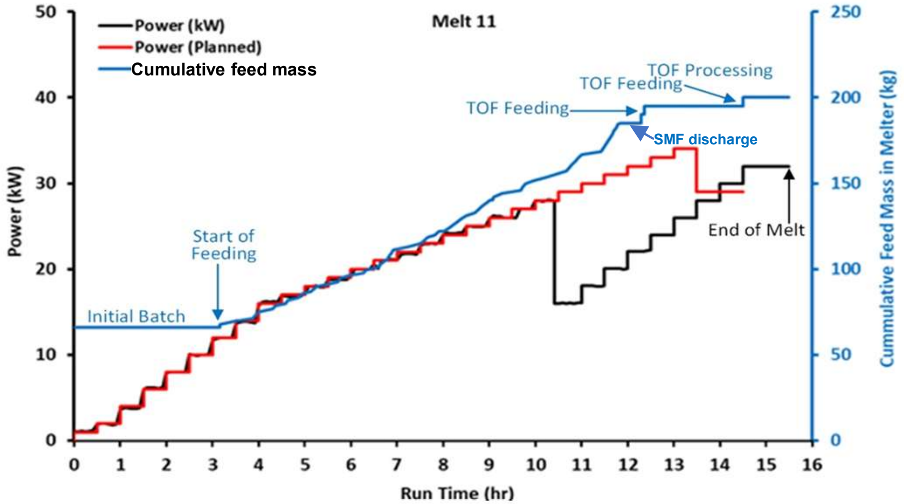
Melt test procedure

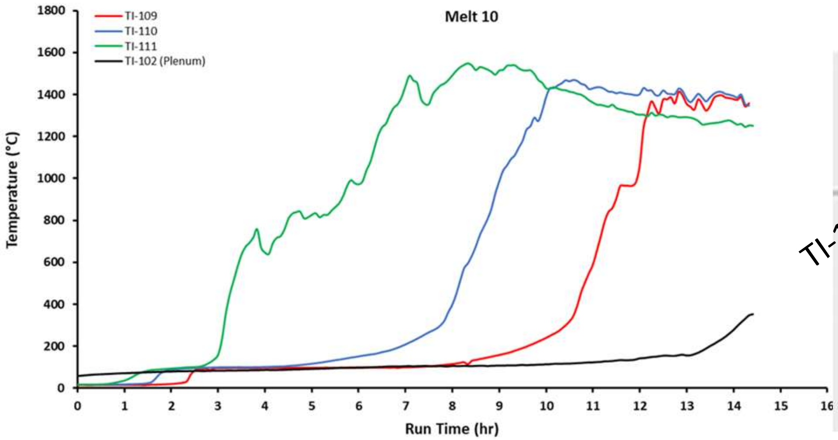
- ➢ The melts start with power applied through the starter path and proceeds upward (“bottom-up melting”). Add the feed of test material.
- ➢ TOF is added at the end after all the waste. The melt ends when all the material in the refractory container has been melted.

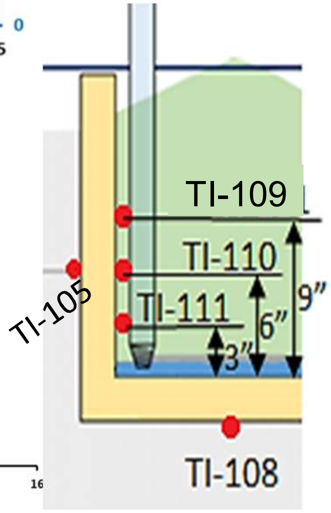
(6) Power ramp, feeding of test materials, temperature in melter and plenum during melting test

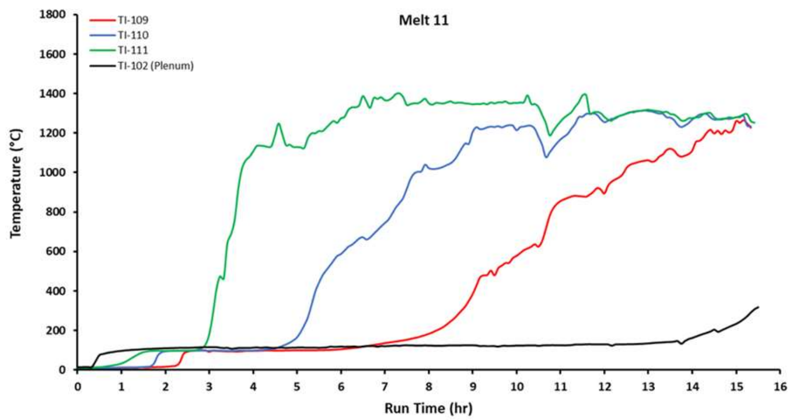
- The melt power ramp was stepwise and decreased 5 kW at the start of TOF stage (to suppress Cs emission) . Melt 11 was an exception; the power ramp was reduced and resumed to control "hazy" CO_2 emissions (Power ramp is modified responding to melt condition)
- Volume was made available in the melter as test material becomes molten glass. Test material was semi-continuously fed in into the melter in order to keep the melter full/maximize the cold cap thickness (cold cap management)
- The temperature in the melter rose as melt proceed from the bottom (bottom-up). Small temperature changes depended on the chemical properties of the test material. Titanate silicate melting temperature (Melts 9,10) was higher than ALPS slurry / Filtercake melting temperature (Melts 11, 12). The temperature and power data of Melt 9 and 12 were almost the same as those of Melts 10 and 11, respectively.
- The plenum temperature remained below 125 ℃ until the TOF begins to melt, then the plenum got hotter (around 300℃ in maximum) as the melt surface becomes exposed.





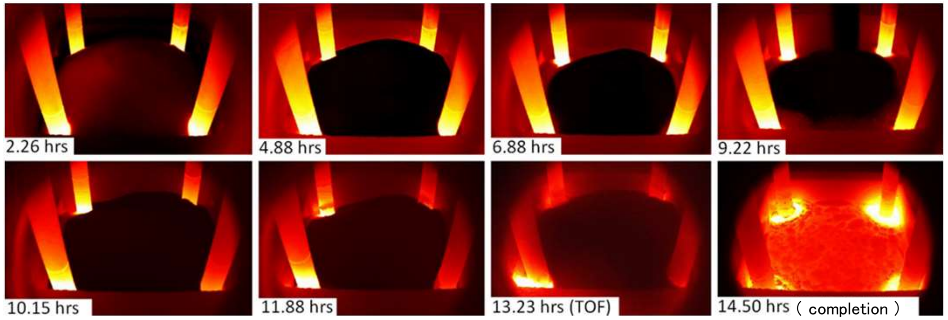




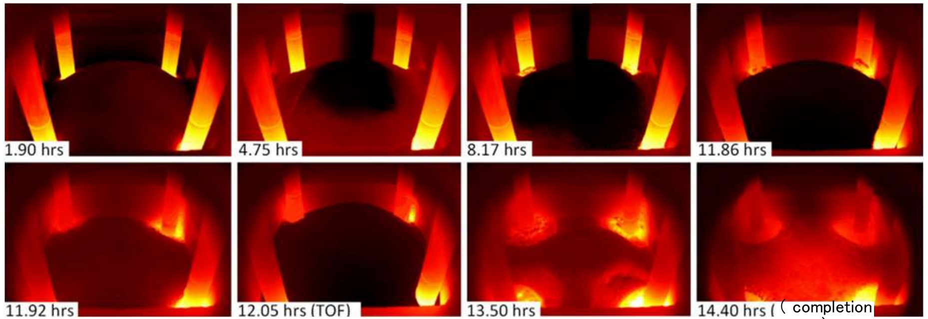


(7) Proceeding of melt (IR camera)

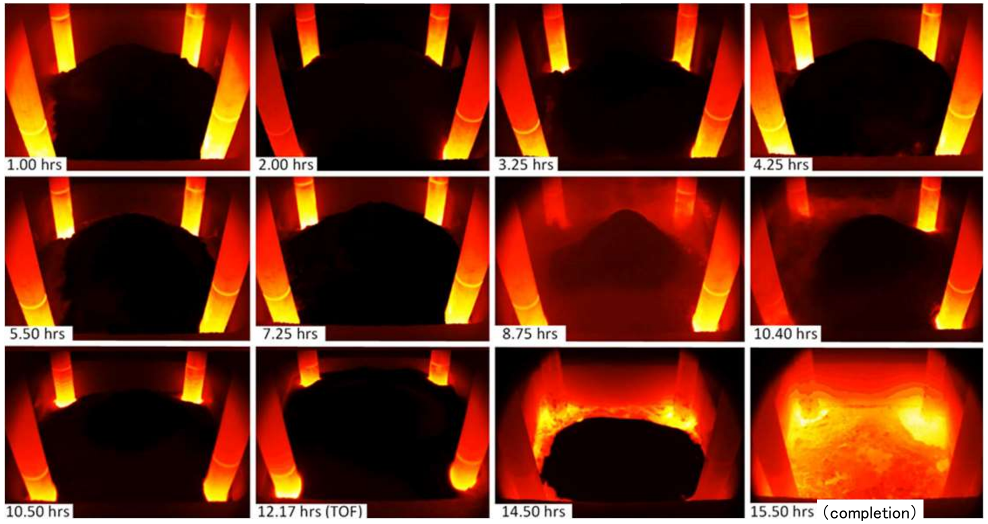
Melt 9[1]



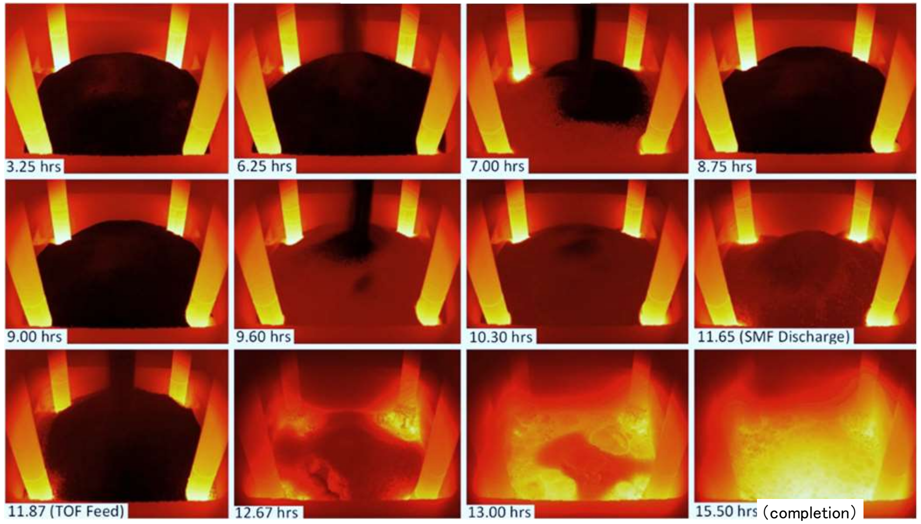
Melt 10[1]

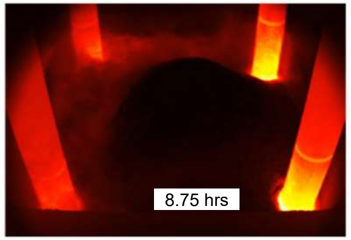


Melt 11

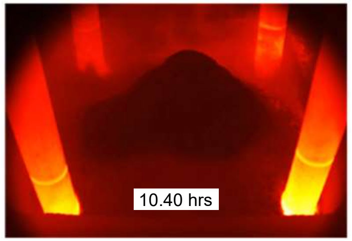


Melt 12

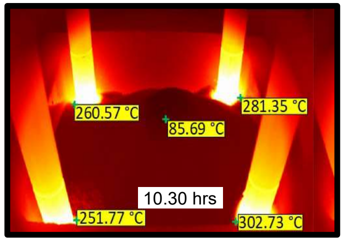




Melt 11
Remarkable CO_2 generation twice (left: 8.75 hours, right 10.40 hours after the start of melting)

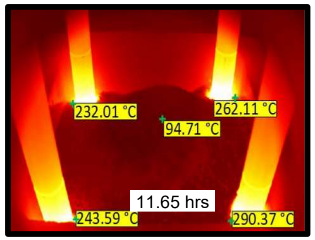


1: Melts 9 and 10 did not cause any unusual events



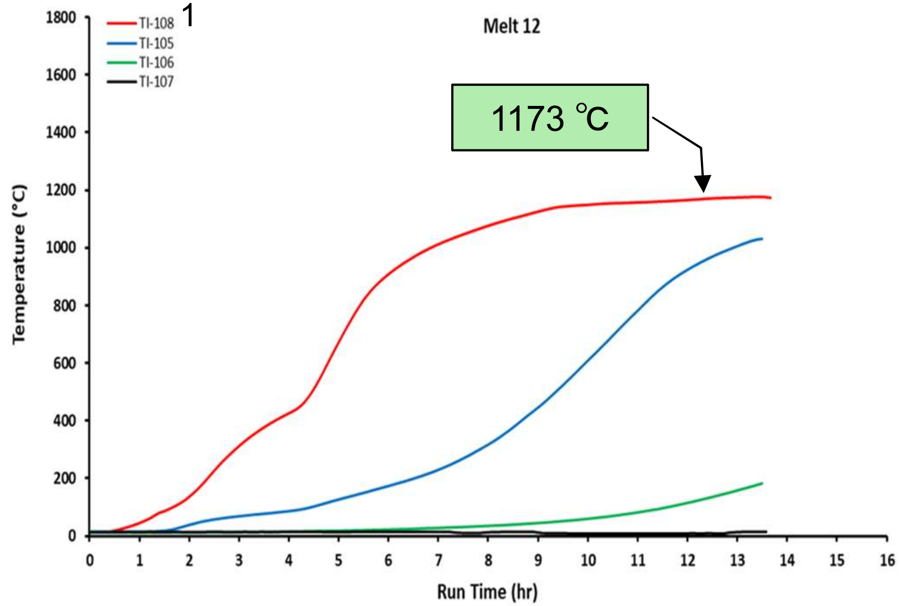
Melt12
Supply of SMF captured particulates
← Immediately before: 10.30 hours after the start of melting,

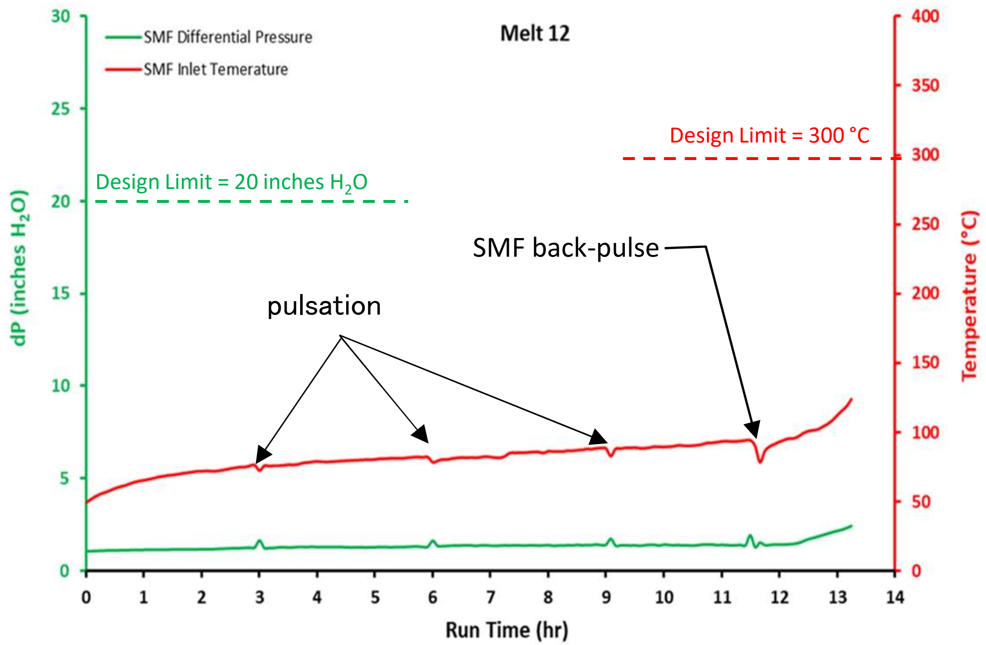
Immediately after: 11.65 hours after the start of melting→

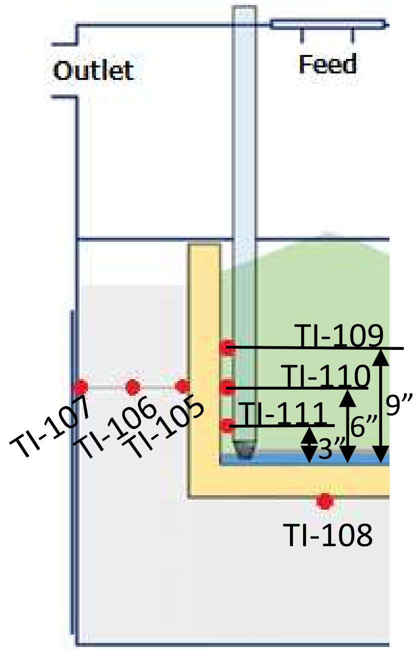


(8) Refractory temperature in melter and SMF temperature・differential pressure

- The thermocouple below the refractory container (TI-108 red line in the figure below left) and side of the refractory container (Ti-105 blue line in the figure below left) remained below the refractory container service temperature (1650℃).
- The SMF performed well below temperature and pressure design limits (temperature = 300℃; differential pressure = 20 inchH_2O
- The SMF was pulsed and discharged during the melt into the melter before the TOF was fed for Melts 10, 11, and 12
- Slight pulsation of temperature and differential pressure were observed at the time of changing of discontinuous stack sampling during melting.





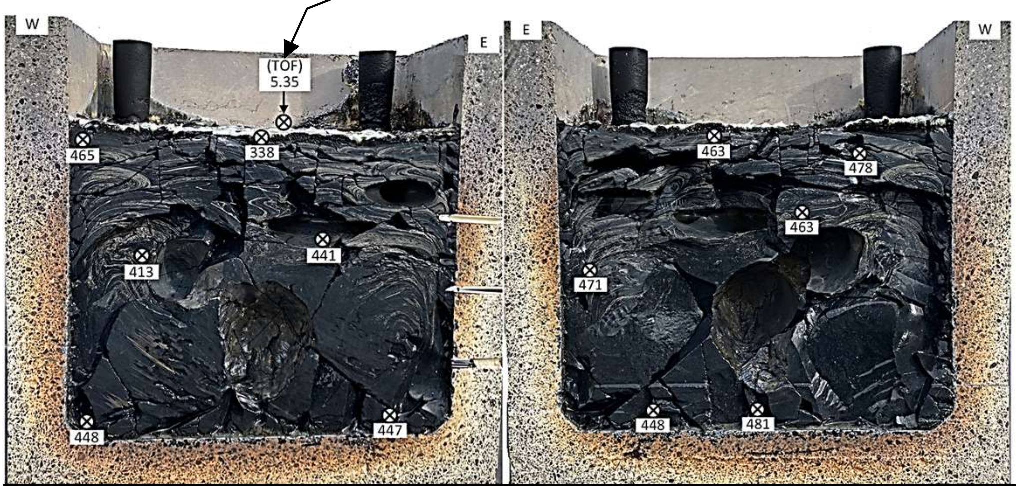


1: The placement levels of the thermocouples that indicate the temperature in the graph on the above are as shown left.

(9) State of produced glass

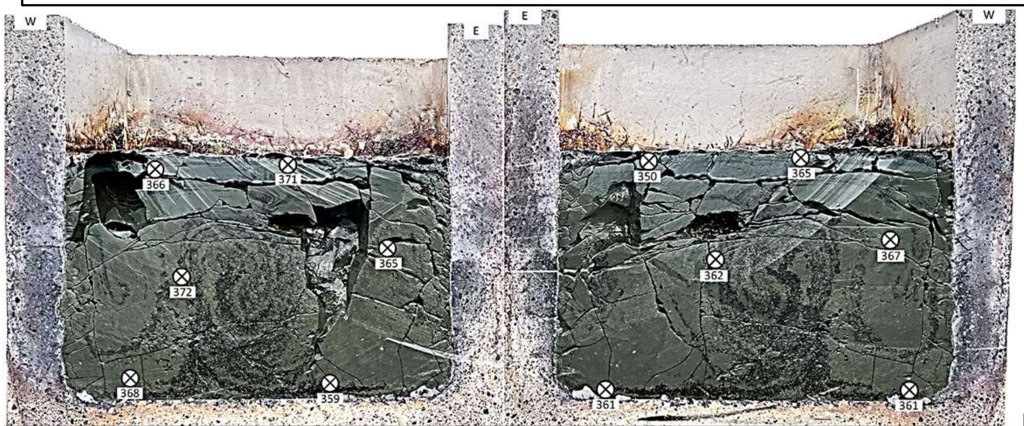
- The glass was cut into 4 section and 3 samples of glass were collected from each section (12 total).
- Cs results show homogenous distribution throughout the glass
- Residual TOF on the surface of Melt 9 was sampled. The Cs concentration in the residual TOF was below the background value of silica sand or refractory and may not be Cs from the melt.

Cs in residual TOF was below the background

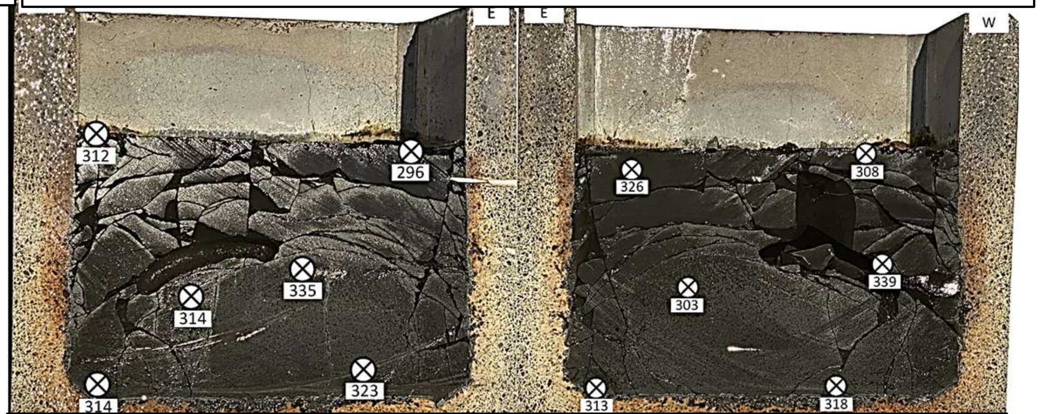


Melt 9 (KUR-EH + KUR-TSG)

Melt 10 (KUR-EH + KUR-TSG)



Melt 11 (KUR-EH + ALPS Filtercake)



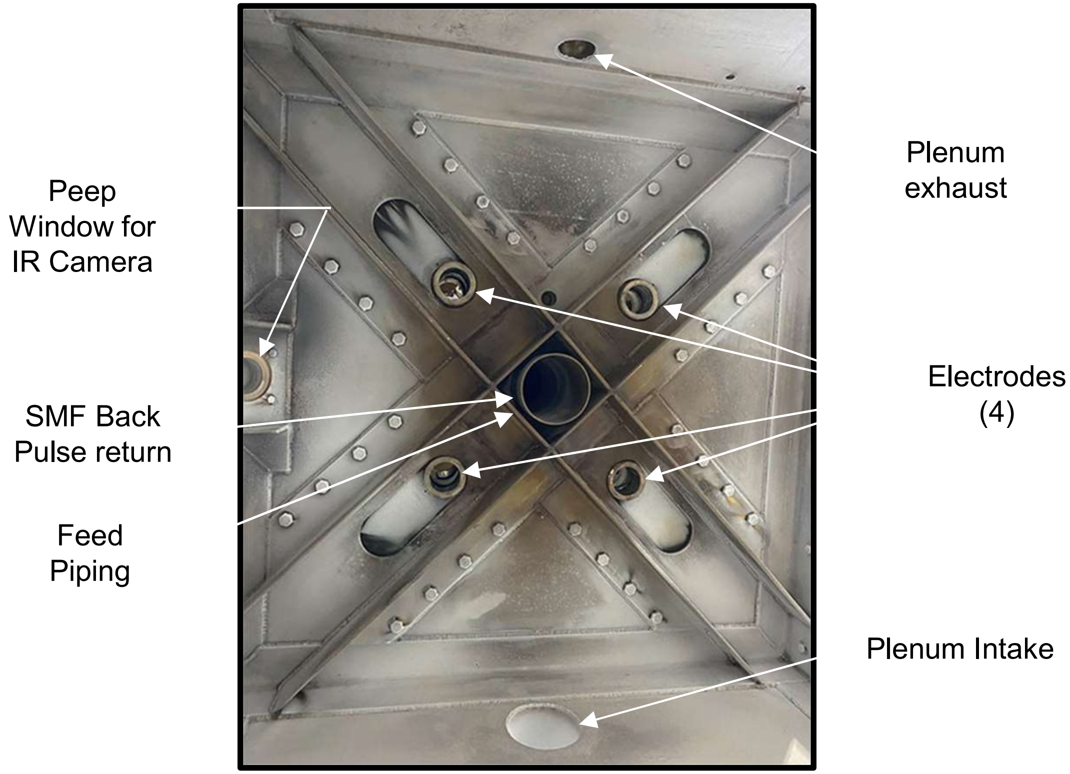
Melt 12 (KUR-EH + ALPS Carbonate slurry)

(10) State of the lower surface of the melter upper hood

- The underside of hood, upper part of the melter are shown with the outlet of feeding pipe (center), insert holes of electrodes and IR camera window.
- By comparison of Melt 9 (water content 15%) and Melt 10 (water content 20%), it turned out no problems (piping blockage etc.) has occurred with increased water content (same for Melts 11 and 12).
- The entire underside of the hood and the first section of off-gas pipe was wipe sampled to quantify total Cs on inner surfaces before first stack sample point. (described later)

Melt 9

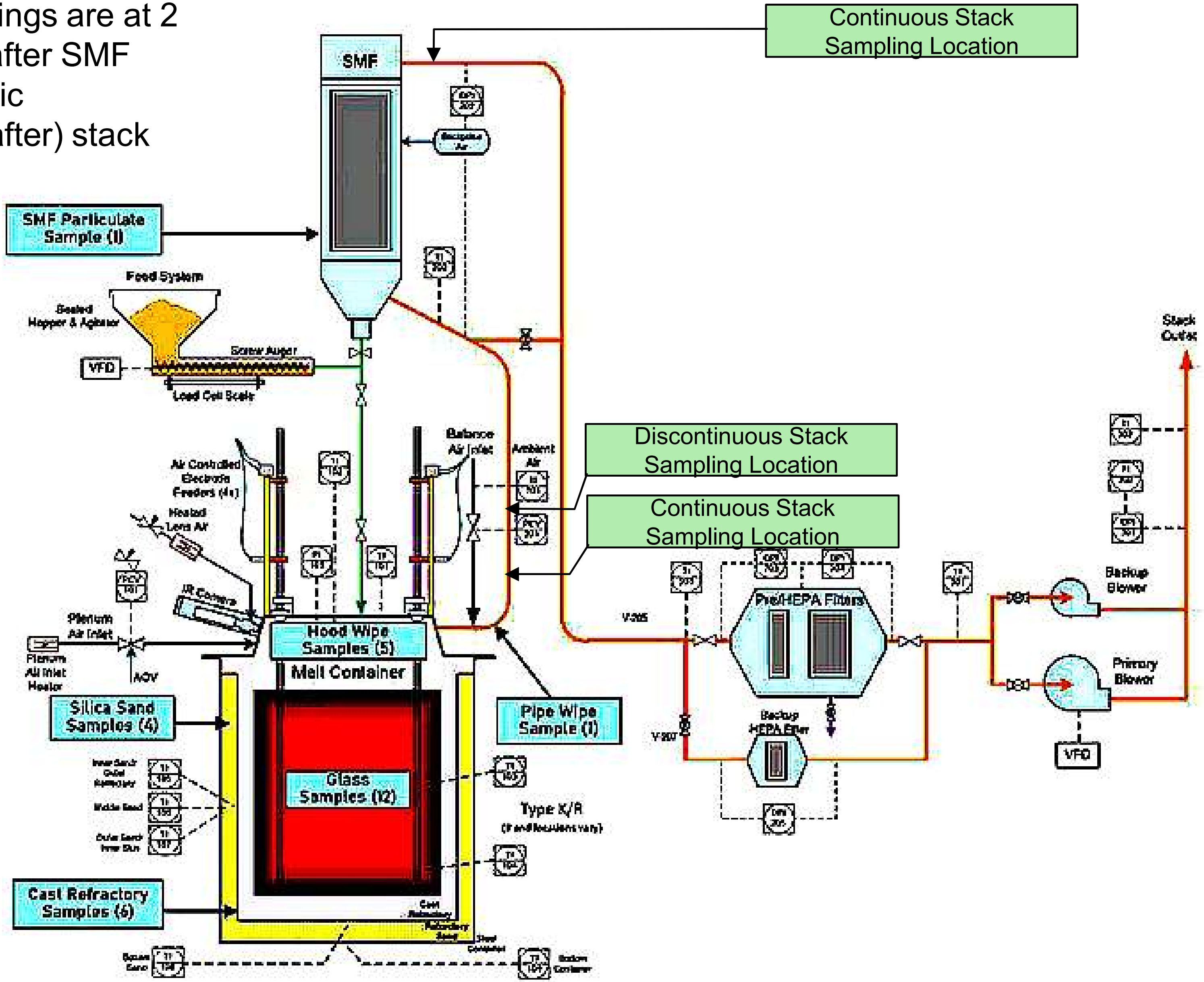
Melt 10



Hood underside before wipe sampling

(11) Location of Off-gas Stack Sampling

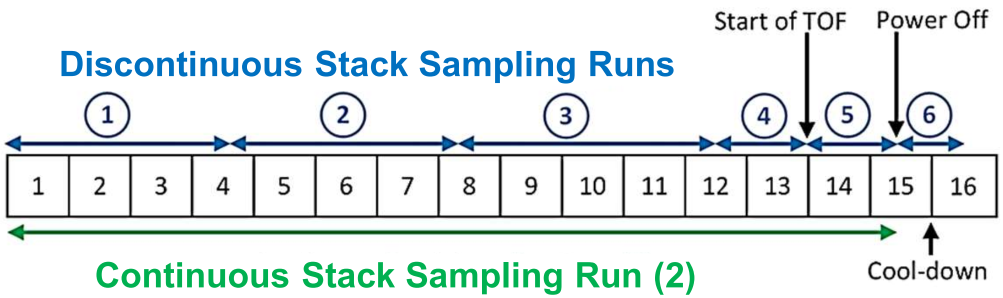
- Continuous isokinetic ("Continuous" hereafter) stack samplings are at 2 positions, before and after SMF
- Discontinuous isokinetic ("Discontinuous" hereafter) stack sampling is at one position, before SMF.



(12) Results of Stack Sampling Measurement

- Off-gas stack sampling was performed according to Method 29 designed by US EPA (Environment Protection Agency)
- Continuous stack sampling was performed through from the start of melting until melt power shutdown. Discontinuous stack sampling was performed from the start of melting until one hour after the melt power shutdown, separating 6 steps responding to the time and stage of melting.
- The measurement results were compared with the melting test results up to the previous year.
- The amount of particulate released in Melts 9,10,12 were almost the same as the test results up to the previous year.
- The amount of particulate released in Melt 11 was especially high in run 4 and 5. This was because the test material was excessively pulverization at the stage of blending. Melt 12 used shorter mixing times to prevent excessive pulverized, resulting in lower particulate emissions.
- Melt 9 and 10 had slightly higher emissions during the TOF stage than Melts 5, 6, and 7. Since the appearance of the supply situation of TOF changed due to the new IR camera angle, the TOF was carefully supplied to avoid overflowing from the refractory container. This may have resulted in a thinner cold cap during the TOF processing stage and slightly higher emissions for Melts 9 and 10.
- Melt 11 had high Cs emissions during the TOF stage primarily because of excessive pulverization, the effect of high chloride concentration in the ALPS Filtercake, and the long duration of the TOF treatment stage.
- Melt 12 had elevated Cs emissions during the TOF stage (Run 5). This was because the particulates remaining in the TOF stage of Melt 11 were also recycled in the recycling of the SMF collected particulates before the TOF supply in Melt12.

Melt 10 sampling (same for other melt tests)



Particulate (g)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Melt 5	1.31	0.52	1.13	26.27		
Melt 6	0.85	0.87	0.75	50.67	25.62	
Melt 7	0.19	0.32	47.69	45.87	20.09	1.73
Melt 9	0.0003	0.002	0.45	0.67	0.59	0.03
Melt 10	0.72	1.10	14.4	28.65	41.18	1.7
Melt 11	0.00	59.7	25.5	150.43	1140.23	77.3
Melt 12	1.8	1.5	1.2	1.76	89.33	9.3

Cs Emissions (g)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Melt 5	0.00	0.00	0.00	1.35		
Melt 6	0.00	0.00	0.00	0.97	0.37	
Melt 7	0.00	0.00	0.06	0.10	0.44	0.01
Melt 9	0.00	0.00	0.45	0.67	0.59	0.03
Melt 10	0.00	0.00	0.28	0.68	0.70	0.02
Melt 11	0.00	0.18	0.02	0.23	9.03	0.05
Melt 12	0.02	0.01	0.00	0.02	2.09	0.14

Orange shading is TOF stage

(13) Measurement results of Cs amount including capture and recovery of Cs by SMF

- Measurement results of each sampling points in each melt test are shown in the table below
  ① Amount of Cs in feed of test material,
  ② Adhesion amount of Cs in the hood and piping (until 1st continuous stack sampling point) (wipe sample)
  ③ Amount of Cs of continuous and discontinuous stack sampling before SMF (The value of continuous + 6th discontinuous run)
  ④ Amount of Cs of continuous stack sampling before SMF
  ⑤ Amount of Cs recycled from SMF
  ⑥ Amount of Cs of continuous stack sampling after SMF.

- Particulate (Cs) captured by SMF was treated as follows in each melt test
  Melt 9: Captured through all course of melt test. Captured particulate (Cs) was not recycled to the melting container but was recovered to the backet to measure the amount of particulate and Cs concentration.
  Melt 10: Captured particulate (Cs) until the start of TOF stage was discharged to the melting container just before the TOF feeding. The amount and concentration discharged were estimated to be the same as Melt 9.
  Melt 11: Captured particulate (Cs) until the start of TOF stage was discharged to the melting container just before the TOF feeding. The amount and concentration discharged were not measured. Captured particulate in the TOF stage was recovered to the backet to measure the amount of particulate and Cs concentration
  Melt 12: Captured particulate (Cs) until the start of TOF stage was discharged to the melting container together with the residual particulates in the melting test 11 just before the TOF feeding. The amount and concentration were not measured. Captured particulate during the TOF stage was recovered to the backet to measure the amount of particulate and Cs concentration.

(unit: metal mass g)

	① Cs in feed	② Cs in hood and piping (before SMF)	③ Cs in stack sampling (con.+ 6th discon. Run) before SMF	④ Cs in stack sampling before SMF (con.)	⑤ Cs recycled from SMF	⑥ Cs in stack sampling after SMF (con.)
Melt 9	73.10	0.04	1.74	1.71	1.02	0.0003
Melt 10	79.36	0.05	1.56	1.54	Not measured	0.00001
Melt 11	60.36	0.08	7.87	7.82	5.51	0.0006
Melt 12	49.64	0.04	2.15	2.01	0.75	0.0001

(14) Capture of Cs by SMF, Calculation of Cs retention rate including recovery and SMF

- The Cs retention rate was calculated and evaluated according to the following three scenarios.

  Scenario A: Cs retention by cold cap (same as previous tests): {(① - ② - ③)/①} x 100 (%)

  Scenario B: Cs retention by cold cap with addition of recycled Cs: {(① - ② - ③ + ⑤)/①} x 100 (%)

  Scenario C: Cs retention by cold cap and recycle of all off-gas emissions prior to SMF outlet (scenario envisioned for the actual treatment plant): {(④ - ⑥)/④} x 100 (%)
- The improvement of Cs retention by SMF is evaluated by comparison of scenario A and B
- As for the actual plant design, it would be adequate to adopt the value of scenario C as Cs captured by SMF was discharged to melter in the same melt batch[1] or following batch[1], in addition, Cs adhering to the inside of the SMF housing and the off-gas piping up to the SMF was washed away with water after the melting was completed, so it was reasonable to use the value of Scenario C.
- The filtration efficiency as a single SMF was evaluated by the ratio of ④ and ⑥. It was demonstrated to be better than the official (catalogue) value (HEPA rate)

Cs Retention for each scenario (%)

Melt	9	10	11	12
Scenario A	97.56	97.97	86.82	95.59
Scenario B	98.96	99.26[2]	95.95	97.10
Scenario C	99.98	100.00	99.99	100.00

SMF Filtration Efficiency (%)

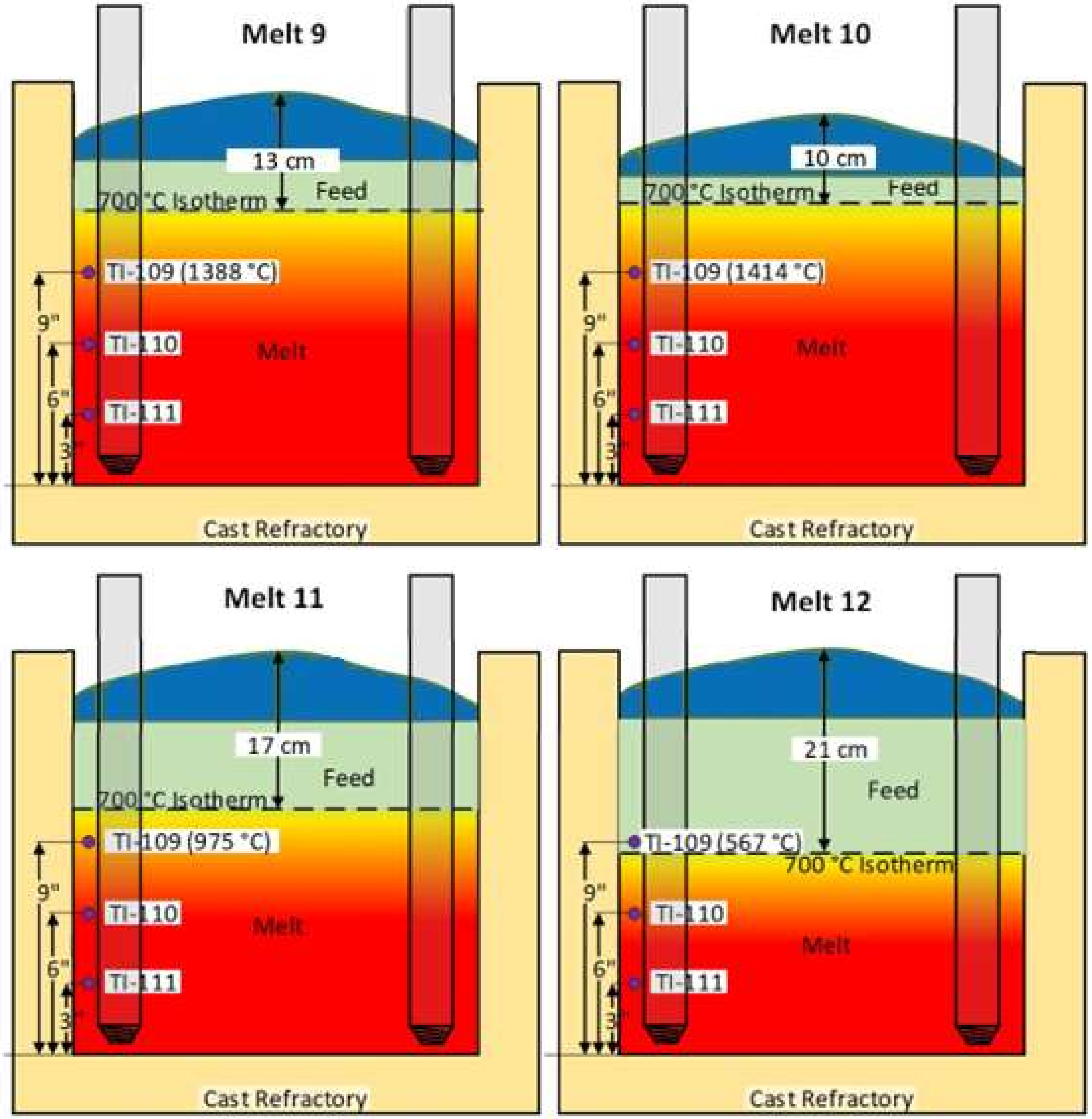
Melt	9	10	11	12
Cs	99.98	100.00	99.99	100.00

1: Melt processing per vitrified waste was called a batch.

2: Since the recycling amount used in the calculation of scenario B of Melt 10 was the same as that of Melt 9, the recycling amount of Melt 9 was used.

(15) Operation condition at the final stage for suppression of Cs emission

- The thickness of cold cap at the TOF stage was evaluated by combination of
  ① IR picture of feed surface at the final feed of test material before the TOF feeding
  ② Temperature gradient and temperature of TI-109 at the TOF feeding.
- Melts 9 and 10 had a thinner cold cap thickness due to the careful feeding of additional test material due to the mounting angle of the new IR camera.
- Improvement of feed method for Melts 11 and 12 produced a significantly thicker cold cap.



(16) Operating conditions at the end of melting to suppress Cs emission (Reflection of basic test on suppression of Cs volatilization at the end of melting)

- The 2021 engineering-scale melting test reflected the "basic test on suppression of Cs volatilization at the end of melting."

Criteria	Result of basic tests	How to reflect to engineering-scale melting tests	Result of engineering-scale melting tests
TOF thickness	Cs emissions were inversely correlated to TOF thickness. Cs emission from wastes under TOF(hTF0=10cm) was ~0.3% of total Cs in wastes using maximum TF (1350℃). Thinner TOF layer on wastes increased Cs emission.	Make the TOF thickness 10 cm or more.	Cold Cap Thickness after the TOF Feed: Melt 9: 13 cm Melt 10: 10 cm Melt 11: 17 cm Melt 12: 21 cm
TOF Feed Timing	Feeding of the TOF on waste mixture was better to be done before subsidence of surface of waste mixture.	Feed the TOF as soon as possible after the feed of the test material was completed.	After the last test material was fed, the TOF was fed as soon as practicable while checking with an IR camera.
Surface temperature of test material before TOF (T_s)	Practically, TS~100℃ just before subsidence of waste mixture because moisture from wastes(~100℃) heats top of waste mixture and kept TS ~ constant until completely dried.	Since Ts with an IR camera could not be measured over time, it could not be used as a guideline for the TOF feed.	The test material Ts before the first TOF feed was a range from 104℃ to 147℃.
Melt surface temperature at the end of mixing of molten TOF and molten waste mixture (T_s)	Melt TS >1100℃ was necessary to complete melting of TOF and mixing with melted wastes; smooth glass surfaces were formed after cooling to solid glass.	For the same reason as above, the melt Ts could not be controlled.	The melt Ts at completion was a range from 232 ℃ to 815℃. This was lower than Tokyo Tech's study because the surface of the GeoMelt®ICV™ melts was cooled by plenum air.
Temperature of TI-109 at TOF stage	In order to suppress the volatilization of Cs at the end of melting, it was necessary to keep the melt TS at <1200℃, and for this purpose the thermocouple TI-109 was required to be kept at <1300℃. (Before performing Melt Test 12).	Melt 12 was performed by a method using the temperature of TI-109 because the melt Ts could not be measured directly.	The maximum temperature of TI-109 at the TOF stage of Melt 12 was 1291℃, below the reflected 1300℃.

(17) Engineering scale Melting tests: Test conditions and Results

Item		Melt 9	Melt 10	Melt 11	Melt 12
Waste		KUR-EH KUR-TSG	KUR-EH KUR-TSG	KUR-EH ALPS Filtercake	KUR-EH ALPS carbonate Slurry
Waste loading (wt%) [not include water] [includes frit]		73% (54% KUR-EH 19% TSG)	73% (54% KUR-EH 19% TSG)	78% (44% KUR-EH ALPS 25% carbonate 9% iron coprecipitate)	66% (40% KUR-EH 26% ALPS carbonate)
Water content (%)		15.00	20.00	16.30	20.00
Melt Duration (hours)		14.50	14.40	15.50	13.33
TOF Optimization	TOF supply	immediately after the last waste feed			
	Power reduction at TOF	34→29 kW	34→29 kW	None (TOF power = 32 kW)[1]	31→26 kW
	TOF amount (kg)	15 kg			
	TI-109 at TOF	1380 – 1287℃	1414 – 1324℃	894 – 1278℃	590 – 1291℃
	TOF Stage Duration (hours)	1.3	1.5	3.3	1.8
Recycle of Cs from SMF		No	Yes	Yes	Yes
Off-gas stack sampling		2 continuous stack sampling (one measurement each) and 1 discontinuous sampling (measuring 6 runs)			
Cs Retention (%)	Scenario A: Cs retention rate	97.56	97.97	86.82	95.59
	Scenario B: Cs retention rate after SMF discharge	98.96	99.26	95.95	97.10
	Scenario C: Retention in glass and SMF	99.98	100.00	99.99	100.00
Sr Retention rate		99.97	99.99	99.74	100.00

[1] No power reduction during TOF because power was reduced earlier in the melt in response to gas generation.

(18) Summary – Engineering-Scale Melting Test (1/3)

- Four engineering-scale melting tests were conducted.
- The performance of the SMF newly installed was demonstrated.
  - It was demonstrated that the filtration efficiency and operability of back pulsing and recycling the particulate captured to the melter during melting.
  - The operation condition (temperature) of SMF was within the design specification and increase of differential pressure during melting was very low.
- The emission of Cs and Sr was grasped quantitatively by continuous/discontinuous stack sampling and used for evaluation.
- It was applied that the findings obtained from the basic tests to the operation at the final stage of melting.
- It was demonstrated that the treatment of waste with high water content (20%) without problem (no piping blockage etc.)
- It was verified that the transportability and feeding of ALPS Filtercake by elemental test. The melting treatment including transportability and feeding by engineering-scale was also demonstrated.
- The melting treatment of ALPS carbonate slurry with higher waste loading (19.49% →29.46%) was demonstrated.
- The homogeneity of Cs distribution in glass by sampling and analysis after melting was verified (Sufficiently small CV values (coefficient of variance) for Cs samples in Melts 9 to 12: 1.56-3.76%).

(18) Summary – Engineering-Scale Melting Test (2/3)

- Cs retention in glass by cold cap (Scenario A)

  Melts 9, 10：Cs retention rates were slightly lower than previous Melts. Since the appearance of the supply situation of TOF changed due to the new IR camera angle, the TOF was carefully supplied to avoid overflowing from the refractory container. This may have resulted in a thinner cold cap during the TOF processing stage and slightly lower Cs retention rates for Melts 9 and 10.

  Melt 11： Cs retention rates were fairly low. This was attributed to the excessive pulverization, the effect of high chloride concentration in the ALPS Filtercake and extended duration of the TOF stage.

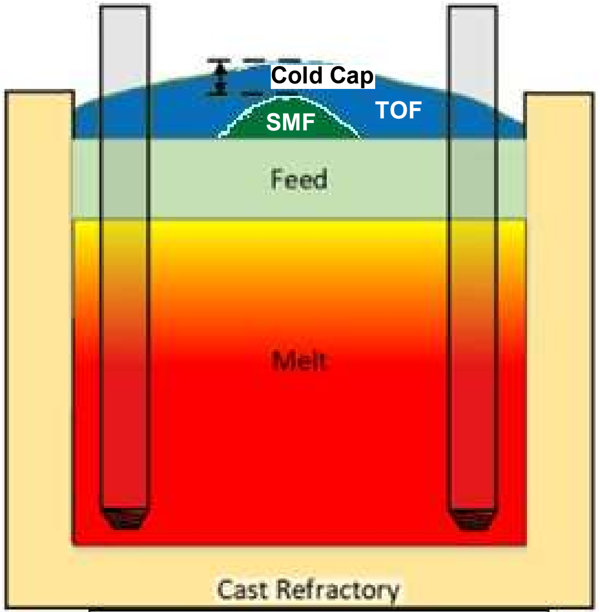
  Melt 12： Cs retention rates were lower than expected. It was probable that the residual Cs captured in the TOF treatment stage in Melt 11 was recycled together with the Cs captured just before the TOF was supplied in Melt 12 .

- Cs retention in glass by recycling SMF captured particulate was improved.(Scenario B)
  - Cs retention in glass（86.82～97.97% to 95.95～99.26%）shown by recycling SMF captured particulate to melter was improved.
- Cs retention in glass by cold cap and SMF was improved. (Scenario C)
  - Very high retention rate (99.98～100%) was obtained for Melts 9,10,11, and 12.

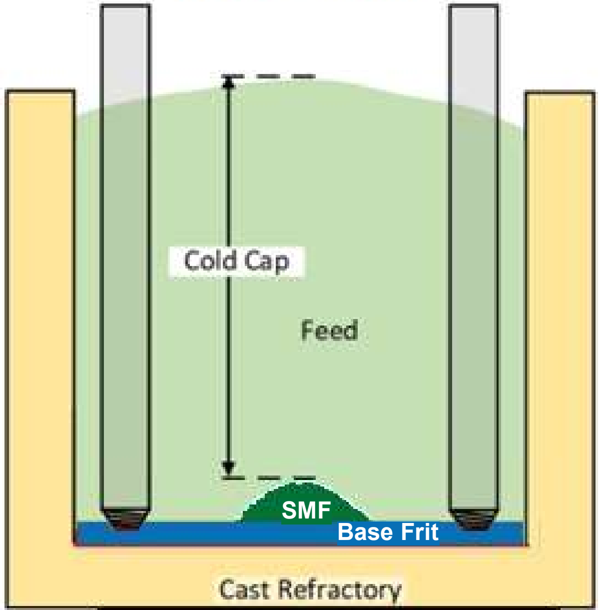
(18) Summary – Engineering-Scale Melting Test (3/3)

- As a design evaluation of the actual treatment plant, the Cs captured in SMF was recycled to the melter not only in the same melting batch[1] but also in the subsequent melting batch, also Cs adhering to the inside of SMF and off-gas pipes was washed out into the melter with water after the completion of melting, so it was considered reasonable to use the value of Scenario C. In addition, equipment for washing away Cs adhering to off-gas pipes, etc. after melting will be examined at the design stage of the melting equipment for the actual plant.
- Cs emissions were highest during the TOF stage in one batch[1] of melt treatment. The Cs concentration in the SMF captured particulates was several times higher than that in feed waste and product vitrified waste. It was important to capture this high condensed Cs particulate by SMF without failure. Cold cap management was also important to obtain high Cs retention, but for some type of waste it would not work well (high chloride concentration in Melt 11). Even in such case, high retention of Cs was obtained by SMF.
- To avoid the re-emission of Cs recycled to melter from SMF, It was considered to be better to recycle at the beginning of the subsequent melting batch[1] (before the first waste feed) rather than just before the start of TOF feed of the same melting batch (runs in Melts 10 to 12). It would result in the particulates with high Cs concentration captured by SMF being covered by the thickest possible cold cap. (see the figures right) Note that this treatment was limited to cases where the same waste is being treated. If recycling is done with different wastes, it was necessary to examine the inventory evaluation method of the produced vitrified waste.
- Long-term outages until subsequent melting batch was supported by back-pulsing the SMF captured particulates and properly storing SMF particulates in the lower holding section within SMF designed as high-dose equipment.

1: Melt processing per solidified glass is called one batch



Melts 10-12



Optimal

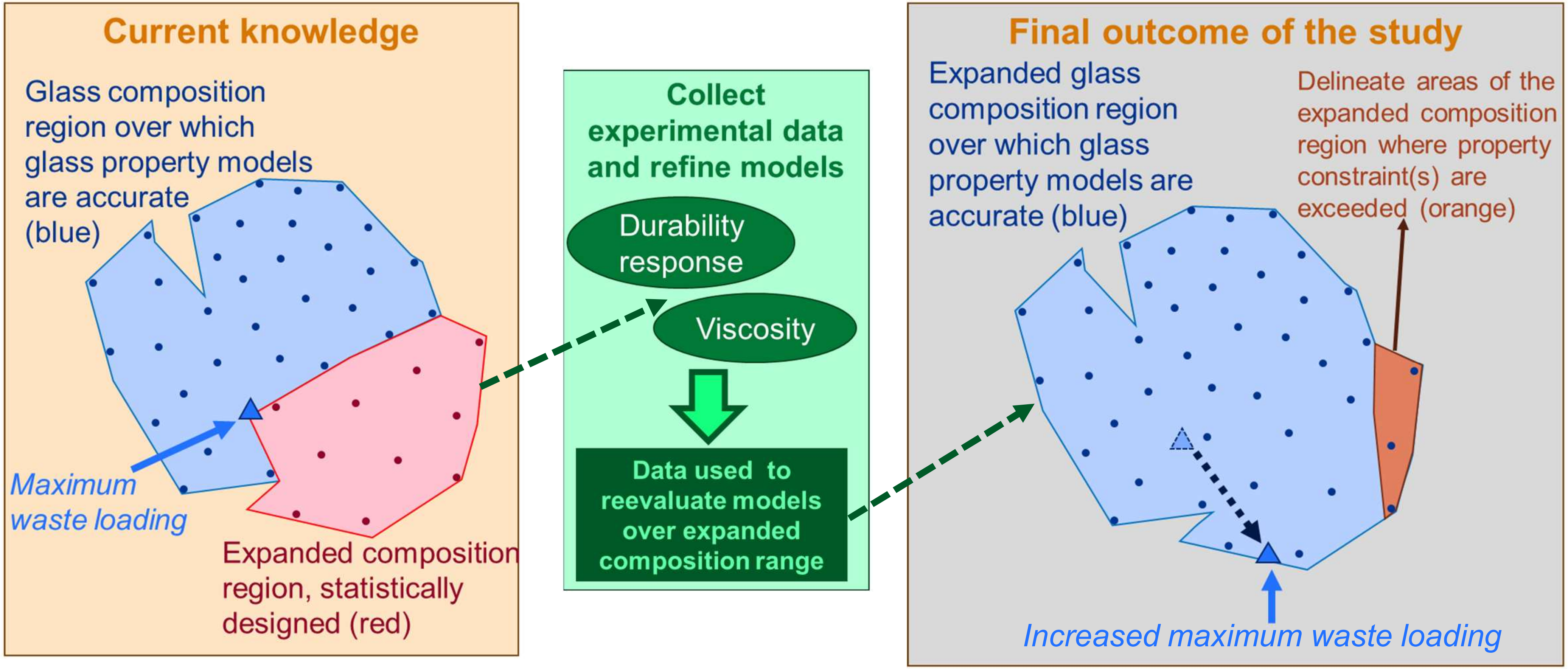
(19) List of Engineering-Scale Melting Test Results by Subsidy Projects

	Melting Test											
	1	2	3	4	5	6	7	8	9	10	11	12
Melter Surface Area/Volume (cm^2/L)	23.17	23.17	23.17	23.17	15.77	15.77	15.77	15.77	23.17	23.17	23.17	23.17
Waste Type	KUR-EH ALPS Slurry[1]	KUR-EH KUR-TSG	KUR-EH AREVA	KUR-EH KUR-TSG	KUR-EH ALPS Slurry[1]	KUR-EH KUR-TSG	KUR-EH AREVA	1F Soil ALPS Slurry[2]	KUR-EH KUR-TSG	KUR-EH KUR-TSG	KUR-EH ALPS Filtercake[3]	KUR-EH ALPS Slurry[2]
Dry Feed Waste Loading (Includes Frit) (%)	75.77	77.44	64.39	77.44	75.55	76.02	64.00	71.00	73.17	72.64	78.25	65.88
Glass Oxide Waste Loading (Includes Frit) (%)	71.10	76.60	63.30	76.60	71.70	79.20	67.00	72.42	76.20	76.20	76.50	72.05
Dry Test Materials Processed (kg)	195.08	182.73	188.90	181.28	185.85	169.76	173.45	122.64	153.00	144.00	150.56	144.00
Water Processed (kg)	10.92	16.77	36.10	18.22	20.15	24.94	26.55	11.36	27.00	36.00	31.08	36.00
Water Processed (% of Total Mass; Not Including Frit)	5	8	16	9	10	13	13	8	15	20	17	20
Frit Processed (kg)	15.00	12.50	15.00	12.50	15.00	15.00	15.00	16.00*	20.00	20.00	20.00	20.00
Total Mass Processed (kg)	221.00	212.00	240.00	212.00	221	209.70	215.00	150.00	200.00	200.00	200.00	200.00
Energy (kWh)	219.82	232.67	336.06	365.02	303.09	345.40	349.04	376.71	290.63	344.34	275.57	314.16
Average Power (kW)	16.19	13.89	22.40	17.11	18.65	19.93	19.39	19.32	20.04	23.91	17.78	23.55
Melt Duration (hr)	13.58	16.75	15.00	21.33	16.25	17.33	18.00	19.50	14.50	14.40	15.50	13.33
Processing Rate (kg/hr)	16.29	12.66	16.00	9.94	13.6	12.10	11.94	7.69	13.79	13.89	12.90	15.00
Processing Efficiency (kWh/kg)	0.99	1.10	1.40	1.72	1.37	1.65	1.62	2.51	1.45	1.72	1.38	1.57
Mass of Glass (kg)	176.60	155.80	169.20	164.26	172.69	166.41	165.00	131.40	148.00	135.10	136.34	129.80
Mass Loss(%)	20	27	29	23	22	21	23	12	26	32	32	35
Volume Processed (L)	267.55	283.23	317.46	282.67	254.02	241.26	236.97	147.06	155.80	225.99	214.70	201.20
Volume of Glass (L)	68.67	63.93	66.00	67.77	60.29	60.29	61.15	51.65	59.71	58.01	52.09	52.09
Volume Reduction(%)	74	77	79	76	76	75	74	65	78	74	75.74	74.11
Sr Retention in Glass (%)	99.76	99.99	100.00	99.99	100.00	100.00	100.00	None	99.97	99.99	99.74	100.00
Scenario A: Cs Retention in Glass (%)	91.46	99.30	93.79	99.44	97.72	98.77	98.47	None	97.56	97.97	86.82	95.59
Scenario B: Cs Retention in Glass with Recycle from SMF (%)									98.96	99.26	95.95	97.10
Scenario C: Cs Retention in Glass and SMF (%)									99.98	100.00	99.99	100.00

1: ALPS Carbonate・Iron coprecipitate slurry, 2: ALPS Carbonate slurry, 3: ALPS Carbonate・Iron coprecipitate Filtercake

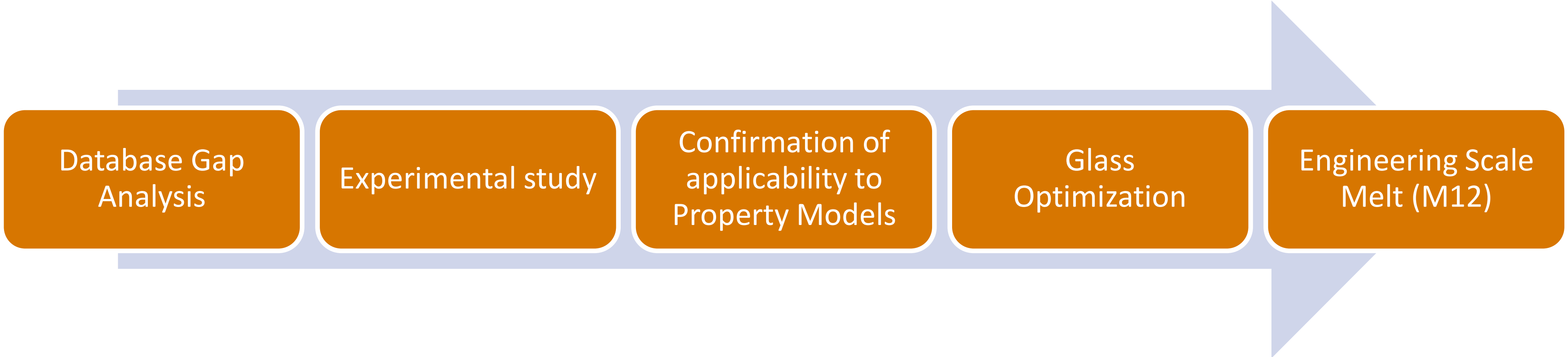
7.4 Glass Formulation・Durability Testing
7.4.1 Increased waste loading of ALPS carbonate slurry (1) Technical approach

Objective: Extend the glass composition region where the glass property model is found to be accurate to enable reliable high ALPS Ca-Mg slurry formulations[1] (alone or together with other 1F waste)



1: ALPS carbonate slurry contains Mg, Ca, and Na. In order to increase the waste loading of carbonate, it is necessary to increase Mg more than before, but since these increase and decrease in the same way, the formulation was studied as a "high ALPS Ca-Mg slurry".

(2) Glass composition settings for Melt 12 using test glass data



- The areas where data was lacking in the current glass property database (high MgO region) was identified.
- The glass composition was set to efficiently fill the unpopulated space of the database, molten glass was manufactured, and the characteristics were measured using samples that have been rapidly cooled and slowly cooled.
- Five characteristic models were developed to predict properties as functions of glass composition using the glass property measurement data such as viscosity, nepheline crystallization, Mg-containing phase crystallization, MCC-1 response of crystal free glasses, and crystal impact on MCC-1 response.
- By combining the new property model and the previous property model, the optimum glass composition that can achieve high ALPS loading rate while satisfying the constraints of glass characteristics (viscosity, durability, phase stability, melting temperature, electrical conductivity, etc.) was set.
- Using the updated glass composition-property model, the glass composition for Melt 12 was formulated and the melt test have carried out.

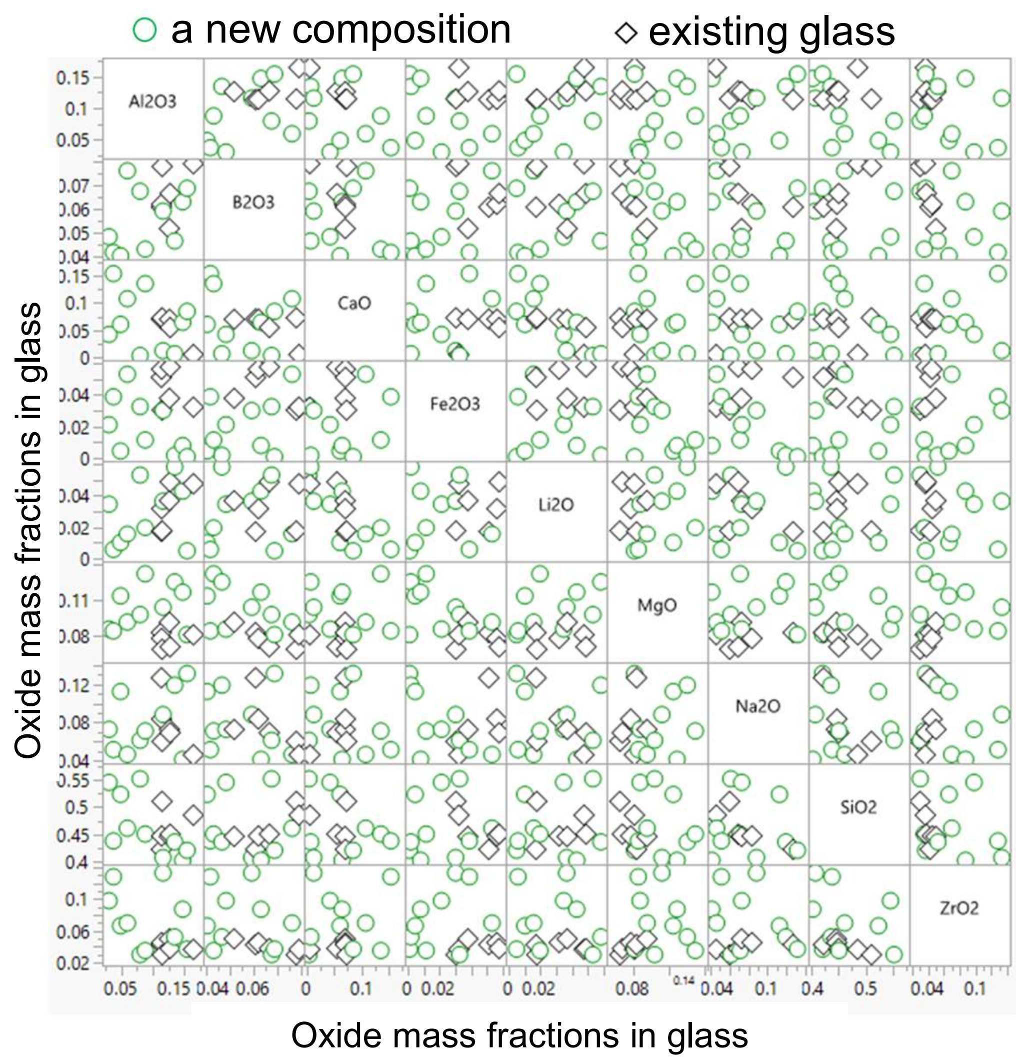
(3) ALPS-MgO Matrix design

Steps:

1. Evaluate composition region of interest (collect existing glasses and model generated glasses with MgO higher than the current 6 wt% limit)
2. Set boundaries for glass components
3. Set property constraints to allow for glass melting (2 < viscosity at 1300°C < 10 Pa.s) (MCC-1 NL_B < 10 g/m^2 at 28d)
4. Apply space-filling design to efficiently backfill existing glasses with 10 new glasses in the composition region of interest

Target glass composition range (oxide mass fraction) for 1F waste glass loaded with high ALPS Ca-Mg

Oxide	min	max	Minors	Concent-ration
Al_2O_3	0.019	0.165	TiO_2	0.005
B_2O_3	0.04	0.08	Cs_2O	0.001
CaO	0	0.16	SO_3	0.00036
Fe_2O_3	0	0.06	SrO	0.001
K_2O	0	0.01	BaO	0.001
Li_2O	0	0.06	Cl	0.005
MgO	**0.08**	**0.135**	Cr_2O_3	0.0001
Na_2O	0.04	0.14	P_2O_5	0.0001
SiO_2	0.4	0.6	NiO	0.0001
ZrO_2	0.03	0.135	SUM	0.0137
Minors	0.0096	0.0178		



Scatter plot matrix of component concentration distribution

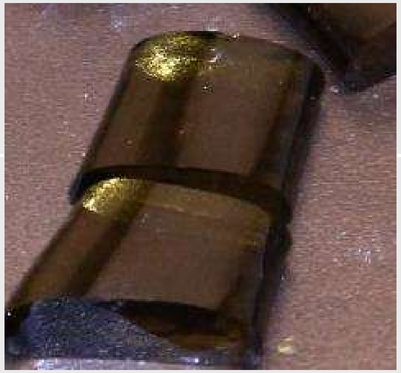
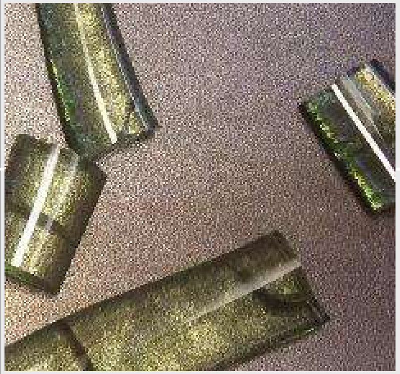
(4) Glasses composition

Glass composition in oxide mass fractions

Glass ID	Al_2O_3	B_2O_3	CaO	Fe_2O_3	K_2O	Li_2O	MgO	Na_2O	SiO_2	ZrO_2	Others
VNS-Mg-01	0.0880	0.0431	0.1359	0.0115	0.0009	0.0196	**0.1322**	0.0712	0.4507	0.0352	0.0117
VNS-Mg-02	0.1160	0.0592	0.0122	0.0301	0.0028	0.0366	**0.1040**	0.0884	0.4073	0.1332	0.0102
VNS-Mg-03	0.0376	0.0417	0.1544	0.0388	0.0098	0.0058	**0.0841**	0.0514	0.4380	0.1283	0.0100
VNS-Mg-04	0.1472	0.0631	0.0646	0.0080	0.0095	0.0429	**0.1167**	0.0413	0.4024	0.0873	0.0169
VNS-Mg-05	0.0597	0.0761	0.1080	0.0531	0.0015	0.0157	**0.0915**	0.0464	0.4613	0.0699	0.0166
VNS-Mg-06	0.1541	0.0688	0.0848	0.0009	0.0057	0.0049	**0.0810**	0.1316	0.4207	0.0370	0.0107
VNS-Mg-07	0.0490	0.0403	0.0608	0.0045	0.0079	0.0101	**0.1136**	0.1126	0.5237	0.0664	0.0110
VNS-Mg-08	0.0799	0.0675	0.0035	0.0326	0.0088	0.0531	**0.0978**	0.0614	0.5524	0.0301	0.0130
VNS-Mg-09	0.1345	0.0466	0.0068	0.0018	0.0037	0.0582	**0.1254**	0.1193	0.4361	0.0523	0.0152
VNS-Mg-10	0.0307	0.0483	0.0423	0.0212	0.0044	0.0347	**0.0856**	0.0729	0.5458	0.0981	0.0160

- Measure the viscosity, MCC-1, and crystallinity of samples (next page) that have been fabricated, cooled rapidly and slowly.
- An updated glass composition-property model to high MgO loading was applied using the measured results to extend the range of glass properties.

(5) Quenched glasses

VNS-Mg-01	VNS-Mg-02	VNS-Mg-03	VNS-Mg-04	VNS-Mg-05
				
VNS-Mg-06	VNS-Mg-07	VNS-Mg-08	VNS-Mg-09	VNS-Mg-10
				

- Quenched glass: 9 visibly amorphous, 1 with crystals (VNS-Mg-02, contained ZrO_2)

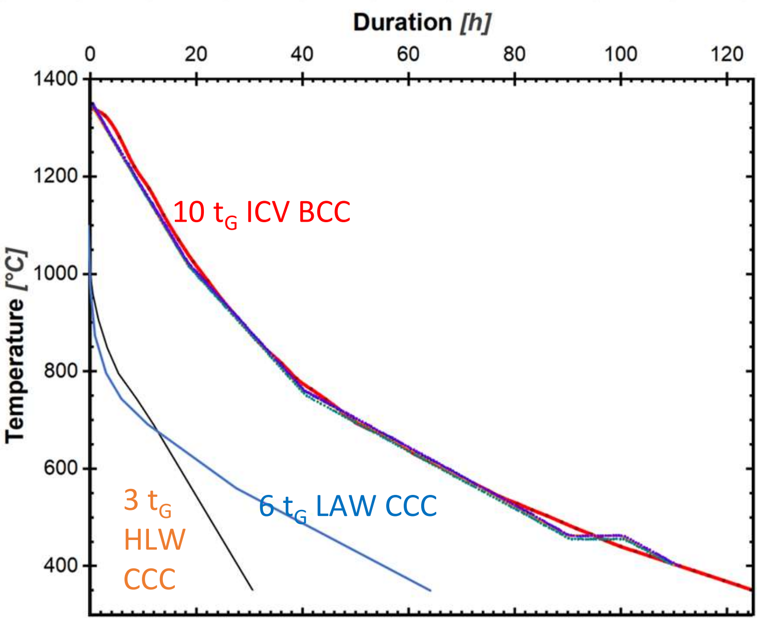
(6) Box center cooling (BCC)

- Glasses were cooled according to the BCC cooling[1] conditions (BCC: Box Center Cooling in the right figure). BCC cooling is:
  - Center of 10 t_G glass in refractory container, the reference for cooling
  - The worst case scenario for MCC-1 durability of cooling in a fireproof box for testing
  - Cooling for 4 days or more from melting to glass transition temperature (Tg)
  - Comparison with 1 day cooling of Hanford Waste Treatment Plant (WTP)
- Since BCC cooling has the slowest cooling rate, crystallization is likely to occur (see the table below), and it is the worst condition for glass properties among cooling methods.

1: The melted glass samples were placed in a fireproof box and cooled by controlling the temperature at the center according to the BCC cooling conditions. The blue line for BCC cooling in the figure below showed the furnace temperature control program modeled on the BCC cooling data for 10 t_G glass, and the red line showed the temperature profile of the glass sample when cooled according to the blue line program.

***NL(B)* at 28 days for all VNS-Mg annealed and BCCed glasses and total crystallinity in BCCed glasses**

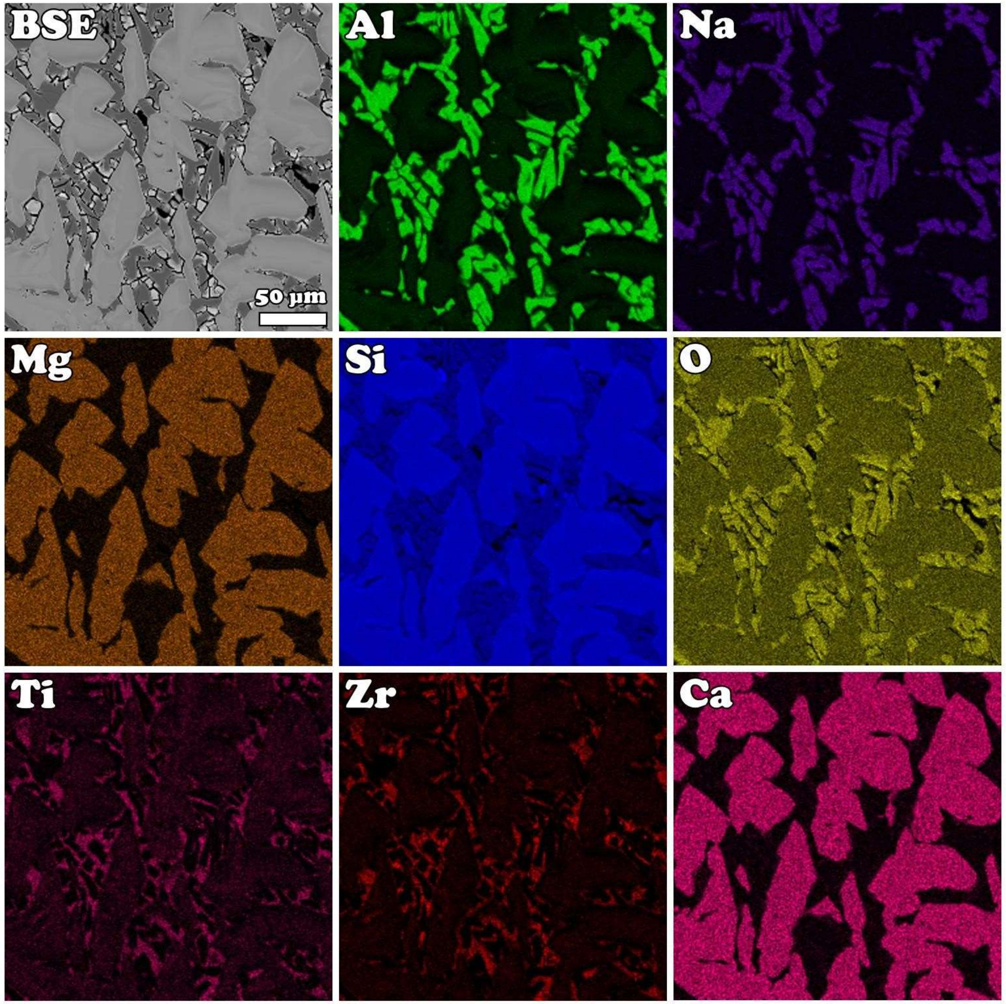
Glass	NLB(28 d) Annealed $g \cdot m^{-2}$	NLB(28 d) BCC $g \cdot m^{-2}$	BCC Total Crystallinity wt. %
VNS-Mg-01	7.5 ± 0.7	2600±250	72.8
VNS-Mg-02	9.7 ± 0.9	17.7 ± 1.7	22.9
VNS-Mg-03	9.1 ± 0.9	33.0 ± 3.2	59.9
VNS-Mg-04	9.4 ± 0.9	117 ± 11	36.4
VNS-Mg-05	8.2 ± 0.8	19.3 ± 1.8	48.6
VNS-Mg-06	11.2 ± 1.1	17.0 ± 1.6	3.8
VNS-Mg-07	12.7 ± 1.2	13.1 ± 1.3	7.8
VNS-Mg-08	7.5 ± 0.7	7.3 ± 0.7	0.1
VNS-Mg-09	9.7 ± 0.9	329 ± 31	54.0
VNS-Mg-10	10.0 ± 1.0	11.5 ± 1.1	7.1



BCC and CCC cooling profiles

(7) Analysis Result of SEM (EPMA)-EDS

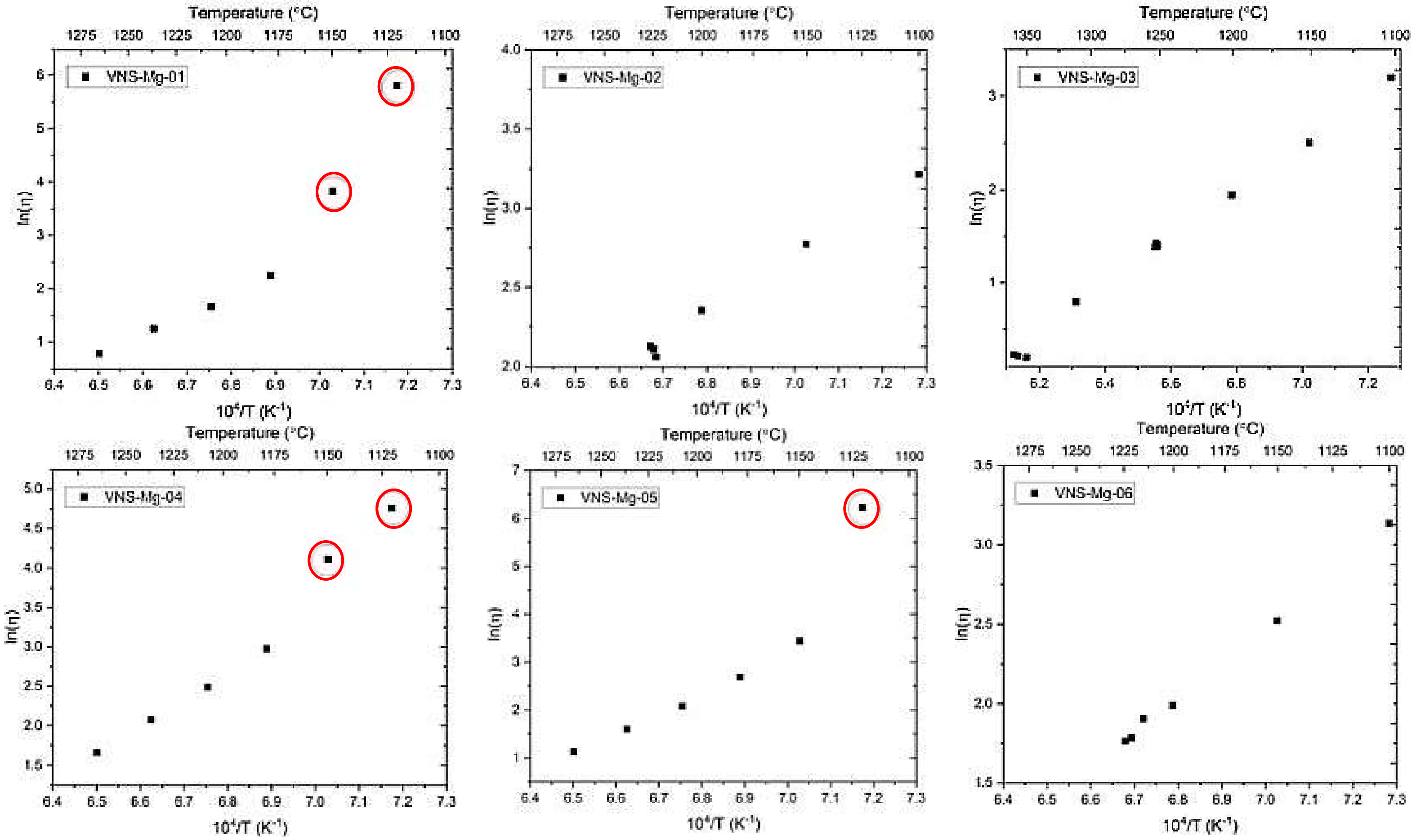
- Among the 20 samples produced under this study (10 quenched, 10 BCCed), 5 were selected for SEM-EDS analysis. Right Figure show the distribution of key elements after crystallization. The elements Al, B, Na, Mg, and Si were collected using WDS and Ca, Ti, Cl, Cr, Cs, Ni, P, S, and Zr were collected by EDS.
- Zr-rich regions were observed in all the samples, which was observed by XRD in these samples as baddeleyite (ZrO_2). In some cases, Ti appeared to be associated with the Zr-rich regions.
- Mg, Ca, and Si were commonly correlated in these samples which matches well with pyroxene group (augite and diopside) and olivine group (forsterite) phases observed by XRD.
- Al, Na, and Si were correlated in all the samples, some samples (VNS-Mg-01, -04, and -09) match well with nepheline that was determined by XRD.
- In other cases, Al, Na, Si, and B were correlated and represent the remainder glass phase, in samples VNS-Mg-03 and -05.
- Al, Si-rich dendrites were observed in VNS-Mg-04 sample that could be eucryptite based on XRD analysis. However, because the Li cannot be measured by the EPMA (neither by EDS nor WDS), its presence had to be assumed.



An example of analysis results: VNS-Mg-01 elemental distribution maps measured by EPMA WDS (Al, B, Mg, Na, and Si) and EDS (O, Ca, Zr, and Ti). Al,Na,Si-rich nepheline, Mg,Ca,Si-rich diopside, and Zr,Ti rich baddeleyite

(8) Viscosity measurement data

- The viscosity results were plotted in Figure below as ln(η) vs. $10^4/T$ with viscosity units of Pa·s and temperature units of K. A secondary (top) x-axis provided temperature in ℃ for easy reference.
- For several glasses, the measurements at 1150℃ and/or 1100℃ deviated from the line formed by the higher temperature data points, likely as a result of crystallization in the melt.
- These data points, circled in red in Figure below, were not used for model fitting for the glasses.



Viscosity measurement example: Viscosity data when measuring VNS-Mg glass. Viscosity is displayed in Pa･s.

(9) Increased waste loading of ALPS Carbonate slurry

- New models based on the glass property data (crystallinity, MCC-1, etc.) obtained in the test (see page 73) was needed to develop in order to enable accurate predictions in the area where can be vitrified with higher waste loaded ALPS slurry.
- New property models were applied to examine the formulation
  - *MCC-1 durability model*
  - *Aluminosilicate crystallization model on BCC*
  - *Mg-containing phase crystallization model*
- 15 glasses with various blends of KUR-EH, ALPS carbonate and ALPS iron coprecipitate slurry by updated glass composition property model was formulated, and the composition of Melt 12 was determined (right table: Melt 12).

- Constraints/assumptions
  - *Melt temperature = 1300°C*
  - *MCC-1 NL_B = 7.46 g/m^2 at 28d (new model)*
  - *PCT response same as US HLW limit*
  - *VHT response same as US LAW limit*
  - *Viscosity between 10 and 100 P*
  - *Electrical conductivity between 10 and 70 S/m*
  - *No Nepheline or Eucryptite (new model)*
  - *< 45 wt% Mg-containing phase (new model)*
  - *No immiscible phase separation (Taylor method)*
  - *No separated sulfate salt*

Glass	Melt 1, 5 (Original model)	Melt 12 (New model)	
Waste loading rate	81.7	75.1	
ALPS carbonate slurry	19.5	$\boxed{29.5}$	⇒ 51 Relative % increase
KUR-EH	57.0	45.6	
ALPS Iron slurry	5.2	0	
Content in glass			
MgO	8.3	$\boxed{12.5}$	⇒ 51 Relative % increase

(10) Summary – Increased waste loading of ALPS carbonate slurry

- This study examined glass compositions containing 8 to 13.5 wt% MgO.
- Testing performed on 10 statistically designed glasses:
  - MCC-1 on quenched and slow-cooled glass (annealed, BCCed), crystallization observed by XRD
  - SEM measurement on 5 glasses
  - Viscosity measurement
- Data collected during testing allowed to update glass composition-property models:
  - Updated MCC-1 durability model[1] for annealed glass samples
  - Updated crystallinity model[1]
  - New MCC-1 durability model[1] for BCCed glass samples
  - Updated viscosity model[1]
- Formulate glass for Melt 12 using the updated glass composition-property model. This glass formulation increased the waste loading of the ALPS carbonate slurry by 51 relative percent (increased from 19.5% to 29.5%).

  Note that since the $Mg(OH)_2$ content in the ALPS carbonate slurry stored in large quantities is a limiting factor for increasing the loading rate of the carbonate slurry waste, increasing the MgO in the glass requires increasing the waste loading of the ALPS carbonate slurry.

1: The property models (viscosity, nepheline crystallization, Mg-bearing phase crystallization, effect of crystal-free glass MCC-1 response and effect of crystals on MCC-1 response) developed as a function of glass composition from glass property measurement data in additional tests, which were the models for analyzing the constraints used in the glass composition-property model for analyzing the final glass formulation.

7.4.2 Impact of refractory on glass durability
(1) Goals and control experiments

Goal: Evaluate the effect of refractory on glass durability

- Two control experiments:
  - A – quantify element release from glass alone
  - B – quantify element release from refractory alone

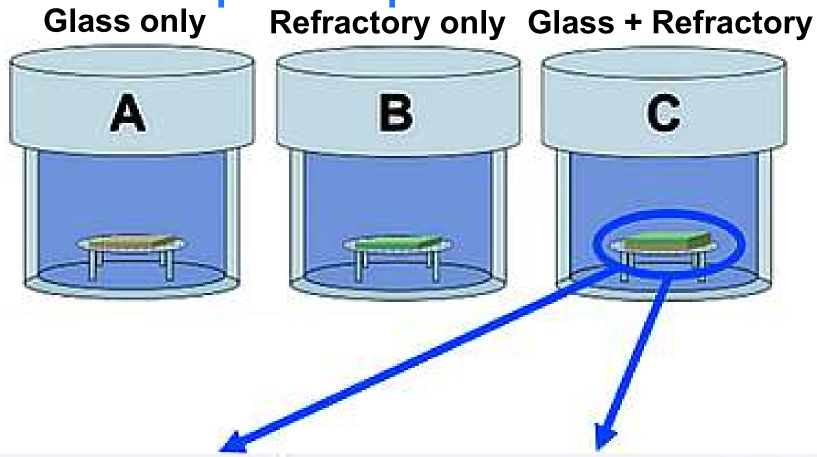
- Glass + refractory experiment:
  - C-Implement in two different configurations

Tight and loose configurations:

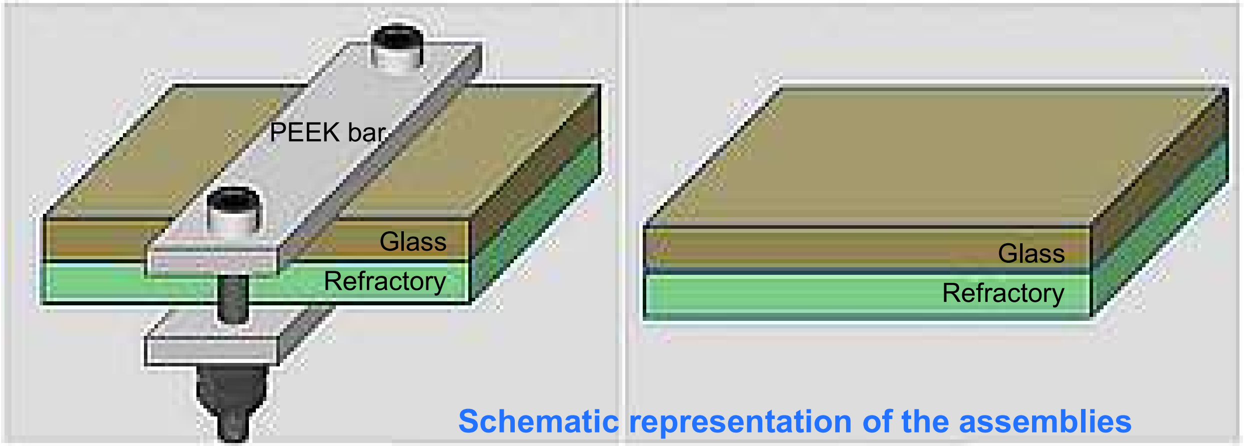
Detailed on the right and next slide

PEEK: **P**oly **E**ther **E**ther **K**etone

Simplified representation

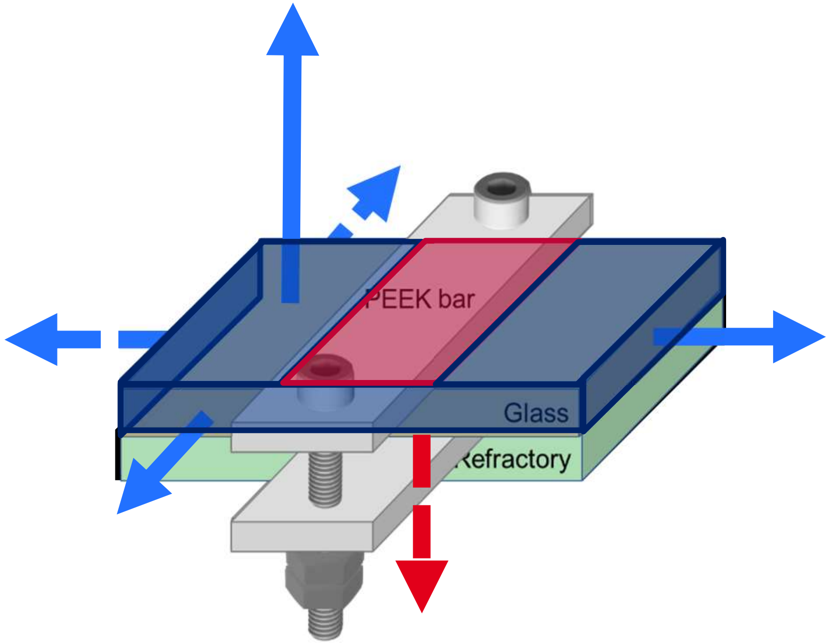


C - Tight configuration	C - Loose configuration
Effect of refractory if water penetration between glass and refractory is none to minimal.	Effect of refractory if water is allowed to penetrate between glass and refractory.

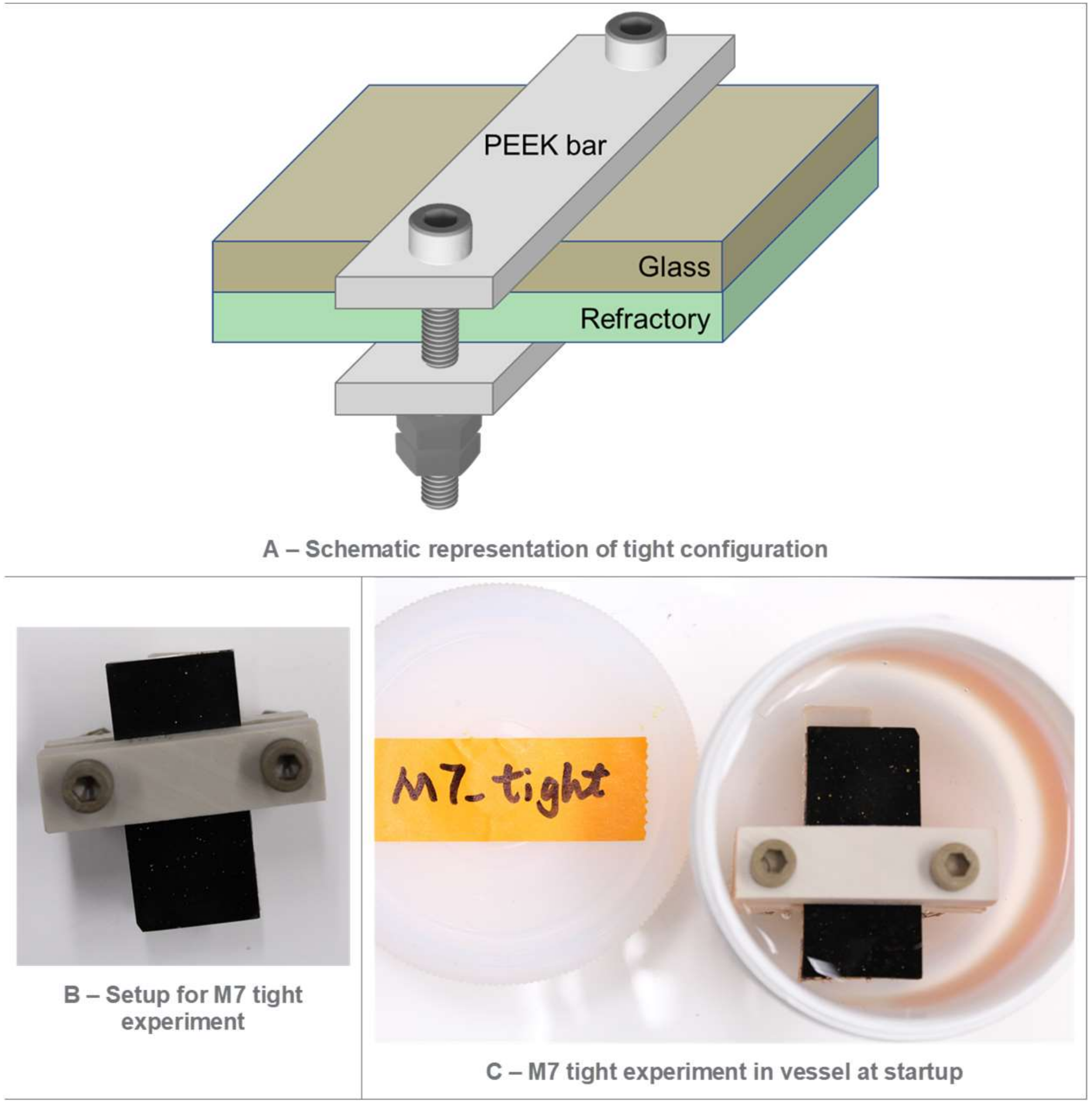


Schematic representation of the assemblies

(2) Tight configuration



5 sides of the glass coupon have their surface area (blue) exposed to water (→), the face contacting the refractory was not exposed (↓) to water (red)
Furthermore, the part ( ) of the upper surface of the glass that was in contact with the PEEK bar was not exposed to water.

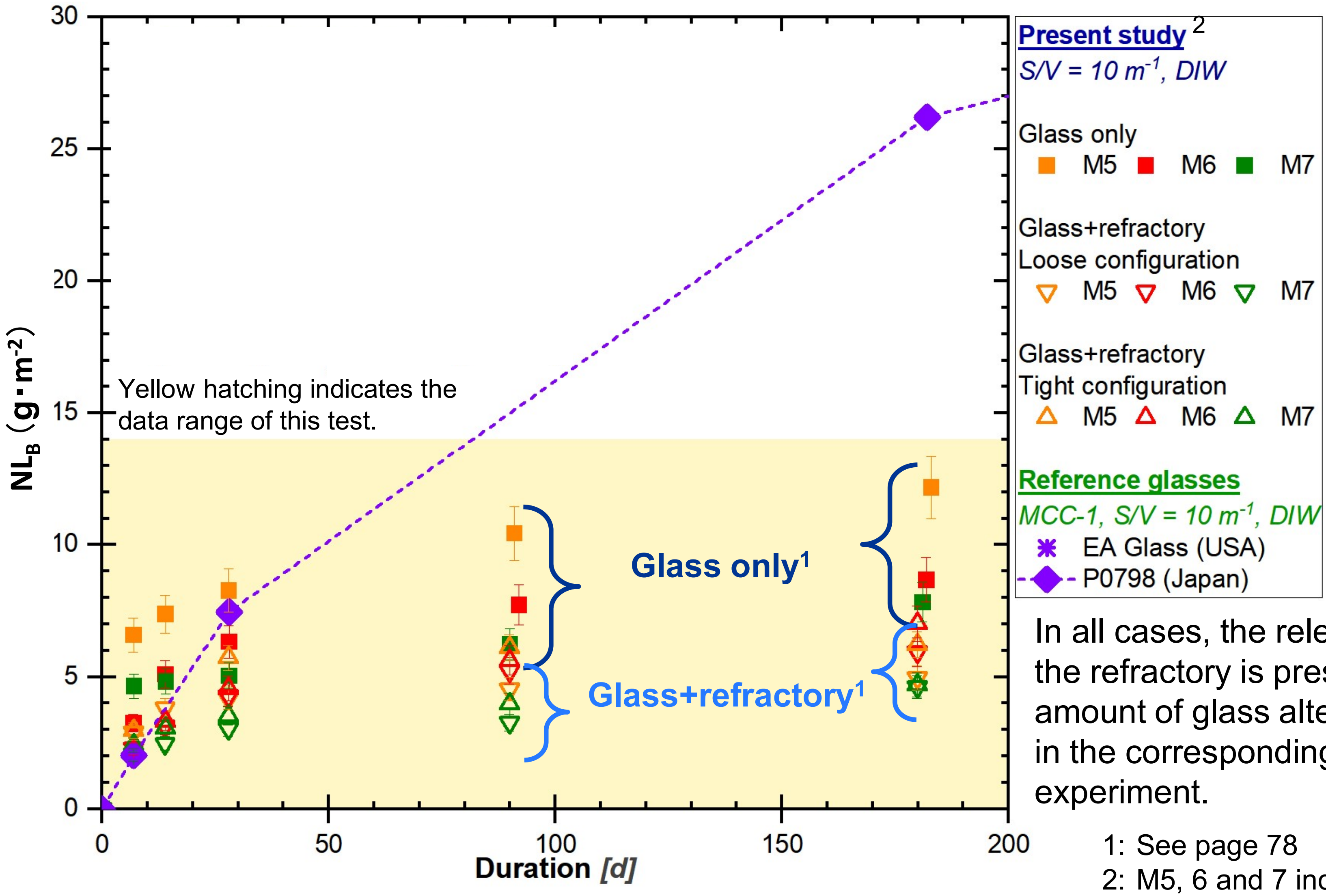


A – Schematic representation of tight configuration

B – Setup for M7 tight experiment

C – M7 tight experiment in vessel at startup

(3) Comparison of glass leaching amount (from boron release)



Comparison of glass leaching amount

In all cases, the releases observed when the refractory is present show a lower amount of glass altered (lower NL_B) than in the corresponding glass-alone experiment.

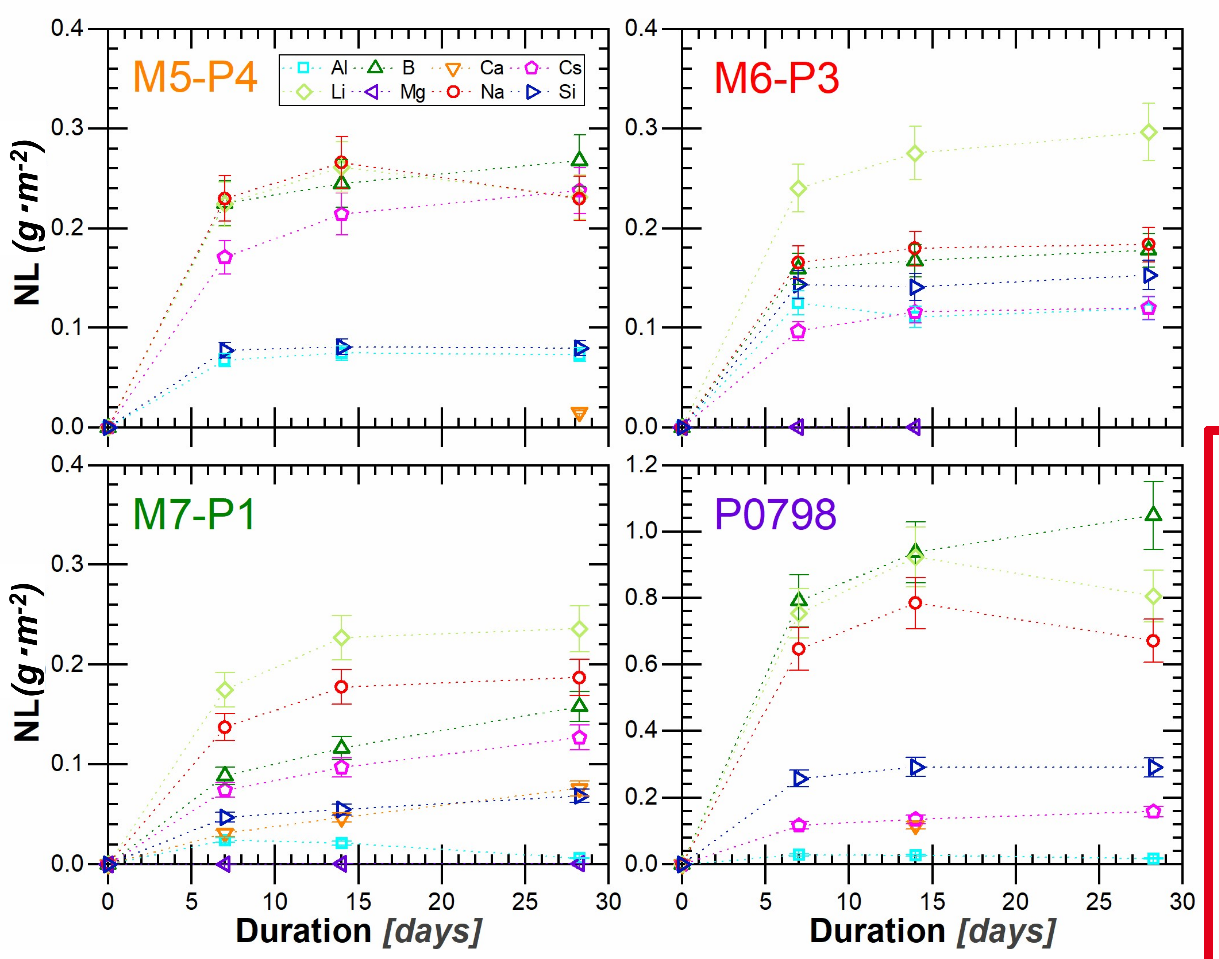
1: See page 78
2: M5, 6 and 7 indicate Melts 5, 6 and 7.
3: Refractory-only results are not shown as they do not affect glass durability.

(4) Summary – Refractory impact on glass durability

- Refractory was co-existing material in the vicinity of glass and could affect the durability of glass.
- Durability of glass and refractory co-existed in the alteration vessel was evaluated.
- The coexistence of refractory had a beneficial effect (reduced leaching of glass at disposal) compared to glass alone.
- There was no significant difference in the effect of different configurations of glass and refractory (tight and loose configurations) on the durability of the glass when the refractory co-existed.

7.4.3 Glass durability test
(1) PCT results

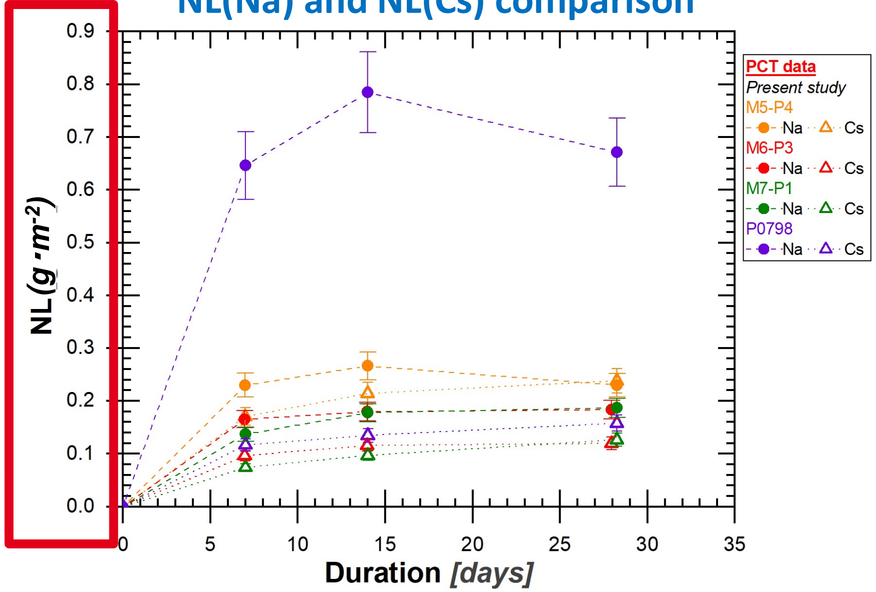
- All 3 glasses (M5/M6/M7[1]) released Na/B/Li (glass alteration tracers) in a similar manner, but the amount is lower than P0798[2].
- Cs release for M5/M6/M7 were similar to P0798, and lower than Na release.



1: M5, 6 and 7 indicate Melts 5, 6 and 7.

2: P0798 glass are Japanese HLW glasses and are the reference glasses for comparison of the glasses evaluated in this test.

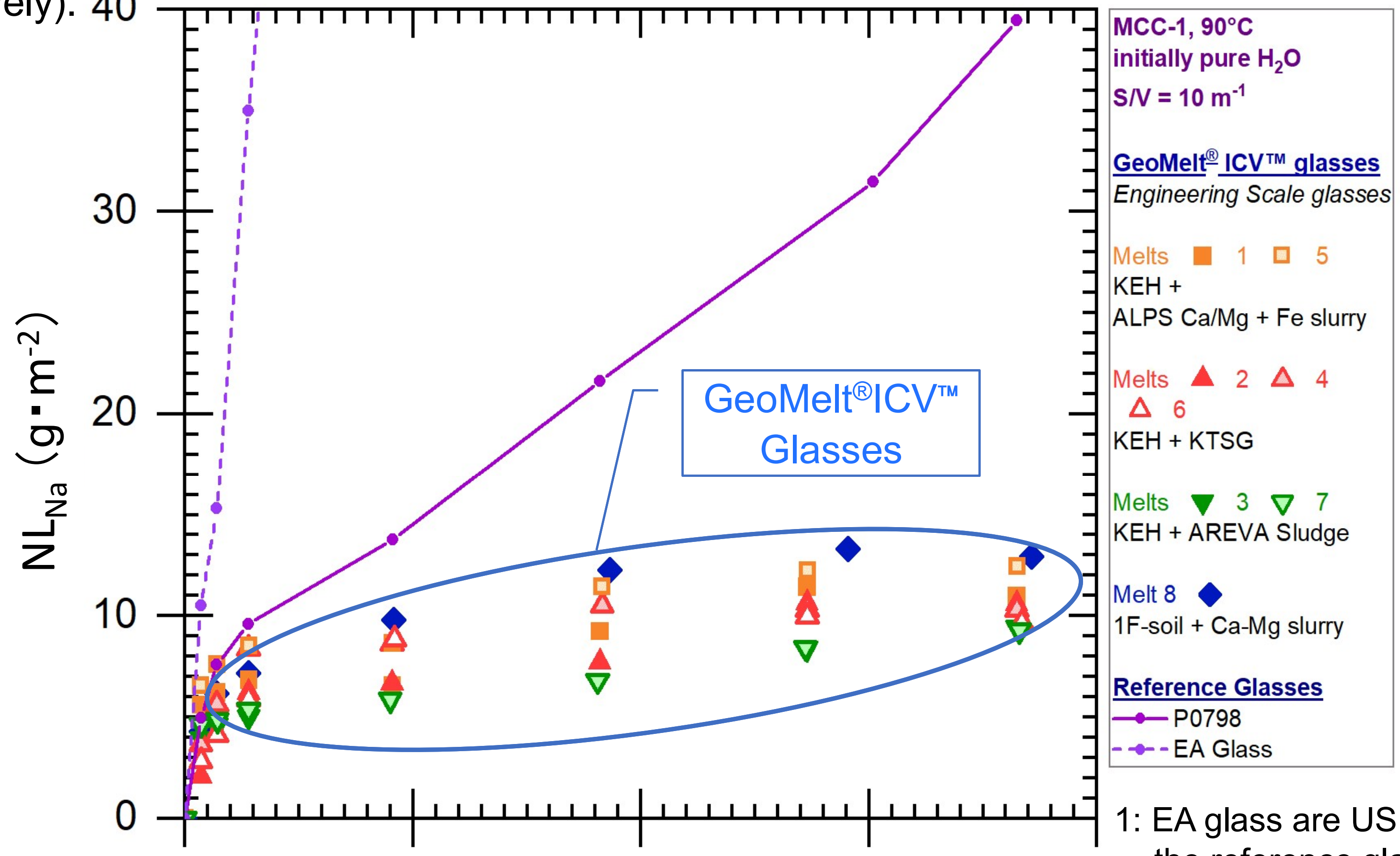
NL(Na) and NL(Cs) comparison



Glass durability test (PCT) results

(2) MCC-1 long-term durability test results

- Average data from 3 samples for each glass (In this project, the melting tests 6, 7, and 8 of the glass were continued to be carried out.
- All NL_{Na} < NL_{Na} for P0798 at 28 day.
- Fast initial release, then slowing down and stabilizing beyond 28-90 day.
- All GeoMelt glasses show a lower release than the Japanese and US reference glasses (P0798, EA glass[1], respectively).



1: EA glass are US HLW glasses and are the reference glasses for comparison of the glasses evaluated in this test.

MCC-1 long-term durability test results

(Reference) Data of MCC-1 long term durability tests

The average results of MCC-1 are shown in the table below.

Updated Na MCC-1 normalized mass loss NL_{Na} and Na leaching rate (average)

Glass	NL_{Na} *at 28 day* (g/m^2)	28–365 day Leach Rate (g/m^2·d)
Melt 1	6.8 ± 1.1	$(1.8 \pm 2.0) \times 10^{-2}$
Melt 2	6.2 ± 0.7	$(1.6 \pm 0.5) \times 10^{-2}$
Melt 3	5.0 ± 0.2	$(1.6 \pm 0.5) \times 10^{-2}$
Melt 4	8.4 ± 2.0	$(6.6 \pm 2.2) \times 10^{-3}$
Melt 5	8.5 ± 0.0	$(1.2 \pm 0.1) \times 10^{-2}$
Melt 6	5.9 ± 1.3	$(7.6 \pm 7.5) \times 10^{-3}$
Melt 7	5.4 ± 0.4	$(1.1 \pm 0.8) \times 10^{-2}$
Melt 8	6.0 to 8.4	5.1×10^{-3}
P0798	9.59	9.0×10^{-2}

Uncertainty = 2 standard deviations; not provided for Melt 8 as only two replicas were made.

7.5 Investigation on the Applicability of GeoMelt®ICV™
(1) Purpose and Method

➢ Purpose

Holistic evaluation on the Applicability of GeoMelt®ICV™ technology to actual processing plants

➢ Method

Based on the results of past tests and preliminary conceptual design, as well as the test results obtained in this project, the following items will be comprehensively evaluated from a technical point of view.

1. Retrieval, Transport and Feeding
2. Solidification Processing Equipment
3. Off-gas and Secondary Waste Treatment
4. Compliance with Regulations
5. Waste Specification and the Influence of Composition Fluctuations
6. Transfer Rate of Cs, etc. to the Off-gas System
7. Leaching Rate of Nuclides from Solidified Materials
8. Integrity of Heat-affected Containers at Disposal
9. Economic Efficiency of Containers
10. Technical Issues of Melting in the 10-ton Melter

(2) Result[1] of Evaluation (1/4)

Items	Results of tests	Results of design study	Evaluation
1. Retrieval, Transport and Feeding	✓ It has been demonstrated that major 1F waste including ALPS carbonate・iron coprecipitate Filtercake (Hereafter referred to as "ALPS Filtercake") would be fed to melter without problems.	✓ The system of retrieval of waste from Kurion and SARRY vessels and transport / feed systems have been designed in Pre-Conceptual Design (PCD)	✓ No problem would be foreseen in GeoMelt®ICV™ for transport and feed of major 1F waste including ALPS Filtercake. ✓ As for retrieval of waste, the equipment designed in PCD would be needed to be demonstrated.
2. Solidification Process Equipment	✓ It has been demonstrated that solidification process equipment (melter and perimeter system equipment) can melt 1F waste. ✓ Melt preparation steps, which was set considering steps in actual plant, has been demonstrated.	✓ 10 tons scale melter and perimeter system equipment have been designed in PCD.	✓ In GeoMelt®ICV™, no problem in operation of solidification process equipment in Engineering Scale Test equipment. ✓ No problem would be foreseen in 10 tons scale melter.
3. Off-gas and Secondary Waste (generated with plant operation) Treatment	✓ It has been demonstrated that Sintered Metal Filter (SMF) installed in off-gas treatment system has high efficiency of particulate (Cs included) capture in Engineering-Scale Tests (EST). ✓ It has been demonstrated that particulate captured in SMF can be recycled to Melter during melting operation.	✓ The off-gas treatment system with SMF, scrubber and HEPA has been designed and the removal efficiency has been studied in PCD. ✓ Recycle of secondary waste water from off-gas treatment system and waste retrieval system and melt treatment of secondary solid waste generated with plant operation have been studied.	✓ The effectiveness of SMF was confirmed by the melting test, and it was thought that there was no problem with the configuration of the off-gas treatment system examined in PCD. ✓ Efficient treatment of secondary waste generated during operation with solidification process equipment would be considered possible.

1: Based on the results of the tests conducted in this project, the PCD conducted in previous projects was reviewed and evaluated in this project.

(2) Result of Evaluation (2/4)

Items	Results of tests	Results of design study	Evaluation
4. Compliance with Regulations	✓ No test implemented.	✓ Compliance with Japanese Law and Regulations has been considered in PCD.	✓ No problem would be foreseen in regard of compliance with Japanese Law and Regulations.
5. Waste Specification and Influence of Composition Fluctuations	✓ Glass formulation corresponding to waste specification has been set and the fabricated glass performance has been verified by crucible tests	✓ Influence of composition fluctuations and melting temperature has been confirmed with PNNL glass modeling (glass composition-property model).	✓ GeoMelt®ICV™ can handle high-temperature and high-viscosity glasses, and is highly flexible in setting glass formulations. It is also possible to minimize the number of vitrified waste while maximizing compositional variation by mixing waste and high melting temperatures. ✓ It is highly applicable to 1F waste treatment where waste of various specifications exists.
6. Transfer Rate of Cs, etc. to Off-gas Treatment System	✓ Transfer Rate of Cs, etc. to the off-gas treatment system in each step of melting process have been measured in EST. ✓ The transfer rate increases in the final stage of melt, but due to the cold cap management the total amount of Cs released is below several percents of Cs in feed. ✓ It has been demonstrated that the most part of particulate captured by SMF can be recycled to melter.	✓ The transfer rate has been set based on the EST results and designed the off-gas treatment system in PCD.	✓ High retention rate (almost 100%) can be obtained by the combination of cold cap management and SMF.

(2) Result of Evaluation (3/4)

Items	Results of tests	Results of design study	Evaluation
7. Leaching Rate of Nuclides from Solidified Materials	✓ Leaching test (MCC-1) was implemented using glass obtained by EST, leaching rate was confirmed. ✓ It has been a lower leaching rate compared to the Japanese and US Reference glasses (P0798, EA glass, respectively). ✓ The leaching rate in the condition of refractory coexistence which is in disposal environment of GeoMelt®ICV™ glass has been confirmed and it has been verified that no factor to accelerate the leaching rate.	✓ If an evaluation model[1] that considers the nuclide confinement performance can be applied, it is evaluated that there is a possibility that it can be classified as pit disposal from the viewpoint of the upper limit of concentration.	✓ It is thought to be possible that GeoMelt® ICV™ glass may be categorized for pit disposal.
8. Integrity of Heat-affected Containers at Disposal	✓ No test implemented.	✓ Influence of heat of melting process on the structure of the 10 tons scale melter has been studied in PCD ✓ Maximum temperature of steel container of melter has turned out to be well lower than softening temperature of steel.	✓ High temperature due to melting process would have no effect on the integrity of the steel in GeoMelt®ICV™
9. Economic Efficiency of Containers	✓ No test implemented.	✓ Economic Efficiency of containers have been studied in the regard of container structure simplicity of function, treatment of high viscosity and high temperature glass, flexibility, robustness and efficiency of energy supplied. ✓ It has an advantage compared to the glass pouring type melter.	✓ GeoMelt®ICV™ has many elements of economic superiority.

1: Created by the projects so far.

(2) Result of Evaluation (4/4)

Items	Results of tests	Results of design study	Evaluation
10. Technical Issues of Melting in the 10-ton Melter			✓ Waste treatment issues were evaluated with PCD and verified with melting tests. ✓ It would be evaluated that technical issues for 10 tons scale melter operation have been solved in GeoMelt®ICV™.
① System Operability, Operational Conditions	① Stable operation of melter (melt treatment) has been demonstrated by EST. It was demonstrated that stable operation will be implemented by adjusting the electric power supply according to the specification of waste.	① PCD is considering applying the operating method based on the GeoMelt®ICV™ design, which has been successfully used for the past 20 years, to the 1F GeoMelt®ICV™ equipment. The effect of SMF is described in "3. Treatment of off-gas and secondary waste generated during operation" and "6. Transfer rate to off-gas system such as Cs".	
② Uniform Supply of Waste	② It has been demonstrated that uniform supply of waste, glass frit and discharged particulate from SMF could be provided by single chute in EST.		
③ Temperature Distribution and Product Homogeneity	③ It has been verified that temperature distribution in the melter can be attained in melter as expected. Sampling and measurement of produced glass has proven the product homogeneity in EST.		
④ Restart of Vitrification after Interruption	④ In EST, the melting was interrupted in the middle of the melting process, and then the melting of the solidified glass was started again. It was demonstrated that melting can be restarted and processing can be completed.	④ Based on the method implemented by EST, the system and equipment for remote re-start of interrupted melt has been studied in PCD	

8. Summary (1/2)

➢ Study on suppression of Cs emission in the final stage of melting:

- ✓ It was obtained that the data on the timing of top-off frit (TOF) supply after the completion of waste supply in the final stage of melting, the supply amount (TOF layer thickness), and the relationship between the melt surface temperature and the amount of Cs volatilization.
- ✓ Cs volatilization was suppressed to ~0.3% of Cs in the waste with a TOF layer thickness of 10 cm using basic test equipment. As the TOF layer becomes thinner, Cs volatilization increases, and when the TOF layer was absent, it increased significantly at a surface temperature exceeded 1130℃.
- ✓ Timing of TOF supply was appropriate to be before the end of water evaporation from the surface of the waste mixture. The operation method of the engineering-scale melting test to supply as soon as possible after the waste supply was appropriate.
- ✓ FEM was used to simulate the vertical temperature distribution of waste molten glass and TOF molten glass. By setting the thermal conductivity in consideration of the presence of a bubble layer and the increase in radiation heat transfer due to the transparency of the TOF molten glass, the temperature measurement results obtained by the basic test could be simulated. The suppression of surface temperature rose due to the increase in radiation heat transfer was also a mechanism for the suppression of Cs volatilization by TOF.

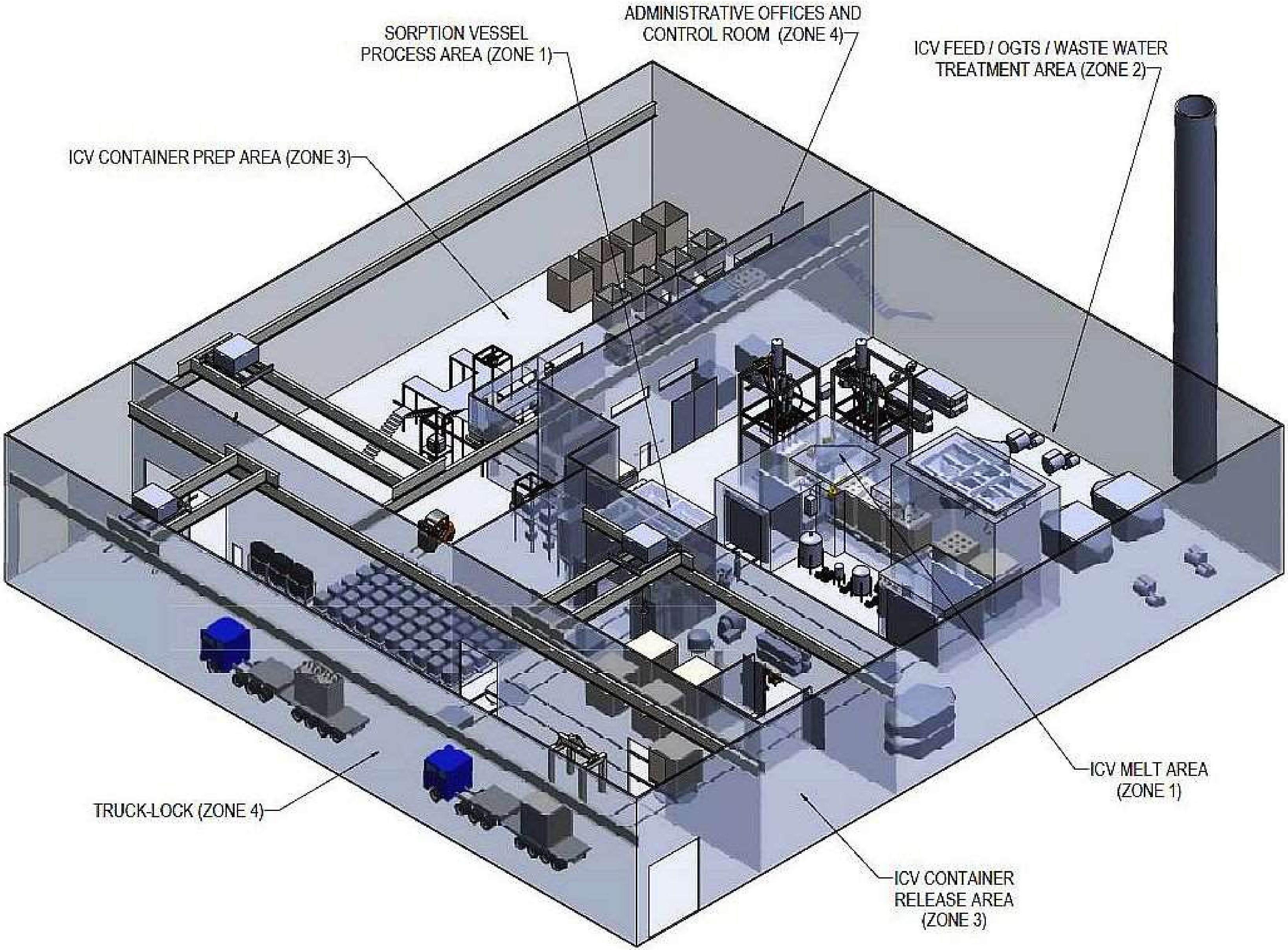
➢ Engineering-scale melting tests:

- ✓ Engineering-scale system was partly modified (installation of SMF etc.) and 4 melting tests were conducted.
- ✓ The waste with water content increased to 20%, ALPS Filtercake and ALPS carbonate slurry with increased waste loading (from 19.49% to 29.46%) were tested and melt treatment of these waste were demonstrated. The transportability and feedability of ALPS Filtercake was verified by elemental test prior to melting test.

Summary (2/2)

- **Engineering-scale melting tests (continued):**
  - ✓ The operability of SMF was demonstrated by recycling of captured particulates to the melter at the timing just before the TOF supply.
  - ✓ Cs retention rate was in the range of 86.82 to 97.97% only by cold cap management. It was improved to the range of 95.95% to 99.26% by taking the recycle from SMF into account.
  - ✓ Cs retention was expected to be more reliable by recycling particulates from SMF to the melter as the first feed waste of the next melt processing batch instead of just before the TOF feed. Furthermore, since the Cs adhering to the SMF housing and the piping to SMF was washed away with water after the melting was completed, it was reasonable to set the Cs retention rate to 99.98% in the design of the actual treatment plant.
- **Glass durability:**
  - ✓ A test was conducted to understand the influence of coexistence of glass and refractory, which were components of the melter, in the disposal environment.
  - ✓ By comparing the durability test results under the condition of glass and refractory coexistence and the condition of glass only, it was verified that there was a beneficial effect (reduction of glass leaching amount) under the condition of coexistence of refractory. Elements (assumed to be Si, Al, and Ca) released from refractory may have an effect.
- **Holistic evaluation on the applicability of GeoMelt®ICV™ technology to the treatment for 1F water treatment secondary waste:**
  - ✓ Based on the results of the tests and pre-conceptual design conducted by the subsidized project, the impacts of solidification equipment, transfer speed of Cs, etc. to the off-gas system, waste specifications and composition fluctuations, etc. were evaluated.
  - ✓ GeoMelt®ICV™ technology was comprehensively evaluated for its excellent applicability to the treatment for 1F water treatment secondary waste. A bird's-eye view of the actual treatment plant was shown (see next page).

Bird's-eye view of Actual Processing Plant (10-ton batch by PCD)



Finally

These are the Results of the Holistic Evaluation of GeoMelt®ICV™ for Treatment of 1F Water Treatment Secondary Wastes conducted as a Subsidiary project of Decommissioning and Contaminated Water Treatment (FY2021) (Research and Development for the Processing and Disposal of Solid Wastes)