Subsidy Project of Decommissioning and Contaminated Water Management
in the FY 2016 Supplementary Budgets

Development of Technology for Fuel Debris Analysis and Characterization

Interim Report

April 2018

International Research Institute for Nuclear Decommissioning (IRID)

CONTENTS

1. Research Background and Purposes

Background of Research

Accident at the Fukushima Daiichi Nuclear Power Station (1F) (March 2011)

Investigate and sort out available knowledge about past incidents, including information on the accident at Three Mile Island Unit 2 (TMI-2) research on severe accidents (SAs), and information related to the 1F accident (2011–2012)

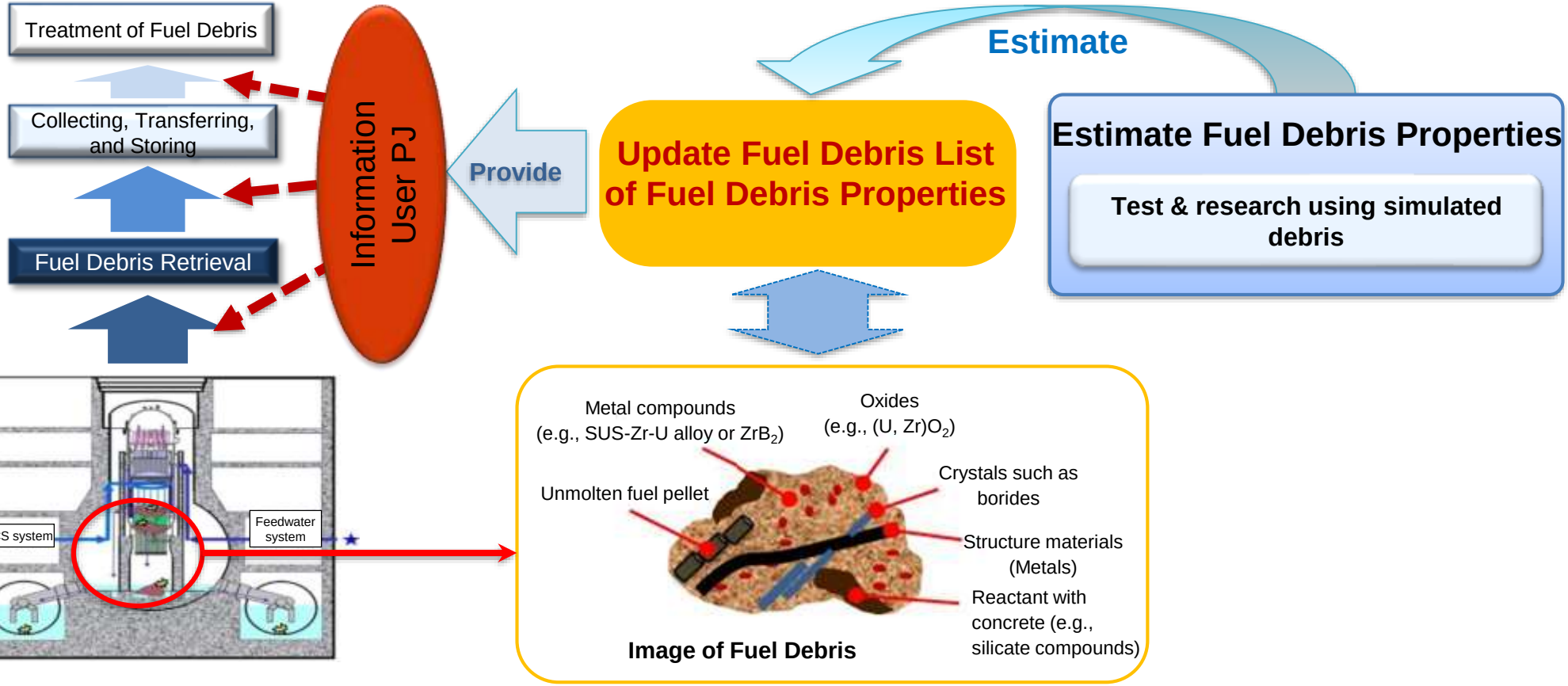
- ✓ Not much has been known about boiling water reactors (BWRs) in the TMI-2 accident or SA research conducted overseas.
- ✓ There is not much information on fuel debris relevant to 1F-specific events, such as the impact of exposure to seawater and the Molten Core Concrete Interactions (MCCIs).

- To execute nuclear decommissioning (retrieval, criticality control, collecting/transferring/storing, material accountancy, and final treatment) safely, steadily, and quickly, it is necessary to sort out and make available fuel debris information that can be leveraged in technical development.
- If accurate fuel debris information cannot be obtained at an initial stage, it is necessary to set up (i.e., assume) fuel debris information based on existing knowledge and research and development projects conducted at home and overseas. This information should be updated and shared among researchers/developers and field workers.
- To determine specific information on fuel debris to be collected, it is necessary to sort out and confirm sufficient project needs and timing requirements (retrieval methods & foundation, collecting/transferring/storing, and criticality control (hereafter referred to as "Information User PJ")) that makes use of such information.

1. Research Background and Purposes

Purpose of Research: (1) Estimation of Fuel Debris Properties and (2) Characterization Using Simulated Debris

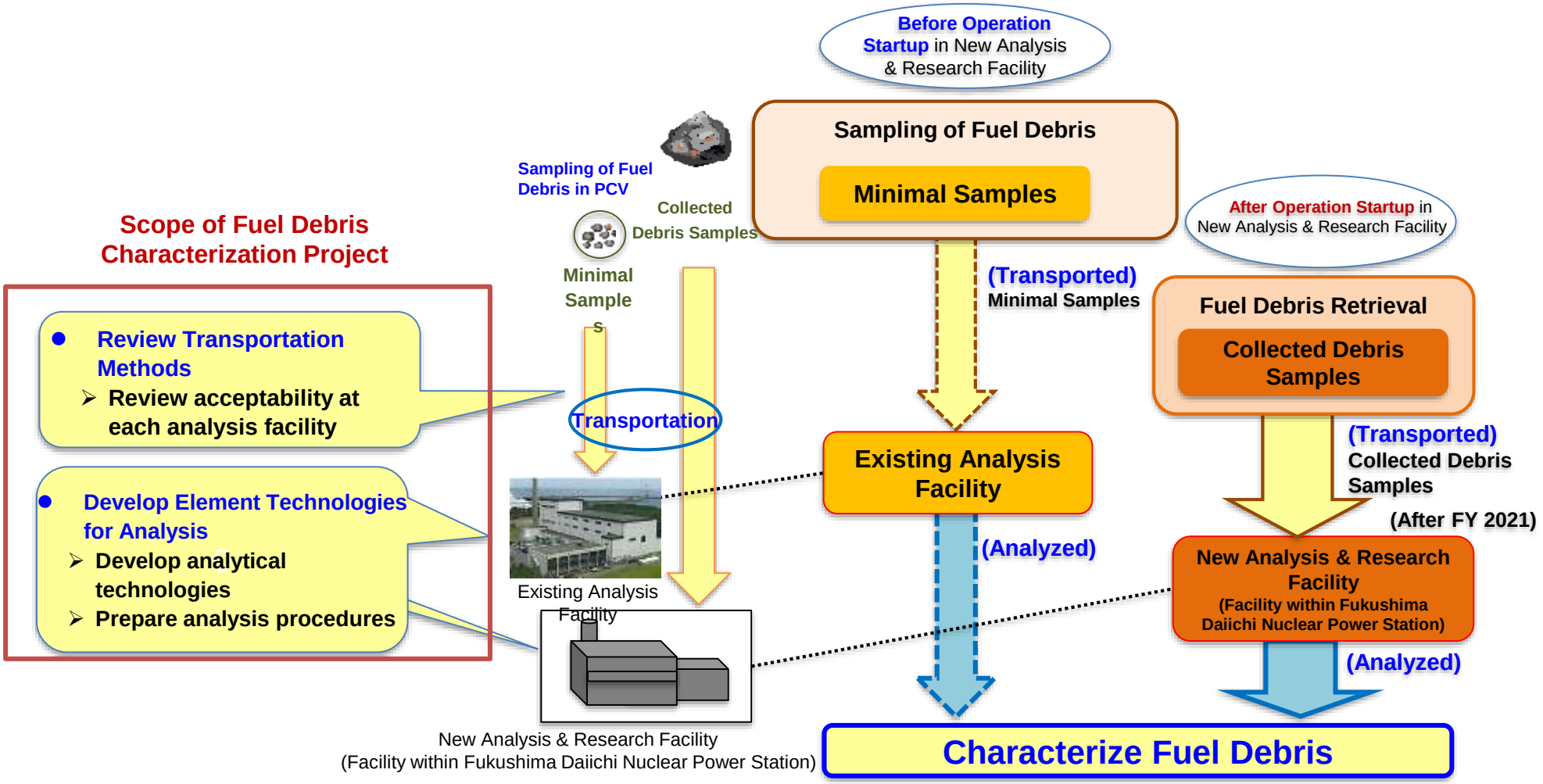
[Purpose] To reflect research results to the "List of Fuel Debris Properties" and provide the updated information to Information User PJ



1. Research Background and Purposes

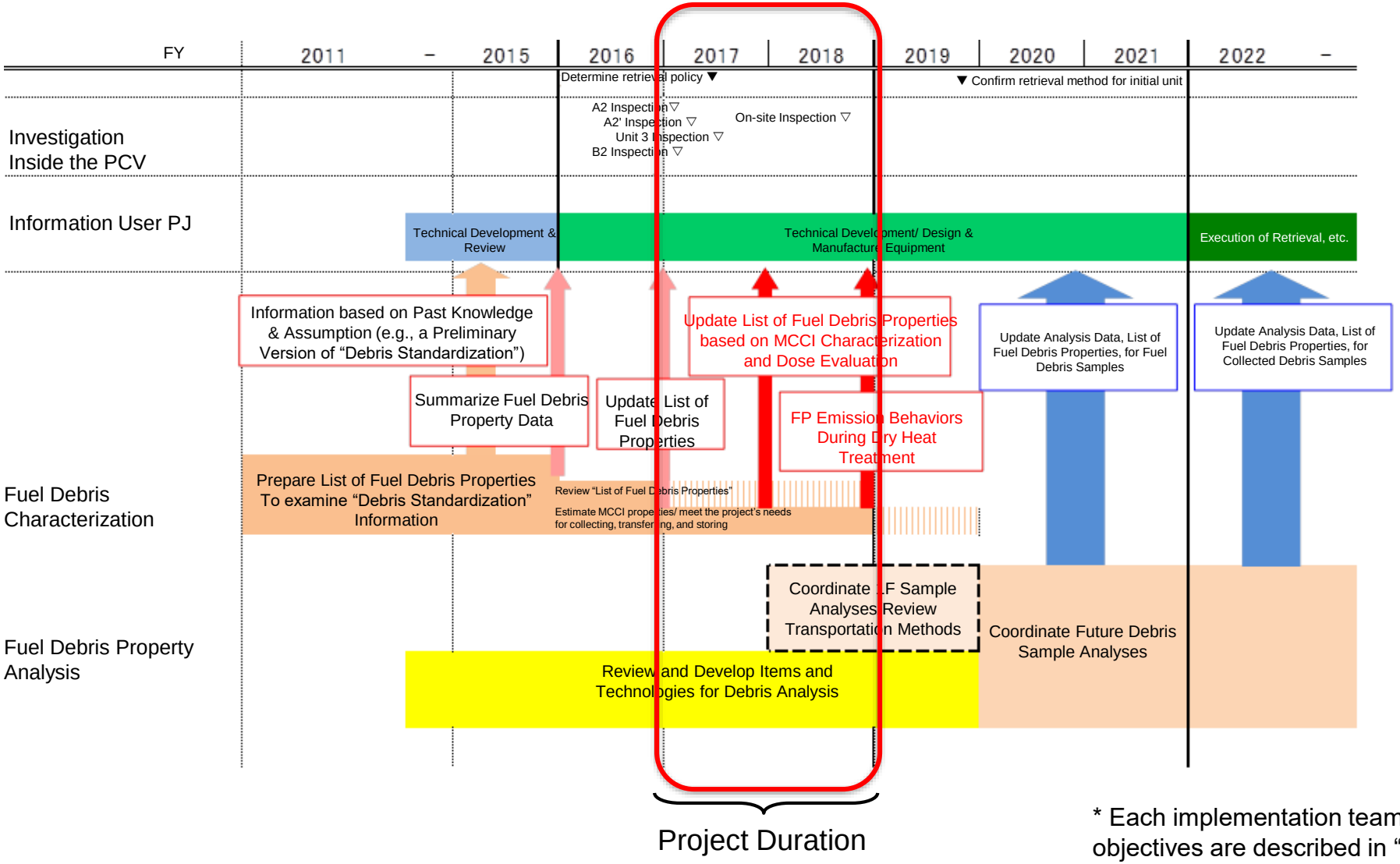
Purpose of Research: (3) Developing of Element Technologies for Analysis on Fuel Debris and Other Materials

[Purpose] To develop analytical technologies while studying transportation methods to analyze facilities for speedy and steady fuel debris analyses



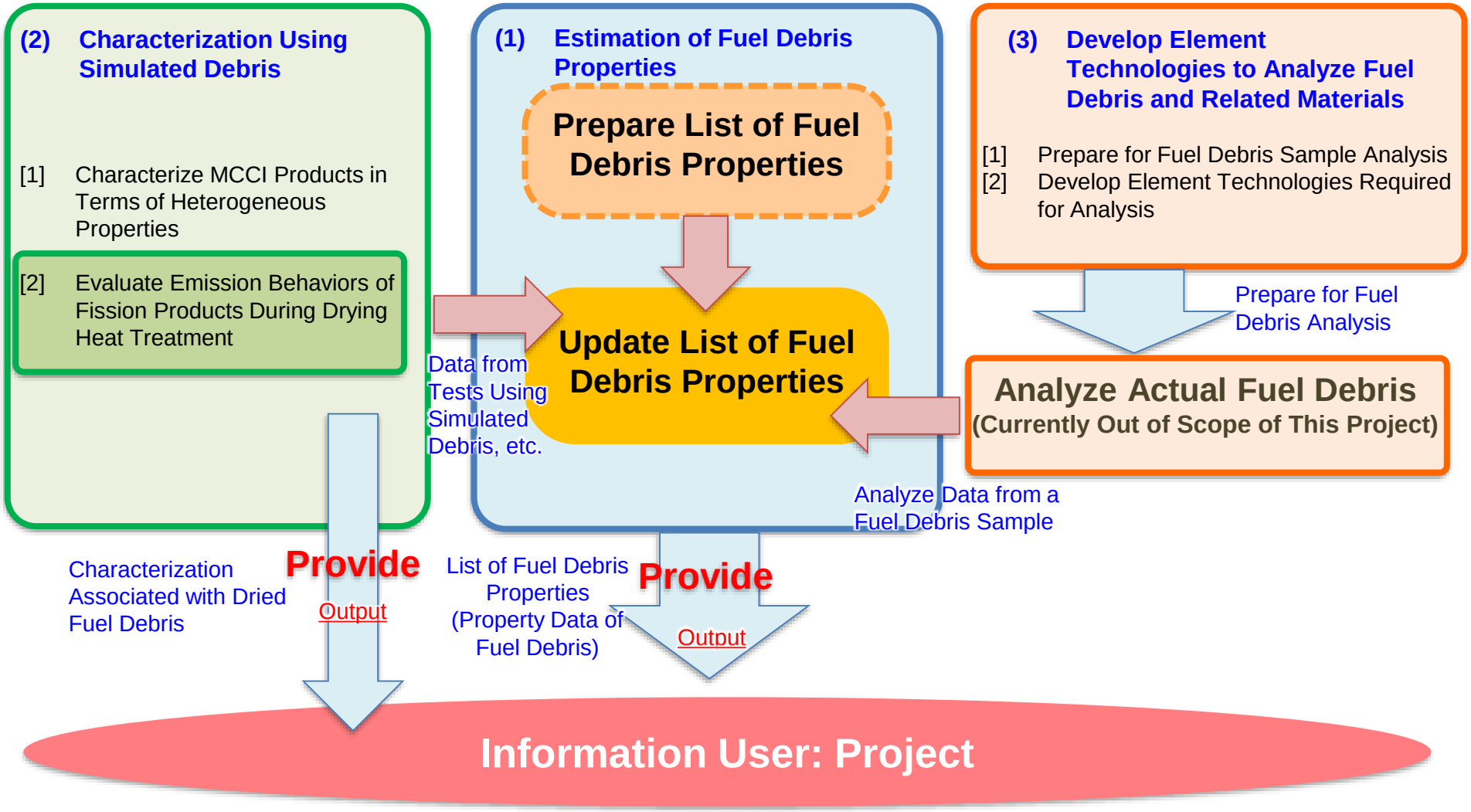
2. Project Goals

Scope and Timing



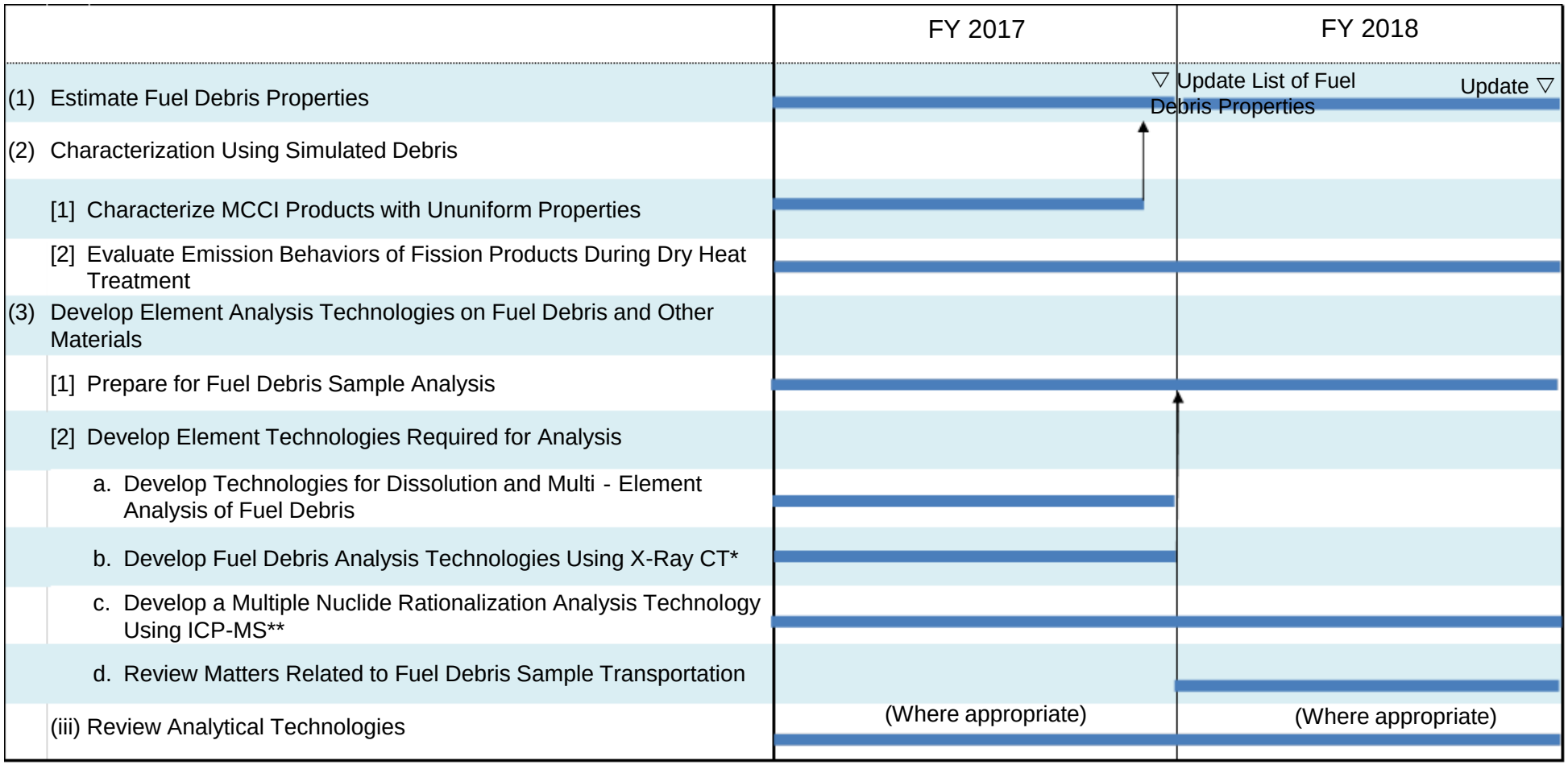
* Each implementation team's objectives are described in "6. Project Items."

3. Implementation Items and Relations with Other Projects



4. Schedule

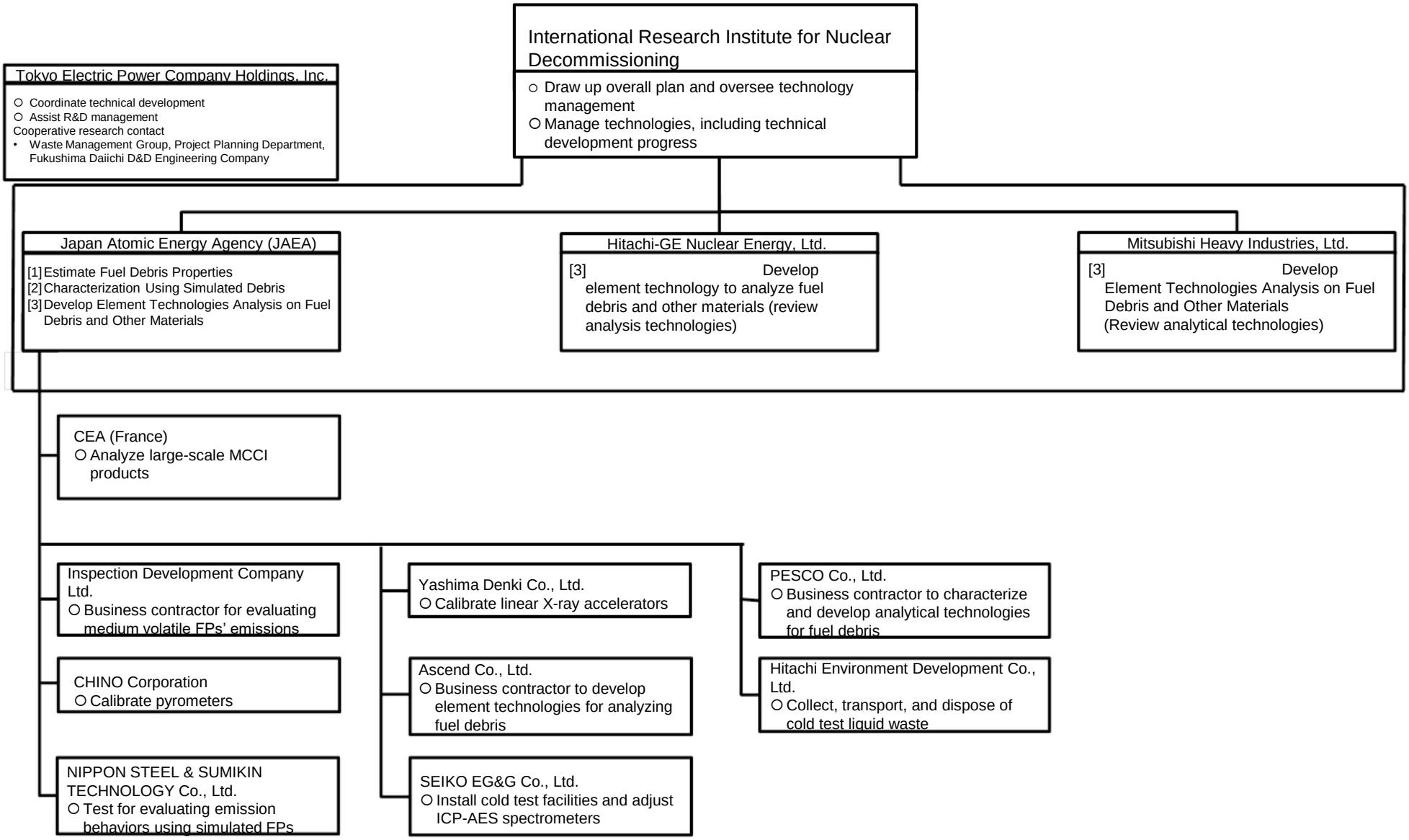
Project Outline and Schedule FY 2017 & FY 2018



* X-Ray CT: X-ray computed tomography

** ICP-MS: High-frequency inductively coupled plasma mass spectrometry

5. Project Organization (FY 2017)



6. Implementation Details

(1) Estimate Fuel Debris Properties (Update Fuel Debris List of Fuel Debris Properties)

(2) Characterization Using Simulated Debris
- [1] Characterize MCCI Products with Heterogeneous Properties
- [2] Evaluate Emission Behaviors of Fission Products During Dry Heat Treatment

(3) Develop Element Analysis Technologies on Fuel Debris and Other Materials
- [1] Prepare for Fuel Debris Sample Analysis
- [2] Develop Element Technologies Required for Analysis
  - a. Develop Technologies for Dissolution and Multi - Element Analysis of Fuel Debris
  - b. Develop Fuel Debris Analysis Technologies Using X-Ray CT
  - c. Develop a Multiple Nuclide Rationalization Analysis Technology Using ICP-MS

(1) Estimation of Fuel Debris Properties (Update List of Fuel Debris Properties)

●Update List of Fuel Debris Properties(FY 2017 and FY 2018)

[Objectives]

To estimate dose rates near fuel debris surfaces under typical conditions.

To reflect the latest results, including dose rate evaluation results, on the “Lists of Fuel Debris Properties,” prepared based on findings over a period up to FY 2016 among other things.

[Criteria for Target Achievements]

- “List of Fuel Debris Properties” was updated based on newly obtained knowledge in FY 2017. (End of FY 2017 - Completed)
- “Lists of Fuel Debris Properties” are updated based on newly obtained knowledge in FY 2018. (End of FY 2018)
- Dose rates near the debris surfaces are estimated.(End of FY 2018)

Achievements in FY 2017

1. Evaluation of Surface Dose Rates of Debris
   Added values calculated by an evaluation formula for surface dose rate, created based on calculation codes.

2. Characterization of MCCI Products with Heterogeneous Properties
   Reflected values in the List including property values based on the product analysis results in large-scale MCCI tests performed in FY 2017.

(1) Estimation of Fuel Debris Properties (Update Fuel Debris List of Fuel Debris Properties)

◆ Evaluation of Debris Surface Dose Rates

To retrieve fuel debris, estimating fuel debris surface dose rates is important because it helps to develop a work plan that takes exposure control into consideration (appropriate shields, task durations, etc.) for workers and other personnel during retrieval tasks.

- Assuming typical fuel debris, based on the fuel debris distribution inside the reactor, the surface dose rate is evaluated for this single fuel debris (under a condition unaffected by radiation from other sources).

Achievements in FY 2017

A preliminary calculation was performed to find the surface dose rate of spherical debris using the Monte Carlo code particle transport code (PHITS) under parameters of fuel debris properties, and the best ways to organize the data (charts and fitting formulas) was reviewed. In FY 2017, surface dose rate evaluation methods, selected a case of fuel debris were reviewed, and preliminary evaluations performed. Minimum parameters were obtained to determine the surface dose rate, and a preliminary evaluation formula was created through function fitting.

Fuel Debris Property Parameters

(i) Type of fuel debris: Melted, MCCI, or metallic debris
(ii) Density and porosity (bulk density)
(iii) Volatile FP emission rate (high to low)
(iv) Size of retrieved debris (about 10 cm or less in diameter)
(v) Primary nuclide composition ratio
(vi) Evaluation period

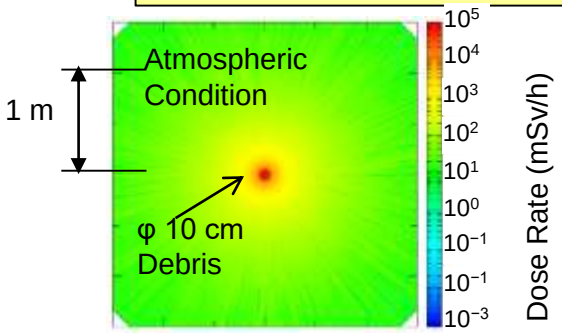


Figure 1 - Example of Dose Rate Calculation under Molten Debris Layer Conditions Using PHITS

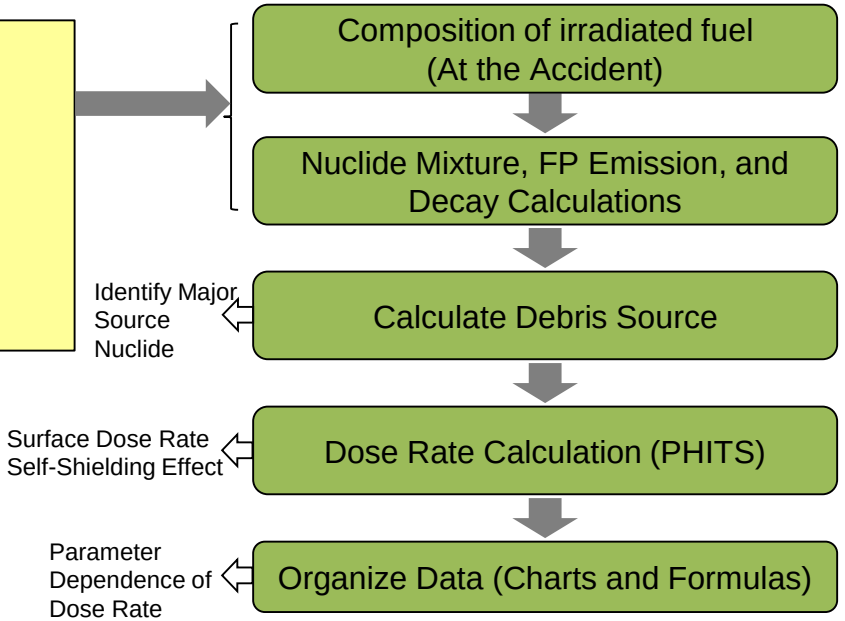


Figure 2 - Evaluation Flow

(1) Estimation of Fuel Debris Properties (Update Fuel Debris List of Fuel Debris Properties)

◆ Evaluation of Debris Surface Dose Rates

- A unitarily applicable evaluation method was established to estimate molten debris (UO_2-ZrO_2) surface dose rates, including MCCI debris (multiple compositions based on the accident progress analyses), and metallic debris (a metallic layer formed at the bottom due to density differences). This method is applicable to fuel debris with diverse element compositions and properties.
  => Through trial and error in combining various property parameters in radiation source and PHITS calculations, minimum parameters were obtained to determine the surface dose rate, and a preliminary evaluation formula was created through function fitting. (See Formula 1 and Figure 3)

$$D_i = P_i(r, \rho, u, t) \cdot R_i(r, u, N_p) \quad \text{(Formula 1)}$$

D_i	Surface dose rate (Sv/h): Evaluated amount	
P_i	Photon emission rate function (number of photons/sec): Fitting formula based on combustion, FP emission, and decay calculations	
R_i	Surface dose rate response function: Fitting formula based on PHITS calculation	
i	FP volatilization model (low emission, most probable, or high emission): Selected according to the intended purpose	
r	Debris radius (cm)	: Set based on the sampling plan
ρ	Bulk density (g/cm^3)	: Estimated from TMI debris measurements, simulation tests, etc.
u	Uranium concentration (wt. %)	: Estimated from accident progress analysis and simulation test results, etc.
t	Elapsed time (year)	: Determined based on the sample analysis plan
N_p	Proton number density (number of protons/cm^3)	: Estimated from accident progress analyses, simulation test compositions, etc.

- The preliminary surface dose rate was evaluated for case of fuel debris based on the established evaluation formula.
  - Example of surface dose rate estimation (average composition of Unit 1, diameter of 6 cm, volatile FP low emission model, 2021)
    Molten debris : 56 Sv/h
    MCCI debris : 6 Sv/h

○ Example of minimum parameter estimation

When r = 3 cm and u = 8.9 wt%

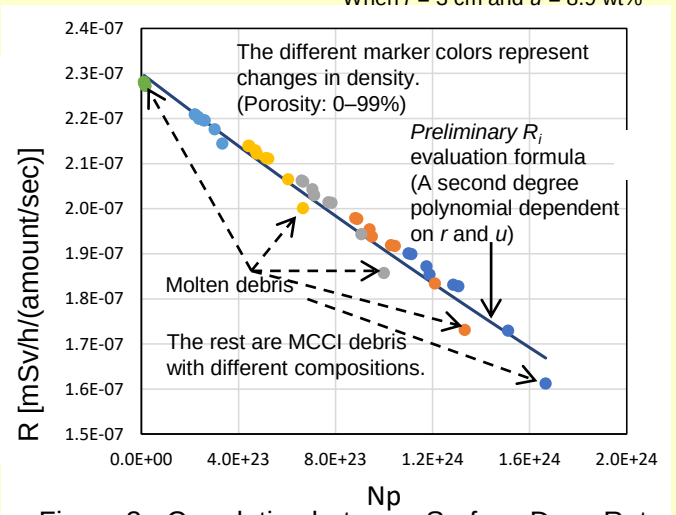


Figure 3 - Correlation between Surface Dose Rate Response Function (R_i) and Proton Number Density (N_p) for Debris with Various Properties

⇒ The impact of elemental compositions and porosity on R_i can be roughly represented as a function of N_p.

What to Expect in FY 2018

In FY 2018, the evaluation formula will be finalized by increasing the number of cases using different FP volatile models and other parameters. The data and evaluation formula to estimate the sampled debris surface dose rates for various cases will be provided to other projects. -> Debris surface dose rates will be reflected in the List of Fuel Debris Properties.

(2) Characterization Using Simulated Debris

(i) Characterization of MCCI Products with Heterogeneous Properties

●Characterization of MCCI Products with Heterogeneous Properties (FY 2017)

[Objectives]

To analyze a large-scale MCCI test product produced in FY 2016 at a test facility owned by France's CEA (taking the 1F conditions into account) and understand its layer structures, formed phases, and hardness, etc. To analyze measurement data from the MCCI test and clarify temporal changes in concrete erosion.

[Criteria for Target Achievements]

- The layer structures of the MCCI test product are illustrated. (End of FY 2017 - Completed)
- Typical formed phases and hardness are shown for each layer with different characteristics. (End of FY 2017 - Completed)
- Temporal changes in concrete erosion from the MCCI tests are shown. (End of FY 2017 - Completed)

- In the 1F's Primary Containment Vessel, reactions (MCCI) occurred between molten core fuel and concrete on the vessel floor. Core materials, such as uranium dioxide, zircaloy, and stainless steel, were melted and mixed with concrete components, producing various compounds (MCCI products).
- Since there is no knowledge about MCCI products even in TMI-2, their behaviors and properties must be reviewed.
- MCCI products' properties, such as formed phase and hardness, are expected to vary depending on their locations in the vessel, and information on such "heterogeneity of properties" is extremely important to understand fuel debris conditions inside the vessel as well as to review retrieval tools and methods.

Large-Scale MCCI Test in FY 2016

- In this large-scale MCCI test, MCCI products were produced while taking the 1F conditions into account and the profile (range of concrete erosion and overview of erosion profile) was obtained for the final test section.
- Metals/oxides were identified based on the obtained products' characteristics, test sample's dismantling status, etc.

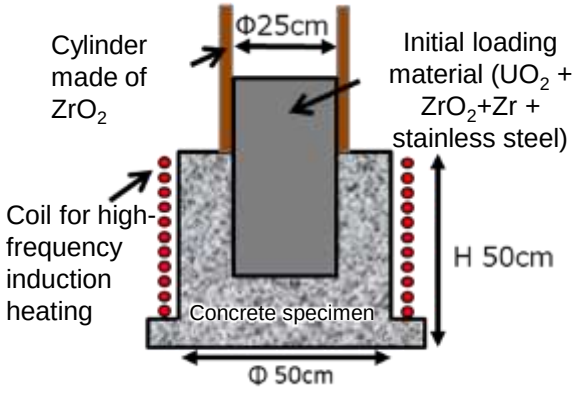


Figure 1 - Cross-Section of Testing Equipment

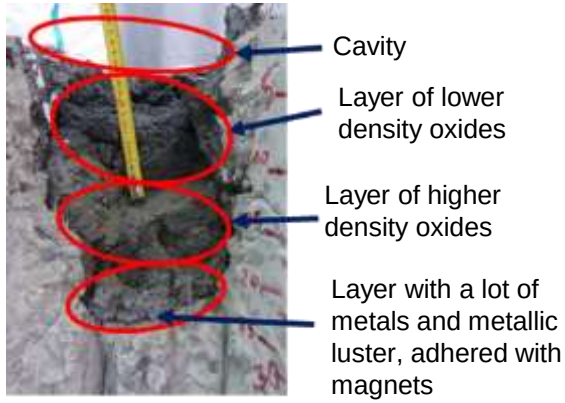


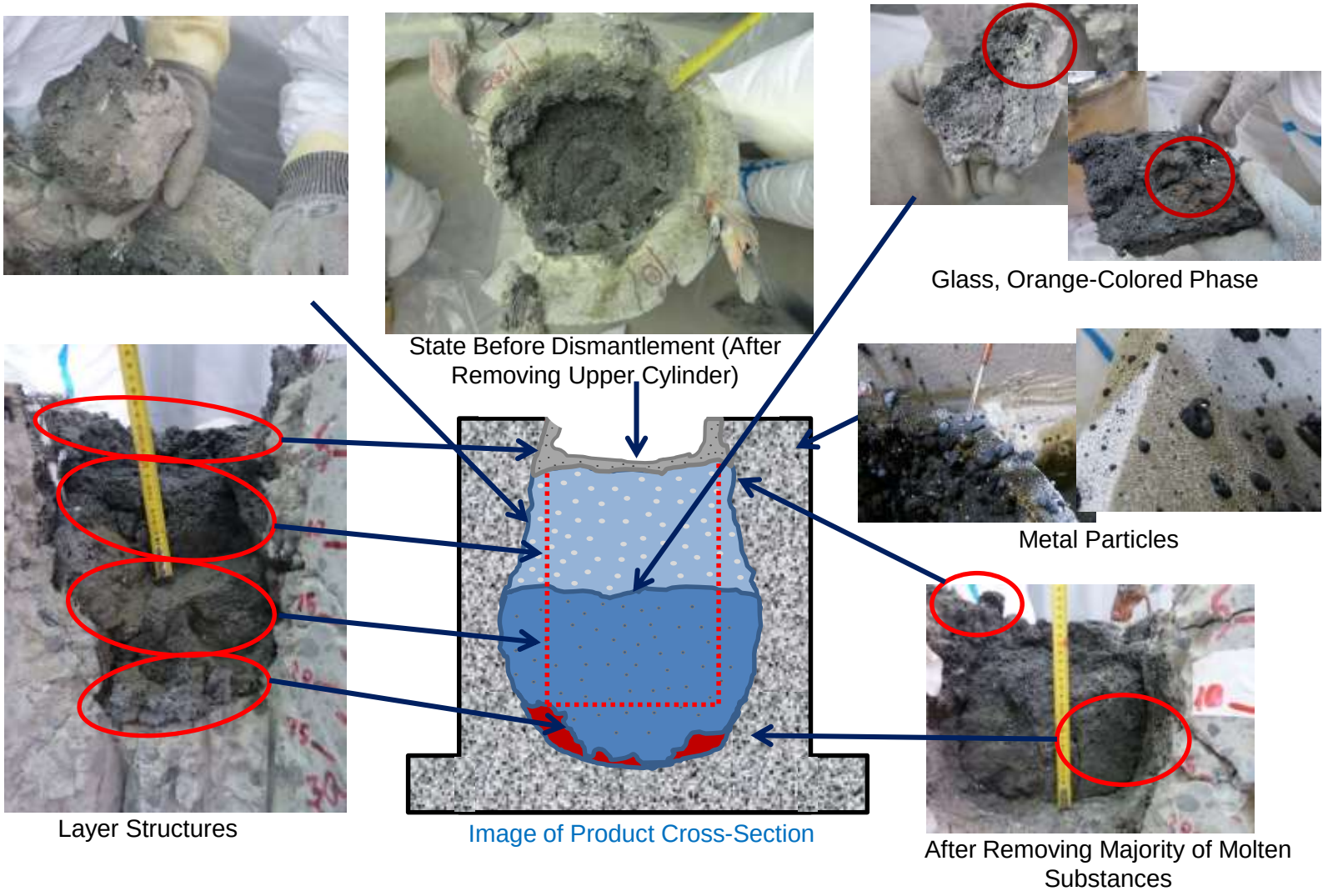
Figure 2 - Cross-Section of MCCI Test Product and Concrete Test samples

(2) Characterization Using Simulated Debris

(i) Characterization of MCCI Products with Heterogeneous Properties

Large-Scale MCCI Test in FY 2016

<Large-scale MCCI Test: Product Appearance>



(2) Characterization Using Simulated Debris

(i) Characterization of MCCI Products with Heterogeneous Properties

Particulate

- Outflowed and scattered powder

Crust

- Solidified surfaces

Heat Deterioration Layer

- Thin heat-deteriorated portion

Composite Phase

- Metal particles of a few millimeters and glass phases are contained in various places.

Air Holes & Stratification

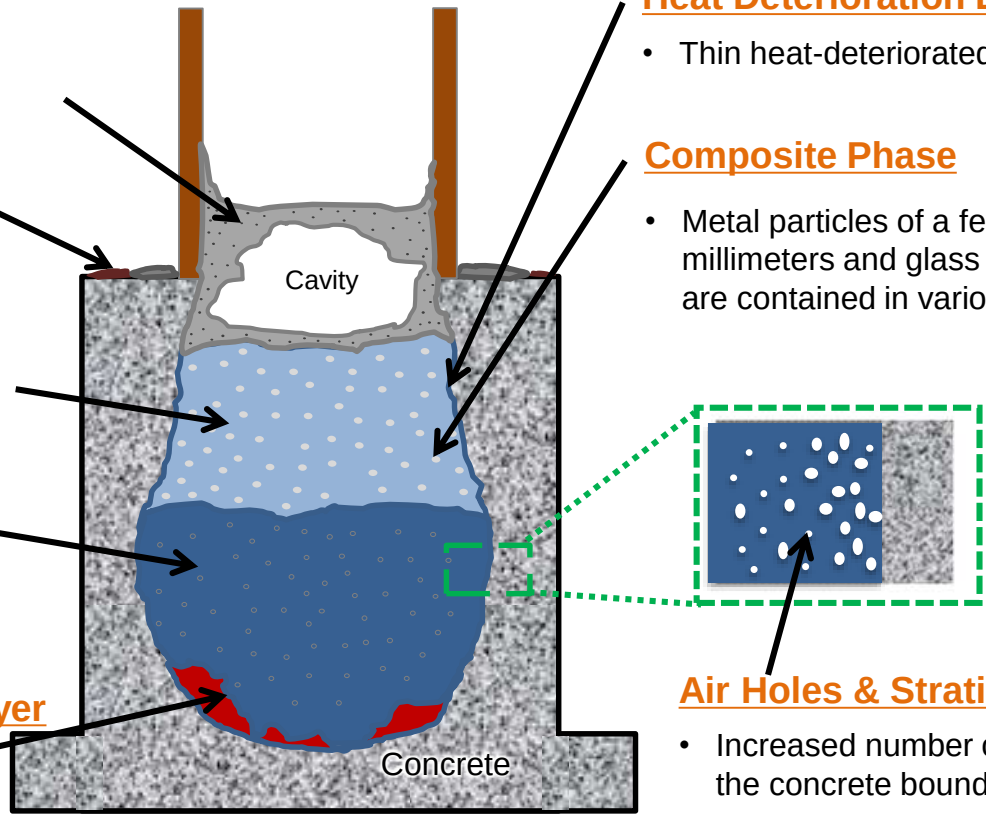
- A low-density molten oxide layer with a number of air holes that is slightly hard to crush.

Air Holes & Stratification

- A high-density molten oxide layer with a few air holes that is hard to crush.

Separated Oxide and Metallic Layer

- A layer with many metals that is hard to crush.



Air Holes & Stratification

- Increased number of air holes at the concrete boundary

Figure - Layer Structure Drawing of MCCI Test Product
(**Large-Scale MCCI Test Product in FY 2016**)

(2) Characterization Using Simulated Debris

(i) Characterization of MCCI Products with Heterogeneous Properties

◆ Analysis of Large-Scale MCCI Test Product

Achievements in FY 2017

- As the main objects of analysis, 10 samples were sampled from each structural layer (see Figure 1) to determine each layer's tendencies in formed phase, hardness, etc.

Table 1 - Analysis Items and Methods

Analysis Item	Method
Microstructure & Local Composition	SEM/EDS
Crystalline Structure	XRD
Microhardness	Indenter Indentation Method
Bulk Density	Dipping Method
Average Composition	Dissolution & Solution Analysis
Particle Size Distribution (For particles generated by severing with a grinder)	Screening

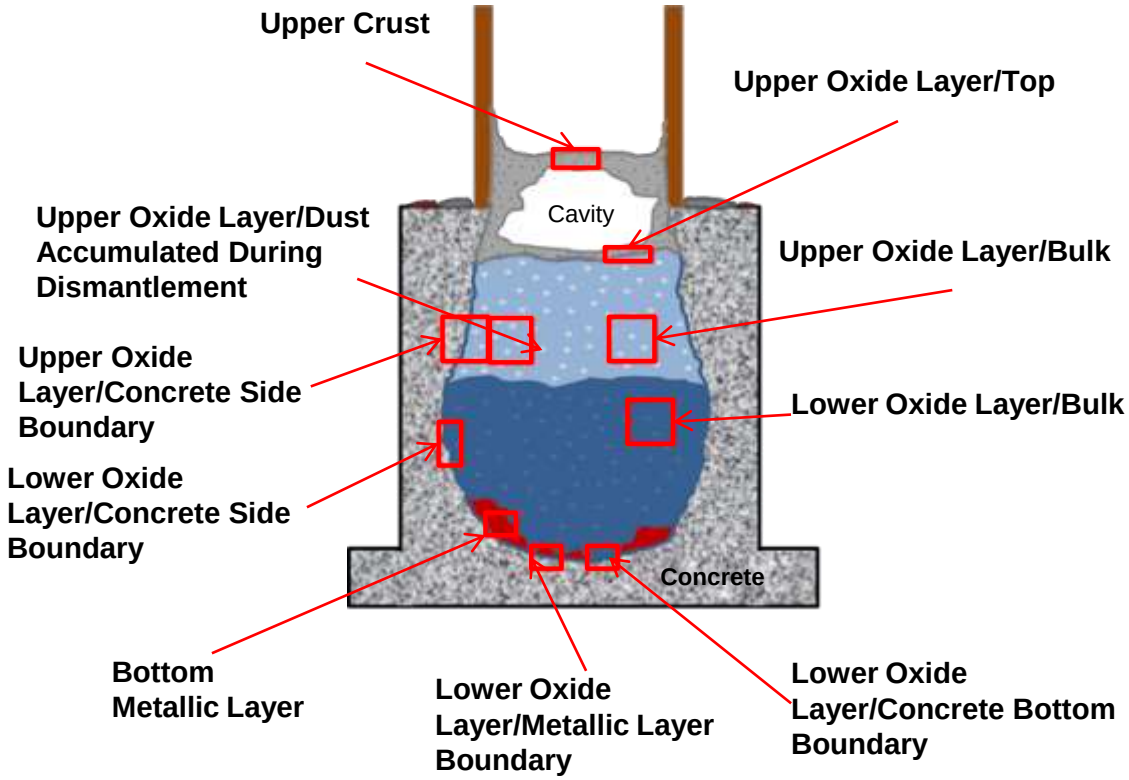


Figure 1 - Test samples Sampling Positions

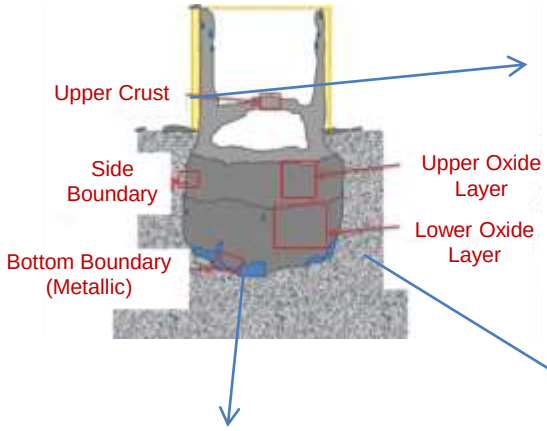
(2) Characterization Using Simulated Debris

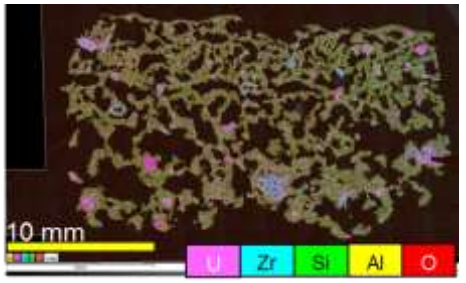
(i) Characterization of MCCI Products with Heterogeneous Properties

◆ Analysis of Large-Scale MCCI Test Product

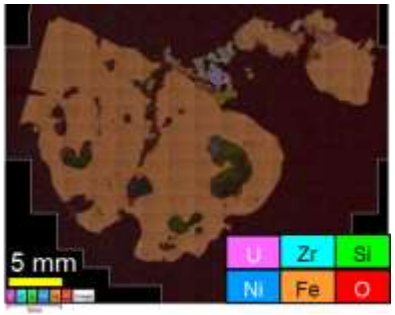
Analysis Results

- Gas pockets of roughly 5 mm were distributed (porous) in every portion.
- In test samples mainly consisting of oxides, such as upper crust and upper/lower oxide layers, U-Zr oxide, and oxides composed mainly of Cr, were deposited in a matrix composed predominantly of Si (and includes Ca and Al). With XRD, compounds were found, including cubic crystal $(U_{1-x}Zr_x)O_2$, tetragonal ZrO_2, spinel phase (e.g., $FeCr_2O_4$), and SiO_2 (cristobalite) in qualitative analysis.
- The metallic layer at the bottom boundary was an alloy composed mainly of Fe.
- No significant differences were found in both formed phases and hardness for different sampling positions.
- For physical properties (e.g., hardness), roughly the same values were obtained as the “Fuel Debris List of Fuel Debris Properties”.

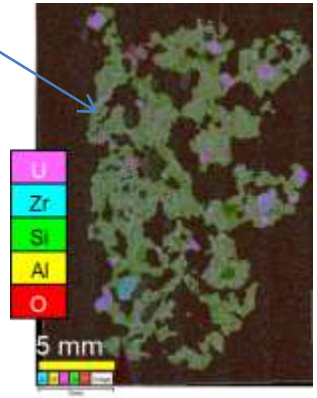




Element Mapping for Upper Crust Cross-Section



Element Mapping for Bottom Boundary Cross-Section



Element Mapping for Lower Oxide Layer Cross-Section

In the large-scale MCCI test that takes the 1F conditions into account, it was confirmed that no significant differences were found in terms of formed phases and physical properties between this test and assumptions that had been made based on the past fundamental test results, etc.

(2) Characterization Using Simulated Debris

(i) Characterization of MCCI Products with Heterogeneous Properties

◆ Temporal Change in Concrete Erosion Profiles

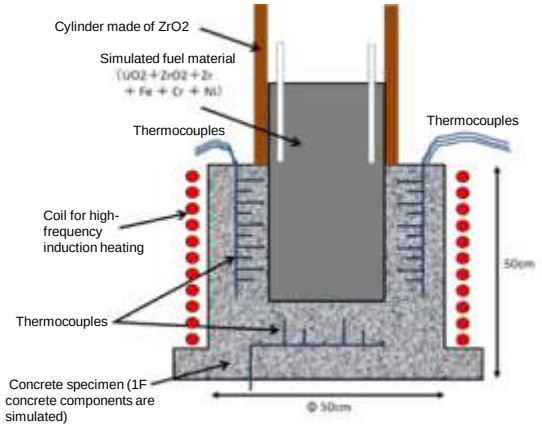
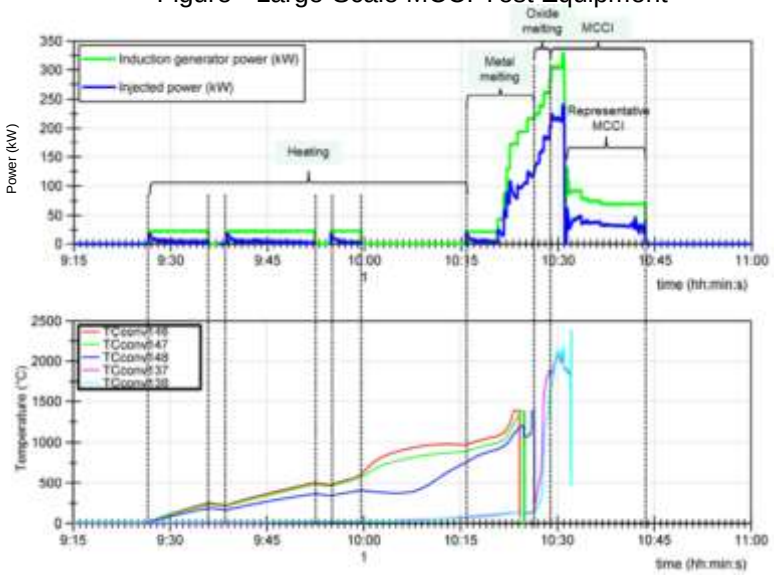


Figure - Large-Scale MCCI Test Equipment



[Heating Started at 9:26 and Ended at 10:44]

Figure - Changes in Heating State of Corium by Induction Heating (FY 2016)

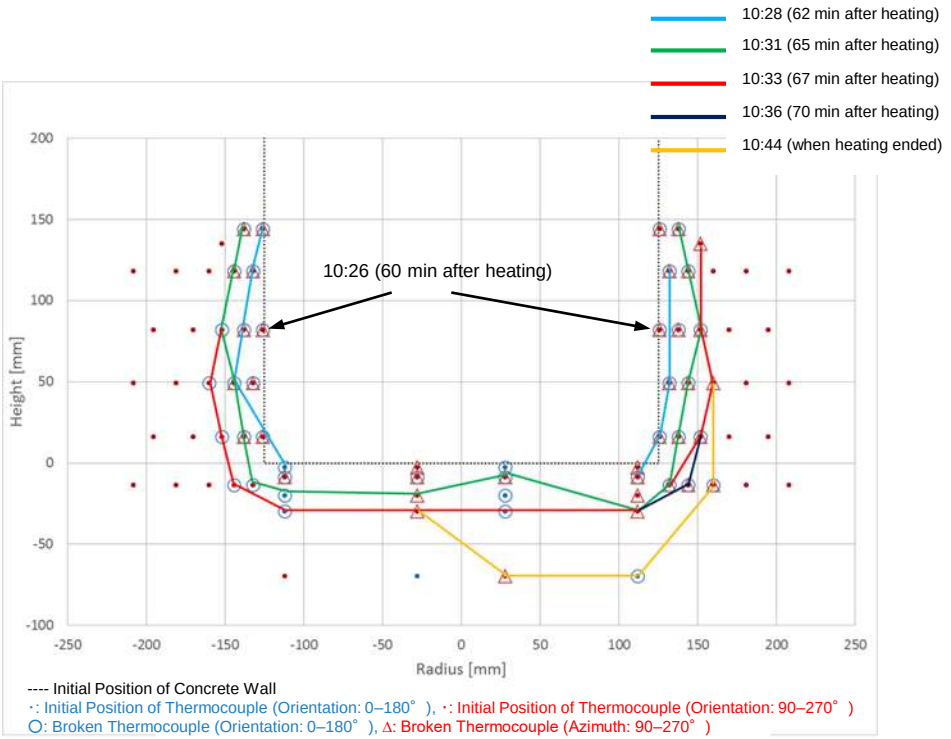


Figure - Positions of Broken Thermocouples at Each Point in Time

- Inspected temporal changes in thermocouples installed in the test equipment (inside the concrete portion) as they broke (melted) to understand the state of erosion in the concrete portion.

=> It was discovered that erosion proceeded radially (i.e., laterally) at the initial stages of fusion and erosion proceeded axially (i.e., downward).

New knowledge has been acquired the state (progress) of erosion under the 1F conditions.

(2) Characterization Using Simulated Debris

(i) Characterization of MCCI Products with Heterogeneous Properties

◆ Recommendations for Decommissioning Work(Cutting and Processing the Fuel Debris) Based on Test Results

Based on the characteristics of the appearance and changes in the working environment observed during the dismantling process, recommendations on how to retrieve fuel debris using mechanical methods while supplementing the sample analysis results were summarized.

Characteristics Observed During Dismantling Process (Appearance & Working Environment)	Sample Analysis Results of This Test (Formed Phases, Hardness, Compositions, etc.)	Recommendations
The debris is highly porous and appears to be brittle, but is actually very tough.	Gas pockets of roughly 5 mm are distributed throughout. Hardness is 5–22 [GPa] for the oxide phase and 1–3 [GPa] for the metallic phase.	It is difficult to select optimal tools based only on observing the air holes. Therefore, it is thought to be necessary to refer to the maximum hardness values obtained in this test and select components made from materials with equivalent hardness (stainless steel or alumina).
Significant quantities of powder dust were generated during the dismantling process.	Properties of a powder dust sample: Particles smaller than 1 [mm] take up about 40% of the powder dust sample's weight. Contains 20–33 [wt%] of U.	During dismantling in atmospheric conditions, measures against rapid visibility deterioration caused by fine powder dusts, including nuclear materials, must be taken, as well as against the possible impact of powder dusts on radiation monitoring.
Crust formation	Properties of upper crust sample: Deposits such as $(U,Zr)O_2$ and $(Cr,Fe)O_x$ are present in a Si-Al-Ca oxide matrix. Hardness is 5–18 [GPa]. Formed phases and hardness are roughly the same as other samples.	In this test, microstructures and hardness of the crust turned out to be similar to those of the molten pool area. However, in an actual accident progression scenario, where surfaces are rapidly cooled by water injection, harder phases may be formed compared to the molten pool portion.
Particulate debris was observed.	-	Handling tools (for suction or scooping) and separation of solid - liquid in the water treatment system may be necessary.
A heat deteriorated concrete layer is present.	-	Not suited for grabbing due to its brittleness.
Air holes & stratification were observed.	Air holes of roughly 5 mm are distributed in both the upper and lower parts.	It is necessary to check for the impact that different degrees of air holes sparsity/density will have on the criticality evaluation.
Oxide and metallic layers were separated.	Metallic layer: Mainly comprised of Fe-Ni alloy. Hardness is up to 3 [GPa]. It is hard to crush this layer while preprocessing analysis samples. Oxide layer: $(U,Zr)O_2$ and (Cr,Fe)Ox were deposited in the Si-Ca-Al oxide matrix (hardness: 5–12 [GPa]).	It is difficult to crush the metallic layer by impact. Since oxide and metallic layers have different mechanical properties, it is necessary to detect the change in layers when different tools are required for each layer.

(2) Characterization Using Simulated Debris

(ii) Evaluate Emission Behaviors of Fission Products During Dry Heat Treatment

● **Evaluate Emission Behaviors of Fission Products During Dry Heat Treatment (FY 2017 and FY 2018)**

[Objectives]

For a drying facility under consideration as a preprocessing facility before storing fuel debris, basic data is required on fission products (FPs)' heat emissions. The data will be used as a basis for considering the design of the off-gas processing facility including its safety.

Behaviors of volatile FPs during the drying treatment are important information when considering the need for, and processing methods of, collected FPs' off-gas processing. Therefore, this evaluation sorts out information on volatile FPs (especially medium volatile FPs with high environmental toxicity) and off-gas design collections of existing plants, and evaluates emission behaviors of medium volatile FPs based on tests, etc.

[Criteria for Target Achievements]

- Medium volatile FPs with high environmental toxicity are identified. (End of FY 2017 - Completed)
- Emission behaviors of medium volatile FPs, such as emission start temperature and emission speed, are evaluated. (End of FY 2018)

○ Highly volatile FPs -> The entire amount is emitted.

- ✓ Cs, I, noble gases, etc.
- ✓ Design based on the assumption that FPs are emitted

○ Medium volatile FPs -> Partially emitted.

- ✓ FPs which are highly likely to be emitted under dry heat treatment conditions
- ✓ It is necessary to consider design loads, etc. caused by emission for each FP

○ Low volatile FPs: Not emitted.

- ✓ FPs which are highly unlikely to evaporate due to their high melting points, such as Ac and its compounds

(2) Characterization Using Simulated Debris

(ii) Evaluate Emission Behaviors of Fission Products During Dry Heat Treatment

Achievements in FY 2017

➢ **Evaluation of FP Emission Behaviors**

Event Specific to 1F (Differences with TMI-2)

(From a viewpoint of impacts on FP emission behaviors)

- The **fuel burnup is higher, and the fuel has a higher FP content,** in the 1F accident.
- **Fuel debris containing concrete is present** due to MCCI.

●The same drying conditions as TMI-2 are highly unlikely to be applicable.

●It is essential to enhance basic data to cover a wider range.

Example: From room temperature to 1,000° C strong (assuming the reduction of concrete's moisture content)

➢**Selection of Nuclides with High Environmental Toxicity**

Environmental Toxicity = (Inventory [Bq] After 10 Years from the Accident) x (Dose Coefficient [mSv/Bq]) ----- (Table 1)

In addition, compounds with greater impacts were identified by **comparing the following conditions and vapor pressure**.

- **Nuclides that can be emitted entirely without any problem: Excluded**
- **Conditions of compound with lower vapor pressure than UO_3: Excluded**

Candidates are Ag, Te, and oxides of Te, Sn, and Cd

Table 1 - Evaluation of Nuclides[1] with High Environmental Toxicity (Unit 3)

	Nuclides	Radioactivity [Bq] After 10 Years from the Accident	Dose Coefficient [mSv/Bq]	Environmental Toxicity (Exposure Dose) [mSv]	Compounds[2] estimated to be generated
1~6 *1	Pu, Am, Cm				PuO_2, AmO_{2-x}, CmO_2
7	Sr90	1.42E+17	7.70E-05	1.09E+13	SrO
8	Cs137	1.91E+17	6.70E-06	1.28E+12	Cs_2O
9~11 *2	Am, Cm				AmO_{2-x}, CmO_2
12	Y90	1.42E+17	1.70E-06	2.41E+11	Y_2O_3
13~17 *3	Eu, Pu, Pm, Cs, Cm				Eu_2O_3, PuO_2, Pm_2O_3, Cs_2O, CmO_{2-x}
18	Ru106	9.67E+14	3.50E-05	3.38E+10	Ru or RuO_2
19	Ce144	3.15E+14	2.90E-05	9.14E+09	CeO_2
20	Eu155				Eu_2O_3
21	Sb125	1.39E+15	3.30E-06	4.59E+09	Sb_2O_3
22	Cd113m	3.41E+13	1.30E-04	4.43E+09	CdO
23	Sm151	8.54E+14	2.60E-06	2.22E+09	Sm_2O_3
24	Te125m	5.17E+14	2.90E-06	1.50E+09	Te or TeO_2
25	Am242				AmO_{2-x}
26	Ba137m	1.81E+17	1.00E-09	1.81E+08	BaO
27,28 *4	Eu, Zr				Eu_2O_3, ZrO_2
29	Tc99	3.15E+13	3.20E-06	1.01E+08	TcO_2
30,31 *5	Fe,Np				Fe_3O_4, NpO_2
32	Sn126	1.40E+12	1.80E-05	2.52E+07	SnO_2
33~40 *6	H, Ni, Co, Sn, Pm, Kr, U, Pr,				H_2, NiO, CoO, SnO_2, Pm_2O_3, Kr, UO_{2+x}, Pr_2O_3
41	Ag110m	2.37E+11	7.30E-06	1.73E+06	Ag
42~51 *7	Sn, Rh, Sb, Np, Pr, Mn, Gd, Rh				SnO_2, Rh or Rh_2O_3, Sb_2O_3, NpO_2, Pr_2O_3, MnO, Gd_2O_3

*1 Pu238, Am241, Pu241, Pu240, Cm244, and Pu239
*2 Am243, Am242m, and Cm243
*3 Eu154, Pu242, Pm147, Cs134, and Cm242
*4 Eu152, Zr93
*5 Fe55 Np239
*6 H3, Ni63, Co60, Sn121m, Pm146, Kr85, U237, and Pr144
*7 Sn119m, Sn121, Rh106, Sb126, Np238, Pr144m, Sb126m, Mn54, Gd153, and Rh102

1) Nuclides whose impact on the environment is negatively evaluated when emitted Specifically, for each nuclide, the product of the mount of radioactivity in fuel debris after ten years and the dosimeter count were calculated and compared.
2) Compounds that may be generated under severe accident conditions

(2) Characterization Using Simulated Debris

(ii) Evaluate Emission Behaviors of Fission Products During Dry Heat Treatment

➢ Review Methods for Measuring FP Emission Behaviors

Test methods were reviewed using simulated debris manufactured with Ru, whose behaviors are well known.

==> **Confirmed that FP emission behaviors and emission speed can be measured** using **TG-DTA***.

Test results: Heating test under air atmosphere (See Figure 1)

- ◆ By measuring the temperature at the point when a specimen's weight starts to decrease ==> Possible to evaluate the emission start temperature
- ◆ By measuring temporal changes in a specimen's weight ==> Possible to evaluate the emission speed

As part of our review of emission behavior evaluation methods, a method using vapor pressure, etc., based on the existing evaluation formula, is under consideration.

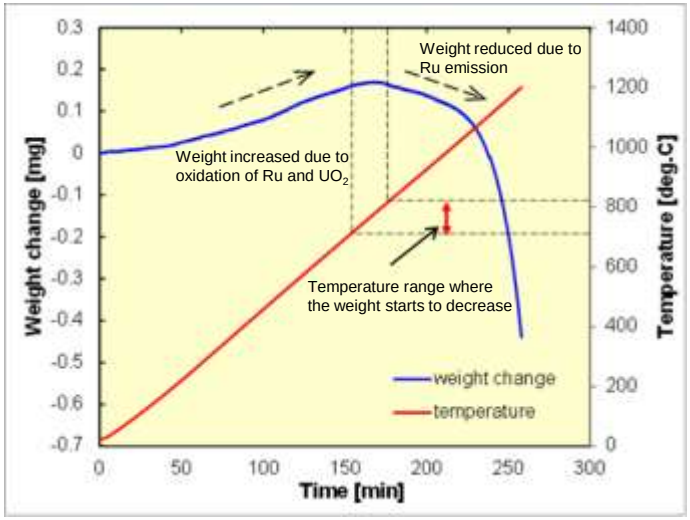


Figure 1 - Weight Change by Heating the Simulated Debris Containing Ru under Air Atmosphere

What to Expect in FY 2018

➢ Obtain & Evaluate Emission Behavior Data for Medium Volatile FP

- **Emission Behavior Evaluation Test**
  Emission behaviors will be measured and evaluated formedium volatile FP nuclides (candidates: Ag, Te, and oxides of Te, Sn, and Cd) by applying the technology described above. Figure 2 shows the vapor pressure curve of candidate oxides.
- **Analyze Emission Behaviors**
  In response to our evaluation method review, as mentioned above, a better understanding of FP emission behaviors and evaluating FP nuclides that are hard to experiment on will be contributed to.

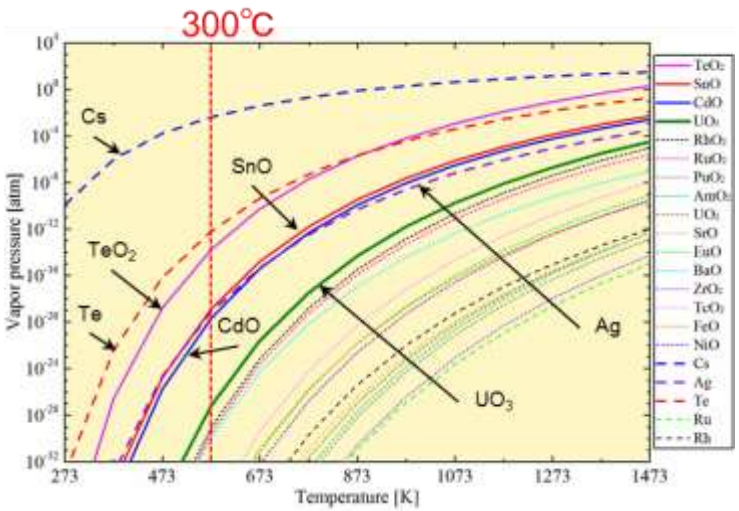


Figure 2 - Vapor Pressure (Calculated Value) of Major Compounds in Nuclides with High Environmental Toxicity

* Thermogravimetry/differential thermal analyzer: Measures weight changes in a specimen when its temperature increases at a constant rate.
By looking at weight changes, it is possible to estimate the specimen's behaviors, including volatilization/evaporation and oxidation.

(3) Develop Element Technologies for Analysis on Fuel Debris and Other Materials

(i) Prepare for Fuel Debris Sample Analysis

●Prepare for Fuel Debris Sample Analysis (FY 2017 and FY 2018)

[Objectives]

To analyze a very small amount of fuel debris that is expected to be obtainable from inside the reactor by sampling before the Okuma Analysis and Research Center starts operating a facility currently under preparation, it is necessary to make preparations so that 1F samples including fuel debris can be analyzed in the existing analysis facility.

To this end, analysis items (including fuel debris composition and mechanical properties) to be conducted in the existing facility are reviewed and appropriate procedures for each item prepared.

[Criteria for Target Achievements]

➢ Appropriate procedures are prepared for each analysis item to be conducted in the analysis facility. (End of FY 2018)

Achievements in FY 2017

Prepare Procedure Documents for Existing Analyzers & Methods

- Of all candidate analysis items, the preparing of procedure documents for 12 high priority items (3 preprocessing items and 9 analysis items, as shown in the table to the right) was started, reflecting considerations and information applicable to debris analyses.

Prepare Procedure Documents for Analysis Methods Developed through Element Development

- Analysis procedure documents for each technical development item of debris specimen dissolution methods, quantitative element analysis using ICP-AES*, porosity measurement using X-ray CT, and measurement of γ ray nuclide distribution were prepared.

Preprocessing Items
Cut out and powderize debris samples
Embed resin and mirror polish debris
Preprocess various analysis samples with solutions
Analysis of Items
Observe shape and measure dimensions with an optical microscope
Observe surfaces/cross-sections using SEM/EPMA and analyze elements qualitatively/quantitatively
Measure chemical structures using X-ray diffraction analysis (XRD)
Determine powder classification and particle size distribution
Analyze elements qualitatively/quantitatively using TIMS
Quantitatively analyze α nuclides
Quantitatively analyze γ nuclides
Measure hardness and toughness
Measure uniaxial compressive strength

* High-frequency inductively coupled plasma emission spectrometry

(3) Developing Element Technologies Analysis on Fuel Debris and Other Materials

(ii) Developing Element Technologies Required for Analysis

a. Develop Technologies for Dissolution and Multi - Element Analysis of Fuel Debris

●Develop applicability of a dissolution method, using alkali fusion and a multi - elementary analysis technology, using ICP-AES (FY 2017)

[Objectives]

To ensure proper elementary analysis in fuel debris, it is necessary to develop a dissolution method for fuel debris with poor solubility and an analysis technology for such solutions. To this end, the applicability of a dissolution method is reviewed, using alkali fusion in preprocessing, for analyzing compounds contained in fuel debris, which have not been reviewed so far. A multi - elementary analysis technology for fuel debris solutions after alkali fusion using ICP-AES is also developed. Note that target elements are 13 elements* that need to be analyzed (U, Pu, Zr, Fe, Gd ,Al, B, Ca, Cr, K, Mg, Ni, and Si).

[Criteria for Target Achievements]

- The conditions are identified for simulated materials to be completely dissolved. For undissolvable materials, complementary treatment methods are provided, including acidic dissolution.
- Analysis procedures are provided for elementary analysis using ICP-AES.

(End of FY 2017 - Completed)

Achievements in FY 2017

◆ Dissolution of Fuel Debris

Of all simulants (test target substances) listed in the List of Fuel Debris Properties, those that had not been tested by FY 2016 (Cr_2O_3, Fe_3O_4, $ZrSiO_4$, B_4C, ZrB_2, and Fe_2B) were reviewed for the applicability of alkali fusion (sodium peroxide) and their conditions were identified.

Major fusion conditions
- Test samples particle size: 90 μm or less
- Fusion agent ratio: 10
  (Fusion agent (sodium peroxide) 0.5 g : specimen 0.05 g)
- Fusion temperature: 750° C

Test Target Substances	Time to Fusion (min)	Tested Year
Oxides		
ZrO_2	15	2015
$(U,Zr)O_2$	30	2016
SiO_2	15	2015
Al_2O_3	15	2015
Cr_2O_3	15	2017
Fe_3O_4	15	2017
$ZrSiO_4$	15	2017
$(U,Pu,Zr)O_2$	30	2017
Metals		
Zircaloy 2	30	2016
Zr(O)	15	2016
SUS316	60	2016
Fe_2Zr	15	2016
Borides, etc.		
B_4C	15	2017
ZrB_2	15	2017
Fe_2B	15	2017
Mixtures		
ZrO2+SUS316	15	2016
$(U,Pu,Zr)O_2$ +SUS316	30	2017

Table 1 - Test Target Substances and Time to Fusion

* Derived from reactor core fuel: U and Pu; from cladding/structural materials: Zr, Fe, Gd, Al, B, and Ni; from concrete: Ca, Cr, K, Mg, and Si

(3) Developing Element Technologies Analysis on Fuel Debris and Other Materials

(ii) Developing Element Technologies Required for Analysis

a. Develop Technologies for Dissolution and Multi-Element Analysis of Fuel Debris

◆ Developing a Multi-Element Analysis Technology

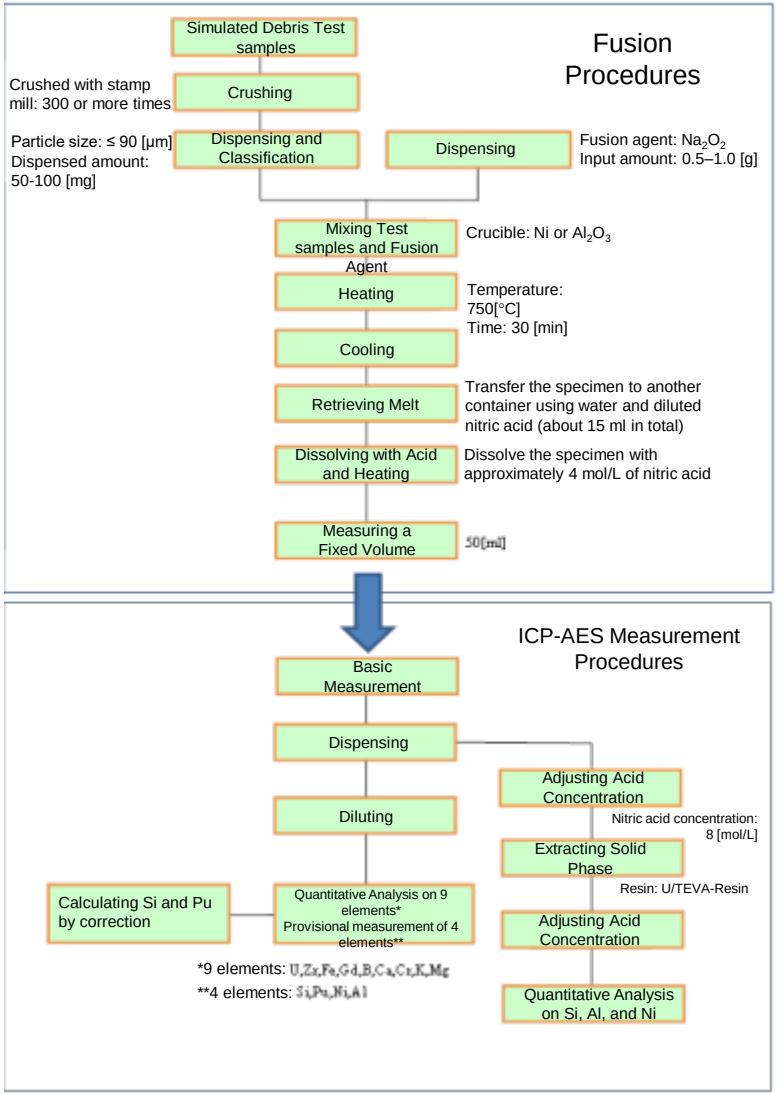
Simulated MOX* debris samples were prepared and tested for applicability of alkali fusion (using sodium peroxide) to acquire data on debris dissolution.

==> It was confirmed that dissolution and elementary analysis using ICP-AES measurement are possible with MOX-simulated debris based on established analysis procedures.

Table 1 - Alkali Fusion Analysis Results for Simulated MOX Debris (Example)

Simulated MOX Debris Test samples	Pu (wt%)	U (wt%)	Zr (wt%)
Round 1	1.1	30.8	43.3
Round 2	1.1	31.8	43.4
Round 3	1.1	31.4	42.0
Average	1.1	30.9	42.9
Cv	2.8%	1.5%	1.9%

* Mixed Oxide: U-Pu mixed oxide fuel



Basic Procedures of Sodium Peroxide Fusion Method

(3) Developing Element Technologies Analysis on Fuel Debris and Other Materials

(ii) Developing Element Technologies Required for Analysis

b. Developing Fuel Debris Analysis Technology Using X-ray CT

●**Establish a Porosity Measurement Technology (FY 2017)**

[Objectives]

To establish a porosity measurement technology. Porosity information is reflected in the estimation of the water and other material content in air holes and contributes to the evaluation of hydrogen generation and criticality control.

●**Establish a Fuel Debris Component Identification Technology (FY 2017)**

[Objectives]

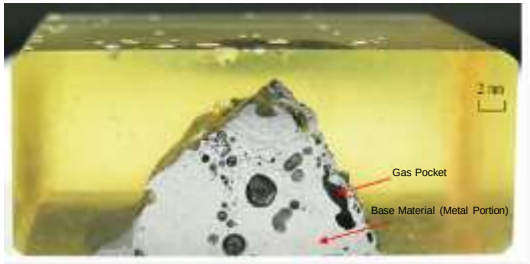
To establish a technology for identifying components with nondestructive measurement methods to confirm fuel debris components in advance.

[Criteria for Target Achievements]

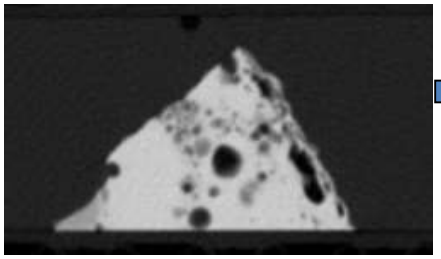
- Analysis procedures are provided that enable the measurement of porosity using X-ray CT. (End of FY 2017 - Completed)
- Analysis procedures are provided that enable component (material) identification by comparing density evaluation results from X-ray CT and nuclide distribution evaluation results from γ ray tomography measurement. (End of FY 2017 - Completed)

Achievements in FY 2017

◆ **Establish a Porosity Measurement Technology**



Appearance of Simulated Debris Test samples



X-Ray CT Image of Simulated Debris Test samples

Porosity Evaluation Formula Based on X-Ray CT Image

(created in FY 2016)

$$\text{Porosity (\%)} = \left\{1 - \frac{Average\ CTValue\ of\ Target\ Substance}{BaselineCT\ Value}\right\} * 100$$

Baseline CT Value: CT value of a portion (base material) without air holes

Porosity Evaluation Results

It was confirmed that porosity can be measured using X-ray CT with an equivalent accuracy to the conventional method that uses optical microscopes.

X-Ray CT Image	22%
Optical Microscope Image (for reference)	23%

(3) Developing Element Technologies Analysis on Fuel Debris and Other Materials

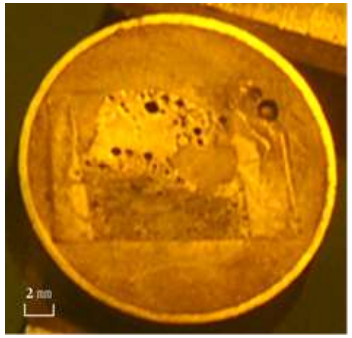
(ii) Developing Element Technologies Required for Analysis

b. Developing Fuel Debris Analysis Technology Using X-ray CT

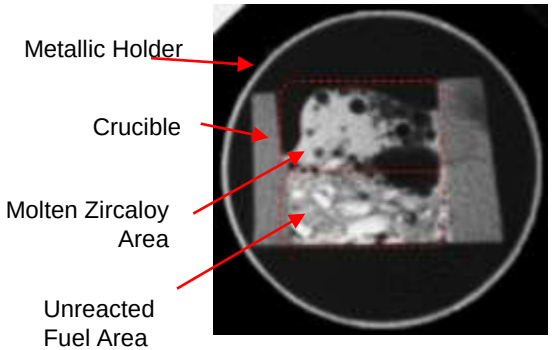
Achievements in FY 2017

- Establish Fuel Debris Component Identification Technology

Fuel debris components are difficult to determine by appearance alone. Understanding their distribution, using nondestructive technologies and reviewing them in relation to their detailed sampling positions, made identifying fuel debris components more accurate.

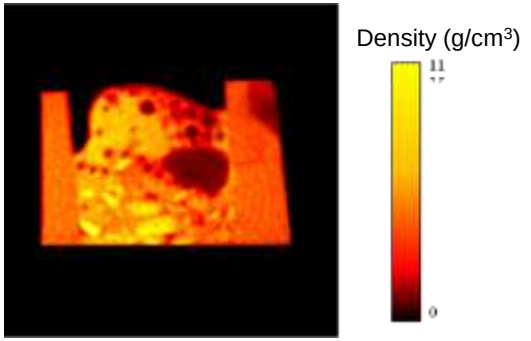


Test samples* Appearance



X-Ray CT Image

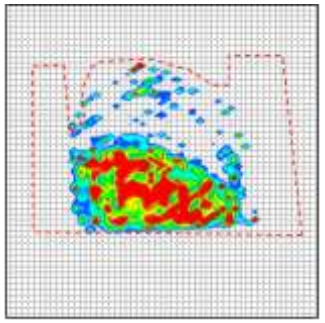
CT Value Is Converted into Density



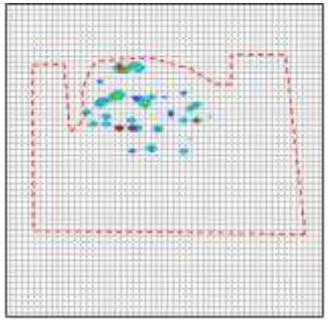
Density Distribution

Test samples: Crushed fuel and shredded cladding (zircaloy) are placed into a crucible, in that order, and heated to a high temperature.

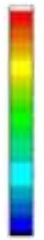
It was confirmed that components of test samples (fuel and cladding portions) can be identified based on the combination of density distribution from X-ray CT image and γ ray emission nuclide distribution from γ ray tomography measurement.



(Eu-154: 1274 keV)



(Co-60: 1332 keV)



γ Ray Emission Nuclide Distribution (γ Ray Tomography Measurement)

(3) Developing Element Technologies Analysis on Fuel Debris and Other Materials

(ii) Developing Element Technologies Required for Analysis

c. Develop Multiple Nuclide Rationalization Analysis Technology with ICP-MS

●Impact Assessment and Removal Test of Interfering Ions (FY 2017 and FY 2018)

[Objectives]

When analyzing a particular nuclide contained in a fuel debris sample using ICP-MS, other nuclides in the sample may interfere with analysis. The new model ICP-MS reviewed in this project may reduce the impact from interfering nuclides significantly. To this end, interfering nuclides need to be identified, their impact on the analysis (i.e., the type and degree of interference) understood, and appropriate analysis conditions to remove their influence reviewed. Furthermore, in cases where their impact cannot be ignored, the interfering nuclides need to be properly removed.

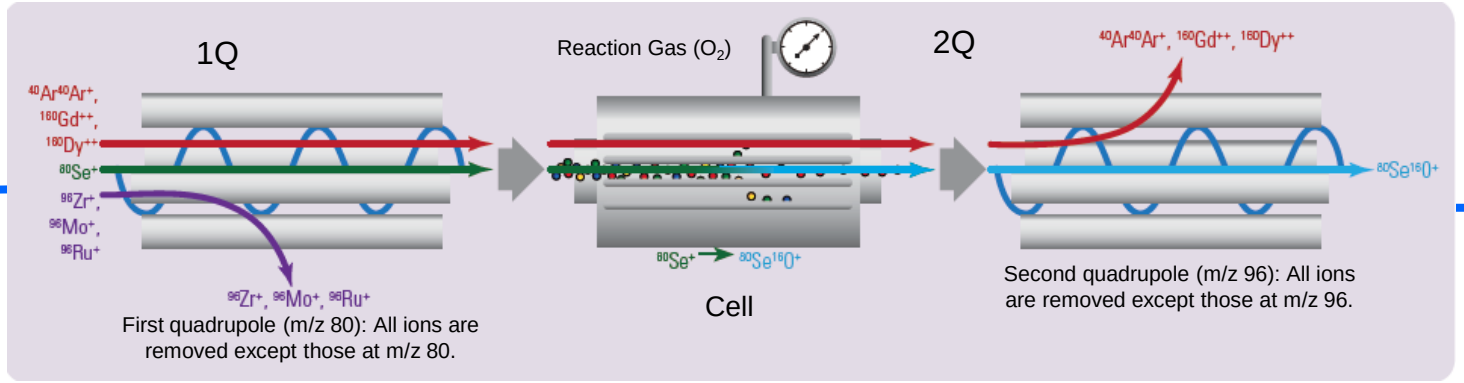
In this project, the impact of interfering ions is evaluated and removal methods for ions established, when necessary, based on the review conducted in FY 2016.

○ Overview of New Model ICP-MS (ICP-QQQ-MS)

Ionization and Introduction of Ions

Interface & Ionization Part

After passing through the first quadrupole, ions react with gas in the reaction cell to change the mass-to-charge ratio of their chemical forms and separated again in the second quadrupole.



Detection of Ions

Detection Part

Through Q1, only ions at m/z 80 ions may enter the cell. Consequently, Zr, Mo, and Ru do not pass through Q1. ^{80}Se reacts with O_2 gas to produce SeO^+. In 2Q, SeO^+ are measured at m/z 96.

(Source: Agilent 8800 Triple Quadrupole ICP-MS Catalogue, Agilent Technologies)

(3) Developing Element Technologies Analysis on Fuel Debris and Other Materials

(ii) Developing Element Technologies Required for Analysis

c. Develop Multiple Nuclide Rationalization Analysis Technology with ICP-MS

[Criteria for Target Achievements]

- Ions that need to be removed are identified. Target removal rates are set. (End of FY 2017 - Completed)
- Methods for removing the above-mentioned ions are identified and the feasibility of such removal methods is verified. (End of FY 2018)

Achievements in FY 2017

◆ Test to Identify Interfering Nuclides

Using ICP-QQQ-MS and solutions that contained potential interfering nuclides, including matrix components reviewed in FY 2016, any peak that affected the mass number of target nuclides was checked for and ions requiring removal were identified.

- Sorted out information on the presence of interfering nuclides and isotopes and lower limits of detection for target nuclides. Target concentrations for removing interfering nuclides were calculated to be 1/10 of the values listed in “Baseline Dose Equivalent Concentration in Vertical Shaft Disposal.” (Table 1)
- Sorted out information on potential interfering ions for target nuclides. (Table 2)
- Gained an outlook that, for Zr, measurements could be made while removing interference from Nb and Mo through a mass shift using NH_3 gas.

Table 1 - Concentration List for Removing Interfering Nuclides (No Gas Mode) using Lower Limit of Detection and the “Baseline Dose Equivalent Concentration in Vertical Shaft Disposal” as Indexes

Target Nuclide		Minimum Baseline Dose Equivalent Concentration (Rubble/Vertical Shaft) (ppb)		Interfering Nuclide		Concentration for Removing Interfering Nuclides (ppb)	
	Lower Limit of Detection (ppb)	1/1	1/10		Lower Limit of Detection (ppb)	1/1	1/10
Ni-59	1.66E-02 (Ni-58)	9.14E+02	9.14E+01	Co-59	2.12E-04	6.92E+02	6.92E+01
Ni-63	1.66E-02 (Ni-58)	7.62E-01	7.62E-02	Cu-63	1.50E-03	4.28E+00	4.28E-01
Se-79	1.57E-01 (Se-78)	4.05E+01	4.05E+00	Br-79	–	–	–
Sr-90	1.90E-04 (Sr-88)	8.28E-05	8.28E-06	Zr-90	1.16E-03 (Zr-90)	1.88E-02	1.88E-03
Zr-93	3.70E-04 (Zr-90)	1.29E+03	1.29E+02	Nb-93	5.00E-05 (Nb-93)	6.72E+02	6.72E+01
				Mo-93	1.60E-03 (Mo-98)	1.17E+04	1.17E+03
Mo-93	1.60E-03 (Mo-98)	3.09E-01	3.09E-02	Zr-93	3.70E-04 (Zr-90)	3.11E-02	3.11E-03
				Nb-93	5.00E-05 (Nb-93)	1.82E-02	1.82E-03
Pd-107	3.80E-04 (Pd-105)	6.30E+04	6.30E+03	Ag-107	6.96E-05	4.71E+04	4.71E+03
I-129	1.42E-03 (I-127)	9.33E+01	9.33E+00	Xe-129	–	–	–
Cs-135	1.60E-04 (Cs-133)	3.05E+02	3.05E+01	Ba-135	5.26E+00	4.36E+03	4.36E+02
Sm-151	3.00E-05 (Sm-147)	5.23E+01	5.23E+00	Eu-151	5.91E-05	2.33E+01	2.33E+00
U-238	–	2.73E+04	2.73E+03	Pu-238	–	–	–
Pu-238	–	5.04E-02	5.04E-03	U-238	–	–	–
Pu-241	–	1.87E-01	1.87E-02	Am-241	–	–	–
Am-241	–	1.89E-01	1.89E-02	Pu-241	–	–	–
Am-242m	–	6.11E-02	6.11E-03	Pu-242	–	–	–

* Concentration of interfering nuclides when the signal strength is at 10% of the baseline dose, the equivalent concentration of nuclides being analyzed

Table 2 - Interfering Ions and

Target Nuclide	Interfering Ion * Shown in red are FP-derived ions	Generation Rate (%)
Ni-59	$[^{118}Sn]^{2+}$	0
Ni-63	$[^{126}Sn]^{2+}$	0
Se-79	$[^{38}Ar^{40}Ar^{1}H]^{+}$	100
Zr-93	$[^{92}Zr^{1}H]^{+}$	0.01 or less
	$[^{92}Mo^{1}H]^{+}$	0.01 or less
Mo-93	$[^{92}Zr^{1}H]^{+}$	0.01 or less
	$[^{92}Mo^{1}H]^{+}$	
Pd-107	$[^{91}Zr^{16}O]^{+}$	0
	$[^{91}Zr^{16}O^{1}H]^{+}$	0.01 or less
I-129	$[^{127}I^{1}H^{1}H]^{+}$	0
Sm-151	$[^{135}Ba^{16}O]^{+}$	0.01 or less
	$[^{134}Ba^{16}O^{1}H]^{+}$	0
	$[^{135}Cs^{16}O]^{+}$ ($[^{133}Cs^{16}O^{1}H]^{+}$)	0
	$[^{134}Cs^{16}O^{1}H]^{+}$ ($[^{133}Cs^{16}O^{1}H]^{+}$)	0.01 or less
Pu-239	$[^{238}U^{1}H]^{+}$	–

Note Percentage of interfering ions generated in target nuclides calculated based on detected signals (i.e., the number of counts)

* The evaluation is based on estimates using stable nuclides since the tests were conducted in a cold environment. Measurements have not been made for α nuclides.

What to Expect in FY 2018

• In succession to Zr, tests for removing interfering nuclides for target nuclides analyzed including Ni - 59 and Ni-63 will be conducted to identify appropriate removal methods.

Project Summary (1/3)

(1) Estimation of Fuel Debris Properties

○ Estimate Dose Rate Near the Surfaces of Debris

By conducting γ ray source calculations based on nuclide decay generation calculations and numerous γ ray transportation calculations simulating sampled fuel debris, dominant factors of the surface dose rate including fuel debris properties were identified, and an evaluation formula to estimate the surface dose rate using these factors as variables was developed. Using this evaluation formula, surface dose rates of Unit 1 fuel debris and MCCI debris were calculated.

○ Update the "Fuel Debris List of Fuel Debris Properties"

The "Fuel Debris List of Fuel Debris Properties" in FY 2016 was updated, with calculated surface dose rates of fuel debris and property data (e.g., hardness) obtained through analyzing the product of a large-scale MCCI test conducted at CEA in France.

(2) Characterization Using Simulated Debris

(i) Characterization of MCCI Products with Heterogeneous Properties

10 test samples collected from various portions of the product obtained in the large-scale MCCI test conducted at CEA in France in FY 2016 were analyzed for their phase state, hardness, etc.

It was confirmed that all product portions were porous and had a structure that contained fine particles, including U-Zr oxide and oxides composed mainly of Cr, in a matrix of Si-Ca-Al oxides. It was also confirmed that the metallic layer near the bottom boundary consisted mainly of Fe alloys.

Physical properties were roughly the same as those listed in the "Fuel Debris List of Fuel Debris Properties."

The greater tendency for erosion in the axial direction by estimating temporal changes in the concrete's erosion profile during the MCCI test based on data from thermocouples installed in the concrete samples was also confirmed.

Recommendations were put together for reactor Decommissioning Work(cutting and processing fuel debris) based on the working conditions observed during a dismantling process for the MCCI test product in FY 2016 and analysis results from this year.

Project Summary (2/3)

(2) Characterization Using Simulated Debris

(ii) Evaluate Emission Behaviors of Fission Products During Dry Heat Treatment

○ Select Medium Volatile FPs with High Environmental Toxicity

Nuclides whose public exposure dose limit exceeds 1 mSv/year according to the ICRP recommendation were defined as “nuclides with high environmental toxicity.” Data on these nuclides based on radioactive nuclides’ activity after ten years from the 1F accident was sorted out. Meanwhile, data on compound forms under dry heat treatment conditions was sorted out, and vapor pressures calculated and compared. FPs whose vapor pressure is higher than that of actinide oxide (UO_3) used as the fuel and lower than that of highly volatile Cs were defined as “medium volatile FPs.”

Based on the evaluation results above, Ag, Te, and oxides of Te, Sn, and Cd were selected as candidates for “medium volatile FPs with high environmental toxicity.”

○ Confirm Evaluation Methods for FP Emission Behaviors

Differential thermal/thermogravimetry measurement were selected as an evaluation method for emission speed, taking dry heat treatment conditions into account. To validate the differential thermal evaluation method, a test using a differential thermal/ thermogravimetry measurement on simulated debris containing FPs with a mixture of UO_2-ZO_2 and Ru was conducted. It was confirmed that the emission start temperature and emission speed could be evaluated.

It was confirmed that, with the differential thermal/thermogravimetry measurement, the evaporation start temperature could be obtained based on weight changes in test samples during a constant-rate heating test where the specimen’s temperature increased at a constant speed. It was also confirmed that the evaporation speed at a specific temperature could be obtained based on the slope of weight changes during an isothermal heating test where a specimen is heated at a constant temperature.

(3) Develop Element Technologies Analysis on Fuel Debris and Other Materials

(i) Prepare for Fuel Debris Sample Analysis

The preparation of procedural documents for analyzing fuel debris, etc. was started at existing analysis facilities using such facilities’ equipment with proven records and applicability for fuel debris analysis.

Project Summary (3/3)

(3) Develop Element Technologies Analysis on Fuel Debris and Other Materials

(ii) Develop Element Technologies Required for Analysis

a. Develop Technologies for Dissolution and Multi - Element Analysis of Fuel Debris

To verify the applicability of alkali fusion for substances listed in the “Fuel Debris List of Fuel Debris Properties,” an alkali fusion test was conducted with sodium peroxide on six types of substances, including chrome oxide, and the conditions that allowed full dissolution of these substances was confirmed. Following the prepared analysis flow, an elementary analysis was conducted using ICP-AES measurement on MOX-simulated debris after dissolving it, the alkali fusion method, and our analysis flow were validated.

b. Develop Fuel Debris Analysis Technologies Using X-Ray CT

To establish a quantitative porosity evaluation technology using X-ray CT, it was confirmed that the technology was applicable to fuel debris with a complex profile. It was also confirmed that, based on the porosity evaluation results, the technology enabled quantitative evaluation with an accuracy equivalent to the conventional evaluation method that uses optical microscopes.

For establishment of a fuel debris component analysis technology using X-ray CT and γ ray tomography, X-ray CT scanning and γ ray tomography measurement on test samples containing a mixture of fuel and cladding components were conducted, and it was confirmed that the technology could be used to analyze fuel and cladding components.

c. Develop a Multiple Nuclide Rationalization Analysis Technology with ICP-MS

In reviewing an analysis technology using ICP-MS, information on interfering nuclides and molecular ions that interfere with measurement of target nuclides was sorted out, and, as an objective for removing interfering nuclides, reference values were set at 1/10 of those listed in the “Baseline Dose Equivalent Concentration in Vertical Shaft Disposal.” Whether the interfering nuclides and molecular ions that were generated interfered with target nuclides was also checked.

Zr is difficult to separate as a target nuclide, and Nb and Mo are interfering nuclides for Zr. It was found that Zr could be measured separately by removing interference from Nb and Mo through a mass shift caused by introducing NH_3 gas during ICP-QQQ-MS measurement.