Fukushima Daiichi Nuclear Power Station Unit 2 X-6 penetration specimen analysis

February 27, 2025

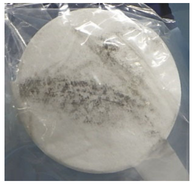
Tokyo Electric Power Company Holdings, Inc.

Power the Future

1. Overview

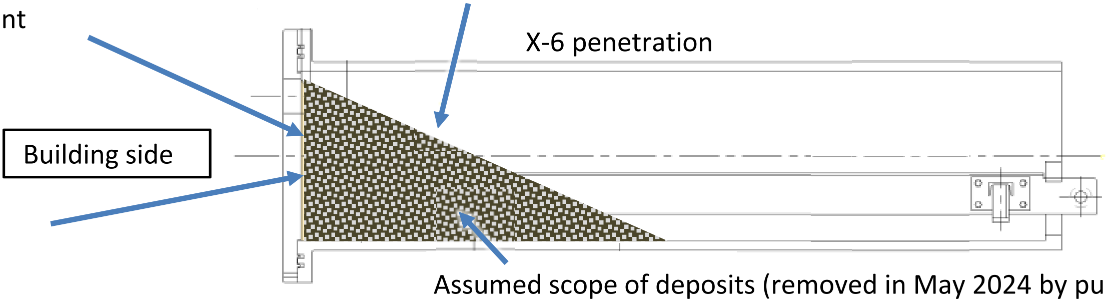
- Specimens taken from various locations are being analyzed in order to deduce the accident mechanism and make assumptions about conditions inside the primary containment vessel, and obtain information that will indirectly help to make inferences about the attributes of fuel debris.
- New specimens of deposit fragments that were acquired when the Unit 2 PCV penetration (X-6 penetration) hatch was opened in 2023 (Specimen ①) and hatch smear (Specimen ②) were analyzed to expand knowledge.
- Based on results that have already been reported, it is assumed that particles, etc. that were churned up into the air when molten fuel fell from the RPV into the PCV accumulated on the cables and formed the deposits.

① Deposit fragment



② Hatch smear

③Material adhered to investigation device (already reported)
（Specimen ③）



PCV side

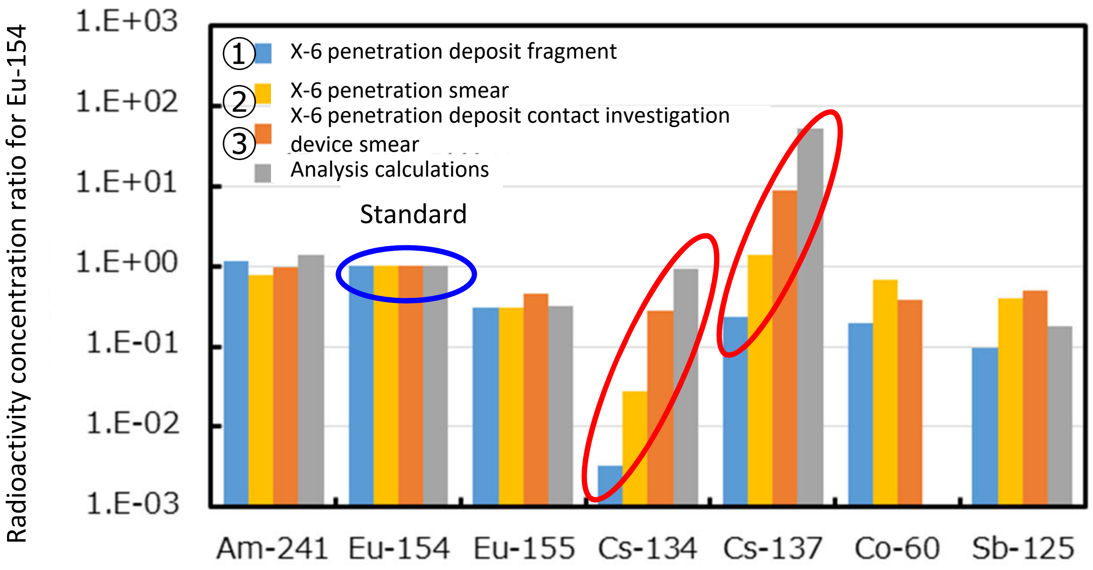
Assumed scope of deposits (removed in May 2024 by pushing them into the PCV)

Specimen	Name	Overview	Analysis agency
①	Deposit fragment	Deposit fragments that fell from the hatch lid went to the X-6 penetration hatch was opened in October 2023.	Nippon Nuclear Fuel Development Co., Ltd.
②	Hatch smear	Taken from the X-6 penetration hatch using a scraper after it was opened. Smear filter paper was used to wipe the scraper and take a sample.	JAEA Okuma Analysis and Research Center
③ （Already reported）	Material adhered to investigation device	Material wiped off of the investigation device with smear filter paper when the deposits inside of the X-6 penetration were investigated in October 2020.	JAEA Oarai Nuclear Engineering Institute Nippon Nuclear Fuel Development Co., Ltd.

2. Radiation measurement results

Gamma ray spectrum analysis（Implemented for Specimens ①, ②, ③）

- Am-241, Sb-125, Cs-134, Cs-137, Eu-154, Eu-155, and Co-60 detected.
- Radioactivity concentration of Am-241, Eu-154 was high.
- Radioactivity concentration ratio for each γ-ray emitting nuclide compiled based on Eu-154（Averages for the Unit 2 core written along side).
  - For all specimens ①~③, the measured presence ratio of Cs-134 and Cs-137 tended to be lower than the calculated value.
    - It is assumed that after Cs volatilized due to the high temperatures when the fuel melted, particles originating from the fuel migrated to the X-6 penetration.
    - Furthermore, it is estimated that the concentration of CS, which is water-soluble, decreased due to long-term steam condensation.
  - This evidence corroborates the water vapor condensation-induced phase flow hypothesis (to be mentioned later) that accompanied.



γ-ray measurement results

※ 1F2 calculated based on JAEA-Data-Code-2012-018

※ The chart shows the Eu-154 radioactivity concentration ratio for each

※ FY2021 measurement values indicate specimen mass values that include the smear paper, and data for 1F2 was corrected on June 10, 2024 based on JAEA-Data-Code-2012-018

α radiation analysis（Implemented for Specimens ②, ③)

- Pu-238, Pu-239+240, Am-241, Cm-244, U-238, U-235
（U-238 and U-235, which have long half-lives, were confirmed using mass analysis)

β radiation analysis（Implemented for Specimen ②)

- Sr-90 detected

3. Composition analysis (analyze elements)

- Elements detected through qualitative analysis (the analysis methods for ①~③ differ).
  - C, which is part of the composition of the material covering the cables, was not detected.

○： Detected
×： Below detectable levels
－： Not applicable

Composition analysis (qualitative) result comparison

	C	O	Mg	Al	Si	S	Cl	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Zr	Mo	Pb	U	Pu
Specimen ①	×	○	○	○	○	○	×	○	○	○	○	○	○	×	×	○	○	○	○	－
Specimen ②	－	○	×	(○)	○	×	×	(○)	○	○	×	○	○	×	×	○	×	×	○	－
Specimen ③	－	－	○	○	×	×	○	○	○	○	×	○	○	○	○	○	○	○	○	○

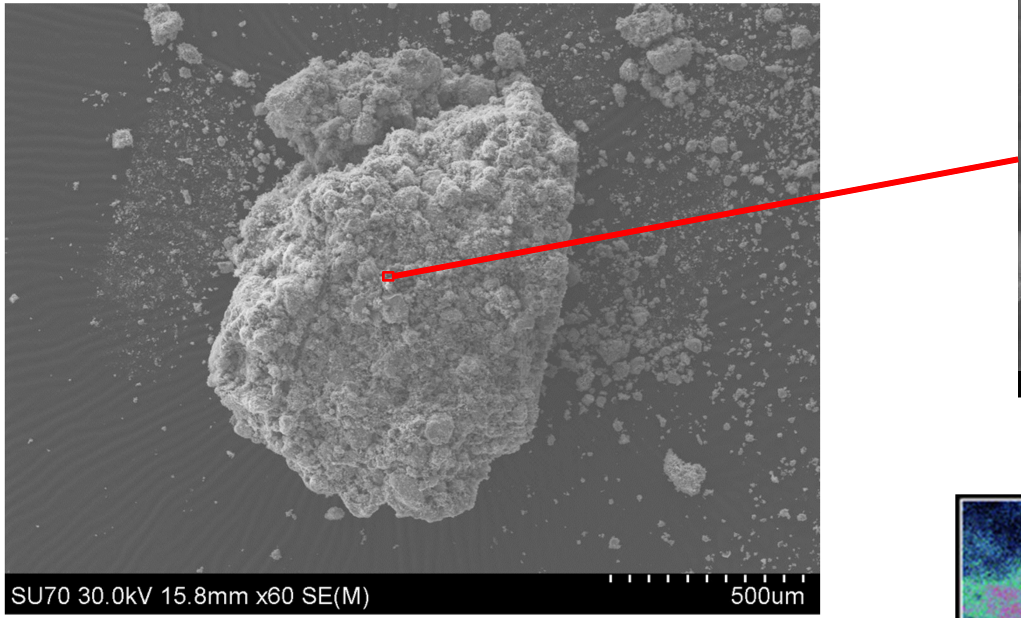
- Quantitative analysis (implemented for Specimen ①)
  - The element composition near the surface of the specimen was analyzed using two methods: A surface analysis that quantifies the elements using SEM-EDS, and a bulk analysis by which a compensating SEM-EDS measurement is produced from the residue from an ICP-MS analysis of the dissolved specimen.
  - A comparison of the primary five metal elements U, Fe, Zr, Cr, Ni was conducted (see the chart below)
    - ➢ The near surface analysis and the bulk (entire specimen) analysis results showed different trends
    - ➢ Compared to Fe, there is a higher ratio of Zr and U inside (bulk) the specimen as compared to the surface, and in light of the results from the fine particle analysis that will be discussed later, it is possible that a Fe vapor deposit formed on/adhered to the surface of particles that have nuclei comprised of Zr or U that are several tens~hundreds μm in size.

Primary element bulk concentration (ICP-MS) and surface concentration (SEM-EDS) comparison

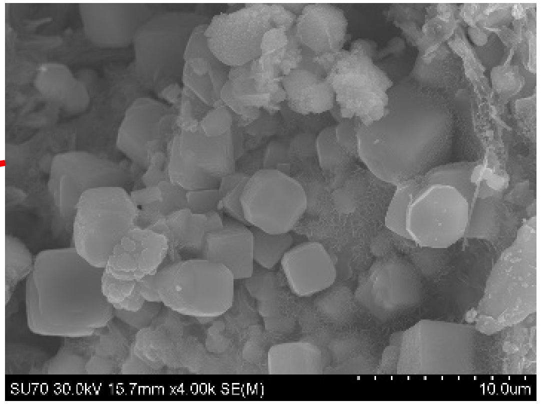
Element	O	U	Fe	Zr	Cr	Ni
ICP-MS+SEM-EDS(bulk)　(at%)	68	6	13	7	3	2
SEM-EDS(surface)　(at%)	47	2	39	5	2	4

- The concentrations of six primary elements identified through the composition analysis and surface analysis and normalized at 100at%.
- O value is for reference (O mass for ICP-MS is assumed to be from the difference between the detected element mass and the mass of the residue, and the mass of the specimen provided for analysis. The quantitative value for O for SEM-EDS has a great deal of uncertainty).

4.1 Solid analysis using SEM-EDS（Specimen ① Hatch deposit fragment）

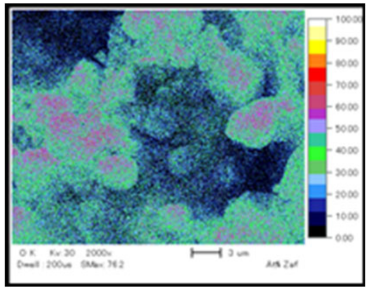


Surface of particle contained in Specimen ①

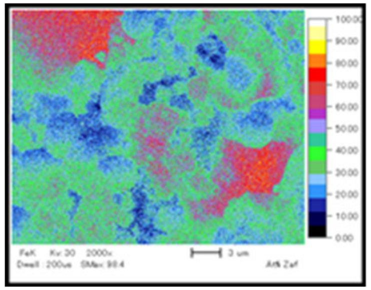


SEM image

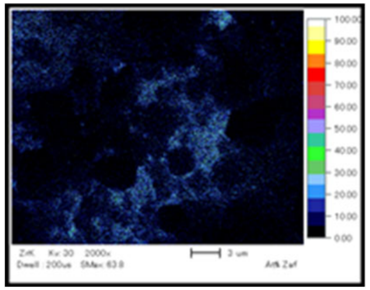
- Agglomerated particle 1mm in size that has tiny iron oxide particles 1~5μm in size on the surface.
- Zr and U are present in small quantities.



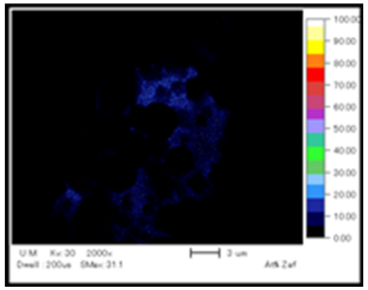
O



Fe



Zr



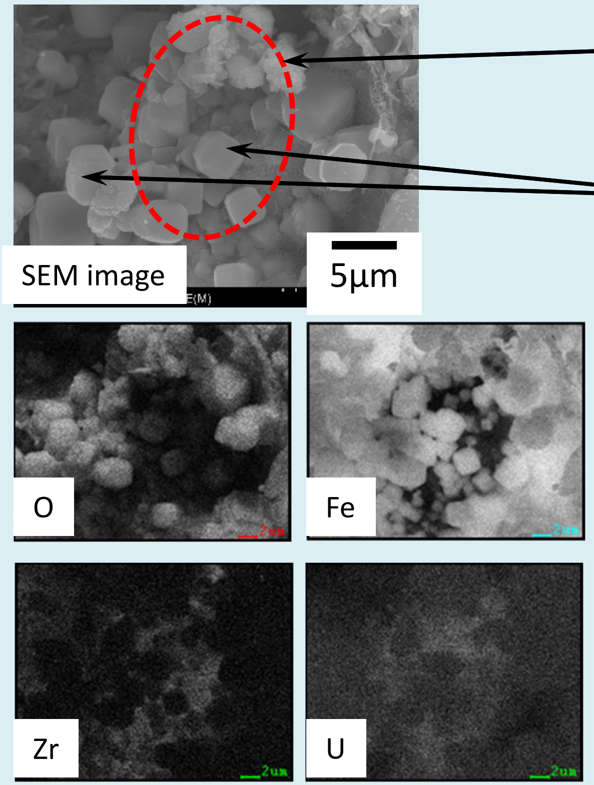
U

Assessment

- Same as the X-6 penetration deposit contact investigation smear sample.
- It is assumed that the small iron oxide particles were formed through evaporation condensation, and that they floated in the air phase for a long time and migrated into the X-6 penetration along with water vapor because the particles are so small.

4.2 Overview comparison of particles sampled from within the X-6 penetration

Specimen ① Hatch deposit fragment



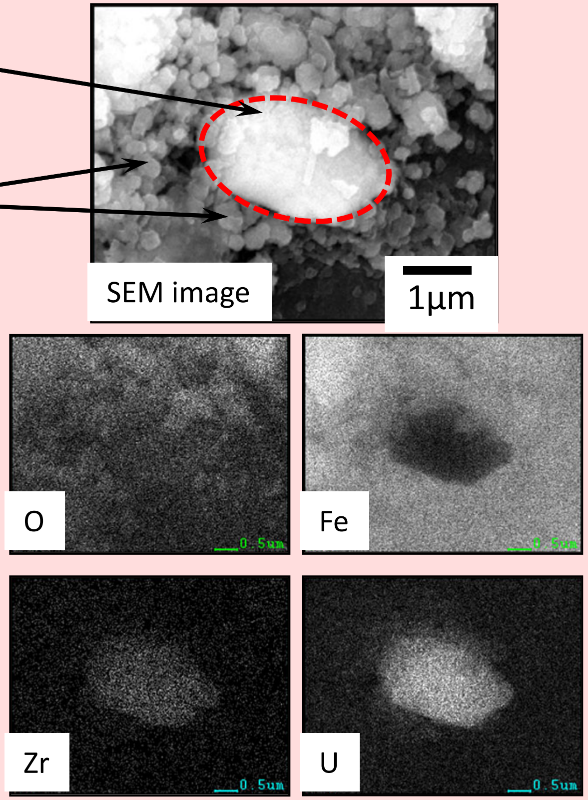
Regions with high U concentrations

Many fine iron oxide particles

Since oxygen and iron are widely present in both specimens it is assumed that the multiple fine particles that exist around the regions of high uranium concentration are iron oxide

SEM image and attribute x-ray image

Specimen ③ Adhered to investigation device



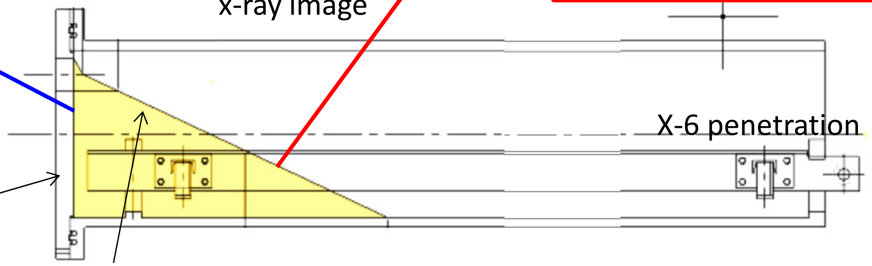


Diagram of deposits

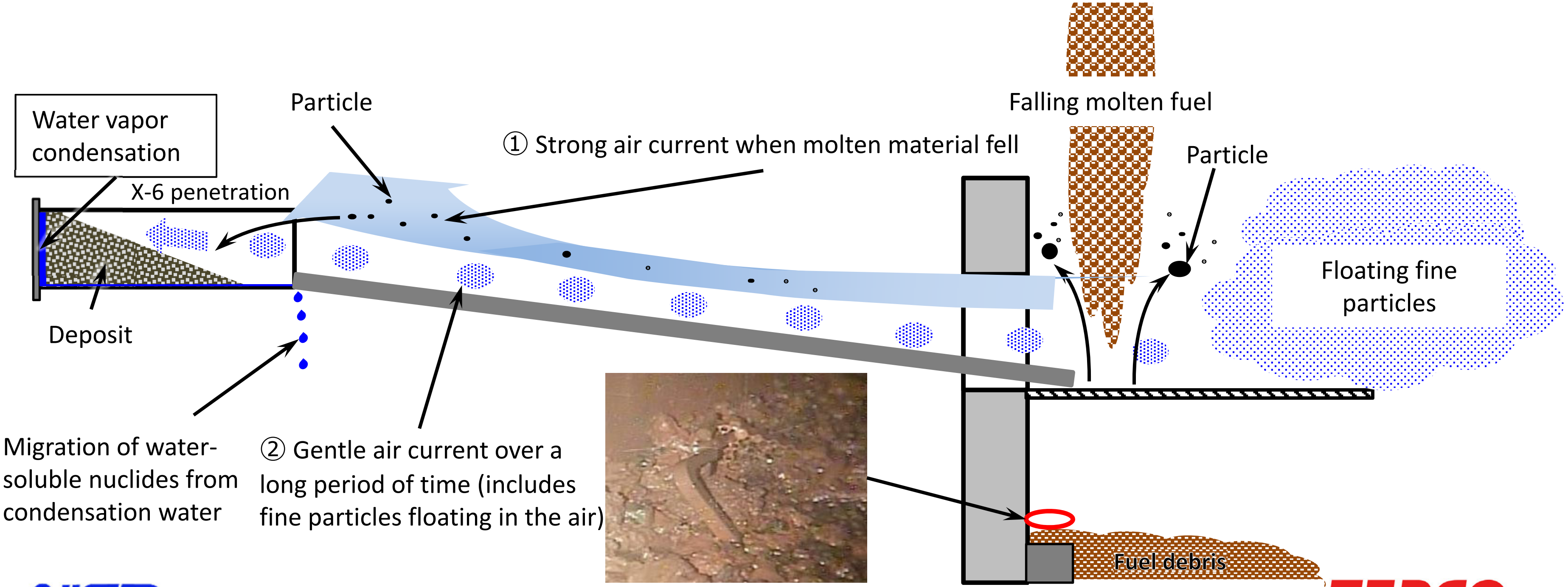
5. Assumed deposit mechanism

It is assumed that the deposits inside the X-6 penetration formed around the cables that were stored inside as a result of the combination of the following two mechanisms:

① Particles created when the molten fuel fell from the damage to RPV were carried by a strong air current and accumulated in different places as the air currents changed （U-Zr-O particles over 40μm are present).

② Fine particles floating in the air inside the pedestal were carried by a relatively gentle but long-term air current produced by the differential pressure that occurred in conjunction with water vapor condensation inside the PCV and deposited themselves on the low temperature X-6 penetration flange (an abundance of iron oxide particles less than a 1~2μm in size are present).

Water vapor condensation was confirmed by the water droplets that poured out when the flange was opened.

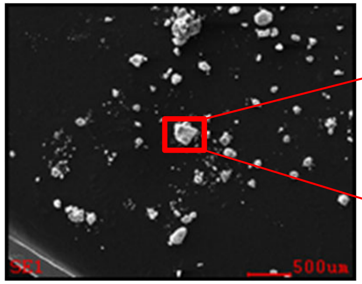


Upper tie plate that didn't melt

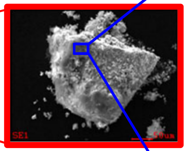
6. Confirming particles related to the presumed accident mechanism
(There are regions in Ni_3S_2 where platinum group FP are scattered)

- Particle specimens taken from the yellowish area seen on the surface of the specimen (particle of interest from the yellow singularity on the surface of A-1) were used to prepare a TEM-EDS specimen that focused around a region of high Ni concentration(Region 03).
- Precipitated Ru, Rh and Pd particles are present in the Ni_3S_2 in the high Ni concentration region (Region 03).
- This indicates a reaction with the UO_2 pellets and zircaloy (cladding tube and channel box) that continued to combust, or with the SUS (control rods, etc.) or Ni base alloy, or with S originating from seawater, etc.

➢ It is assumed that when the particles were reacted with S at high temperature conditions in the RPV, so this is corroborating evidence that seawater was injected into the RPV.

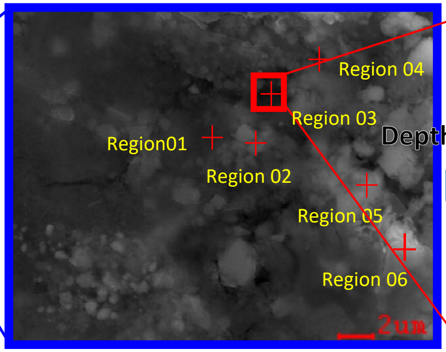


Yellow singularity on A-1 surface

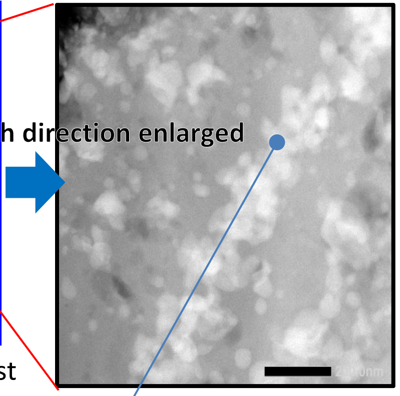


Particle of interest

Plate specimen SEM image

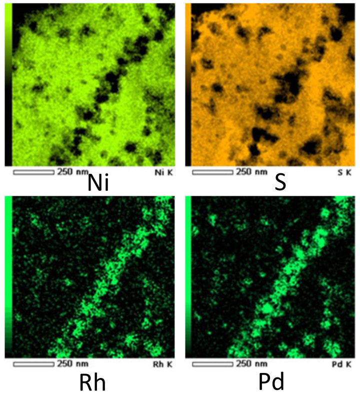


Enlarged surface of particle of interest



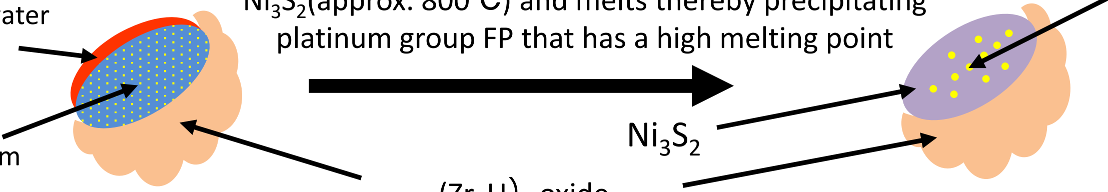
200.0nm

Trigonal crystal Ni_3S_2 (Includes Ru, Rh, Pd)



Element map

TEM observation results



$H_2/H_2O \gtrsim 0.2$

S lowers the melting point of Ni which becomes Ni_3S_2(approx. 800℃) and melts thereby precipitating platinum group FP that has a high melting point

Adhered S from saltwater composition, etc.

Metal Ni containing platinum group FP

Platinum group FP

Ni_3S_2

(Zr, U） oxide

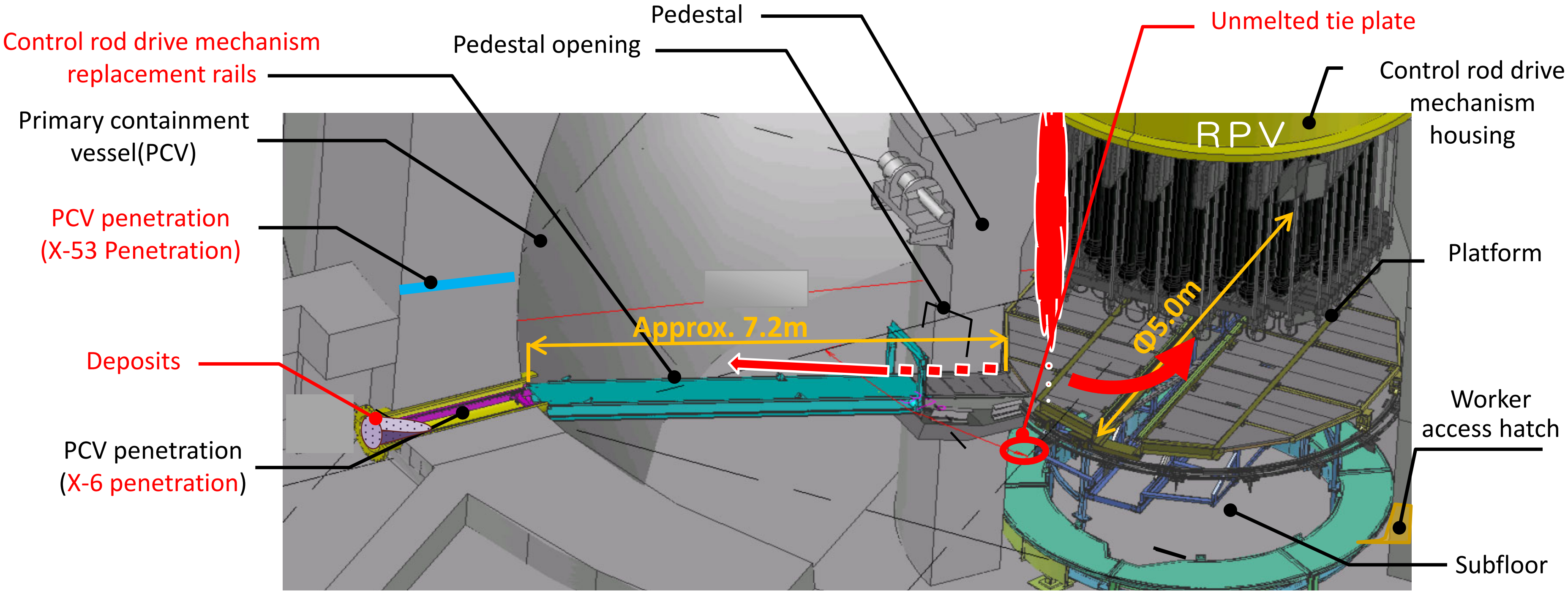
Presumed deposit structure of platinum group FP inside Ni_3S_2

Conclusion

- Radiochemical analysis, composition analysis, and solid analysis (SEM-EDS, TEM-EDS) were performed for specimens ① Deposit fragment, ② Hatch smear, and ③Material adhered to investigation device (already reported) .
- Radioactive concentrations of the deposits showed small percentages of Cs-134 and Cs-137, which are volatile nuclear fission products, and large percentages of Am-241 and Eu-154.
- The main elements of the deposits originate from structures made of Fe, Cr, and Ni, and are mixed with elements originating from the combustion of U and Zr. C was not detected. Furthermore, the deposits comprise tiny iron oxide particles less than 1~3µm in size and particles ranging in size from several 10~several hundred µm that contain U.
- Almost none of the elements from the melted cable covering remain in the deposits.
- When the molten material (or molten-solidified material) fell from the RPV into the PCV, some of the particles from this substance remained in the air and migrated into the X-6 penetration suggesting the possibility that a large amount of the deposits formed as tiny iron oxide particles were supplied in this manner over a long period of time.

[Reference] Specimen sampling location

- In the X-6 penetration the control rod drive mechanism replacement rails face opposite the opening of the pedestal.
- An unmelted tie plate was found to have fallen near the inside wall of the pedestal in the vicinity of this opening suggesting that there is a relatively large rupture in the bottom of the RPV above this point.
- There is an abundance of deposits inside the X-6 penetration and it is assumed that these deposits were carried from inside the pedestal.

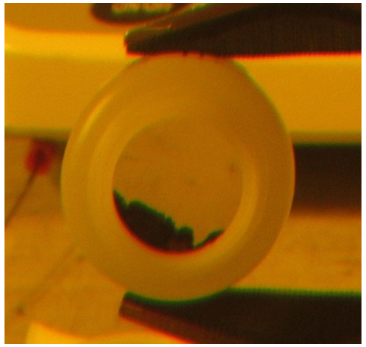


Positional relationships inside the Unit 2 X-6 penetration

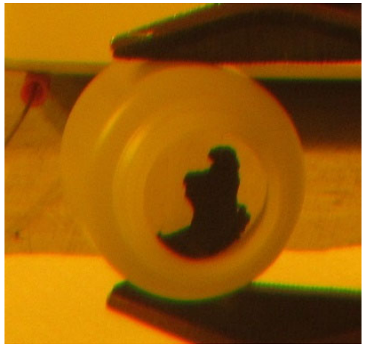
[Reference] Specimen ① X-6 penetration deposit fragment

- Fragments fell on the absorption mat when the X-6 penetration flange was opened.
- The fragments were put into two containers.
- The fragments are extremely brittle and can be easily crushed.
- The specimens in the two containers were transported to the Nippon Nuclear Fuel Development Co., Ltd. hot lab in Ibaraki Prefecture and analyzed.

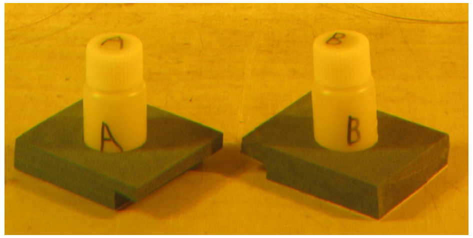
Transported to hot lab



Specimen A



Specimen B



Specimen	B.G.	Dose rate (γ)
A	180 [μSv/h]	18.6 [mSv/h]
B	180 [μSv/h]	15.2 [mSv/h]

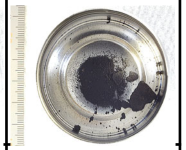
An ionization chamber was sealed to the wall of the container and maximum doses were recorded while rotating the unit

Specimen A

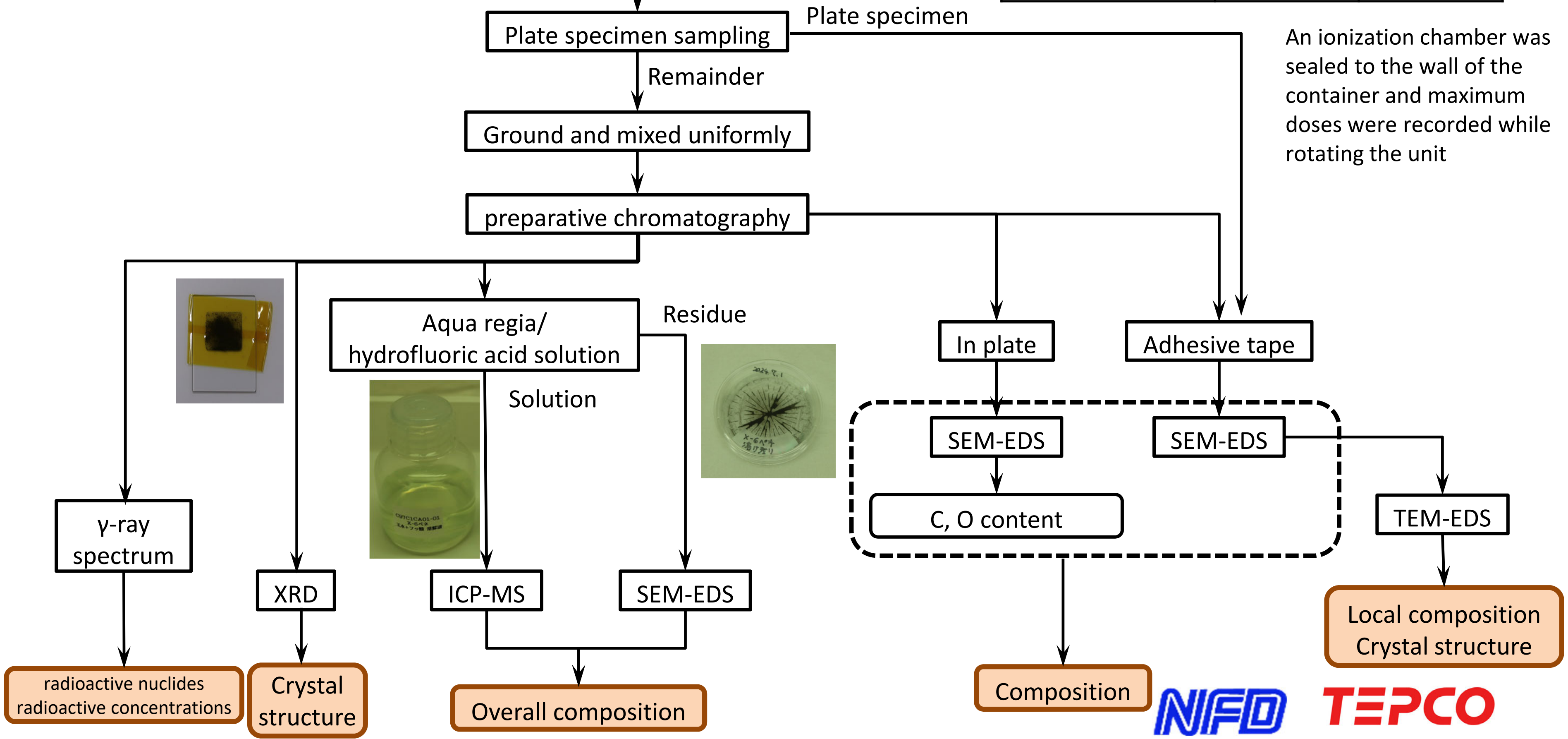
Specimen B

External appearance of specimen when received

[Reference] Specimen ① Analysis flow

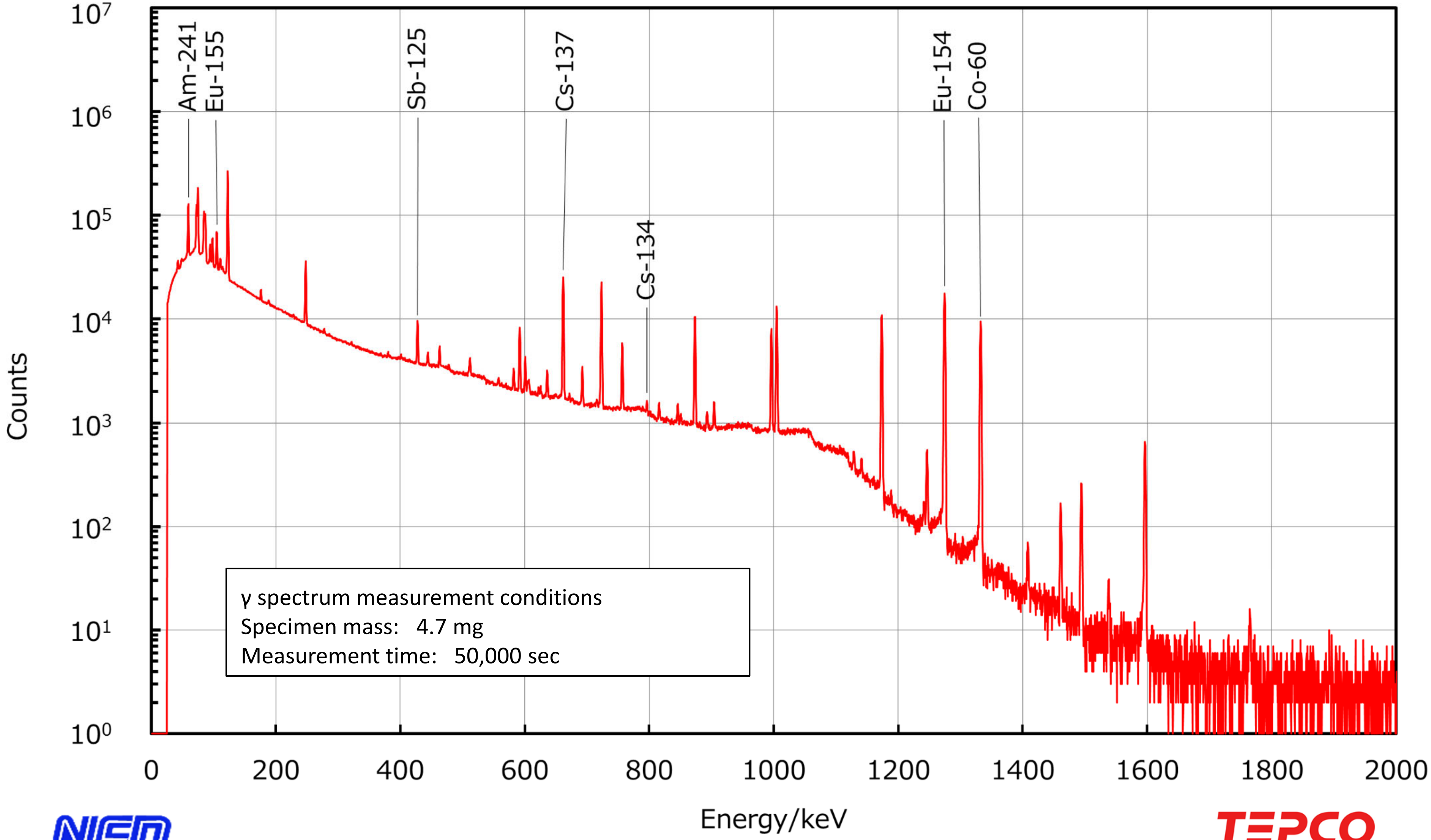
	A	B
External appearance		
Mass [g]	3.186	1.879
Dose rate [mSv/h]	18.6	15.2
B G [μSv/h]	180	180

An ionization chamber was sealed to the wall of the container and maximum doses were recorded while rotating the unit



[Reference] Specimen ① γ-ray spectrum measurement results

- Primary nuclides detected: Am-241, Eu-154, Eu-155, Cs-134, Cs-137, Co-60, and Sb-125.



γ spectrum measurement conditions
Specimen mass: 4.7 mg
Measurement time: 50,000 sec

[Reference] Specimen ① γ-ray measurement results

- γ-ray spectrum measurement were taken after the specimen was uniformly crushed and batched.
- Am-241, Sb-125, Cs-134, Cs-137, Eu-154, Eu-155, Co-60 were quantified.
- FY2021 measurement values indicate radioactivity for mass of the specimen sampled from the X-6 penetration deposit contact investigation device smear that includes the smear paper.
- Change over time has been simplified, and the radioactivity ratio of Eu-154, which is a highly radioactive nuclide, was assessed (Co-60 was excluded).
- With the exception of water-soluble Cs, These analysis results, and the FY2021 measurements were the same as the analysis results for the radioactivity ratio of Eu-154.

Nuclide	Productivity concentration(Bq/g)		Radioactivity concentration ratio of Eu-154 ※2			
	Values from this analysis	FY2021 measurements ※3	Values from this analysis	X-6 penetration smear	FY2021 measurements ※3	Analysis calculations ※1
Am-241	2.8E+07	2.0E+03	1.137	0.755	0.963	1.339
Eu-154	2.5E+07	2.1E+03	1.000	1.000	1.000	1.000
Eu-155	7.6E+06	9.3E+02	0.308	0.298	0.452	0.318
Cs-134	8.1E+04	5.8E+02	0.003	0.027	0.282	0.900
Cs-137	5.8E+06	1.8E+04	0.235	1.366	8.936	52.511
Co-60	4.7E+06	7.9E+02	0.192	0.676	0.383	—
Sb-125	2.4E+06	1.0E+03	0.098	0.390	0.484	0.180

Normalized on June 10, 2024

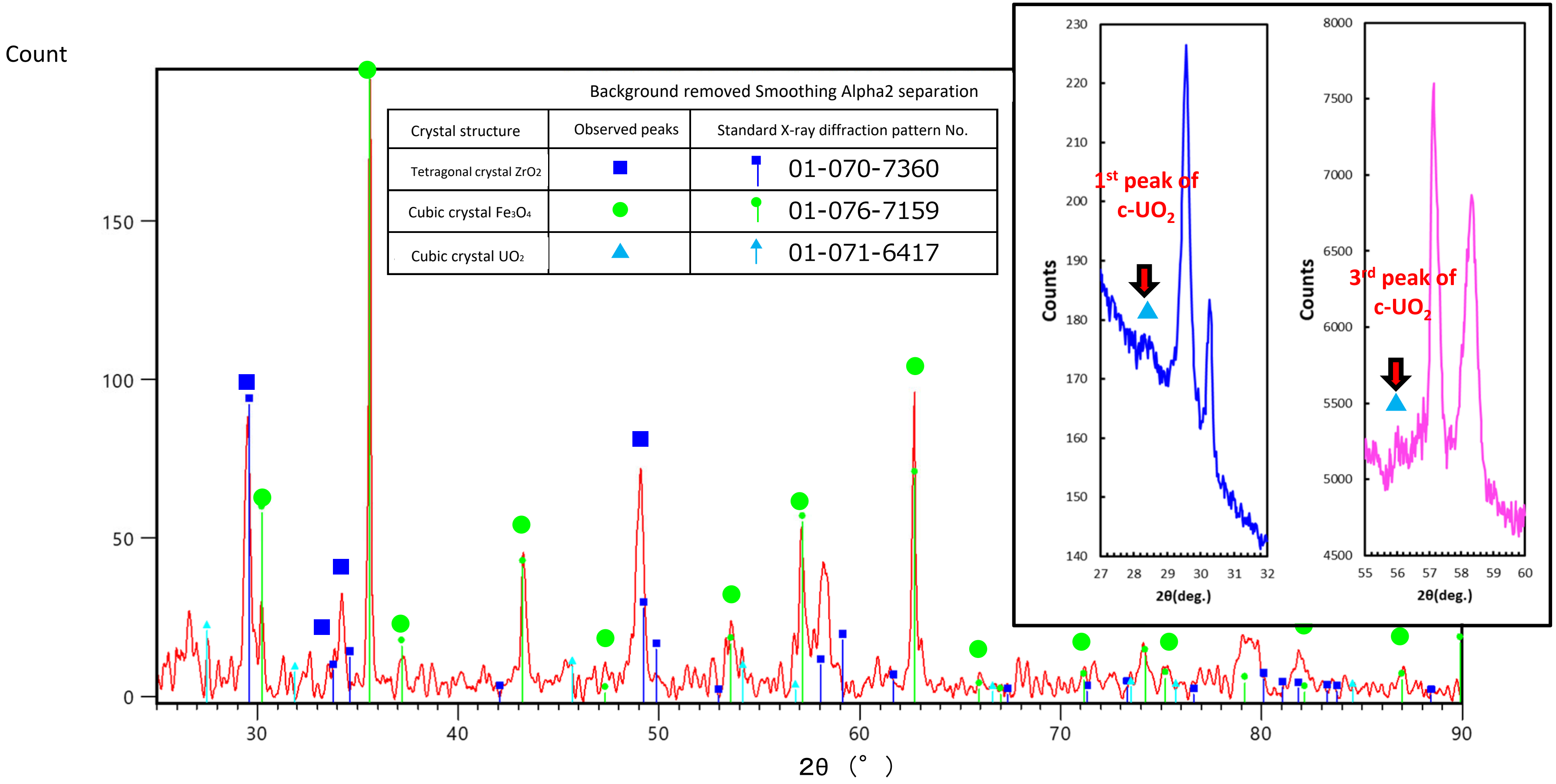
※1 1F2 calculated based on JAEA-Data-Code-2012-018

※2 The chart shows the Eu-154 radioactive concentration ratio for each

※3 FY2021 measurement values indicate specimen mass values that include the smear paper, and corrected on June 10, 2024 based on 1F2 ORIGEN analysis results

[Reference] Specimen ① Uniform powder specimen crystal structure （XRD）

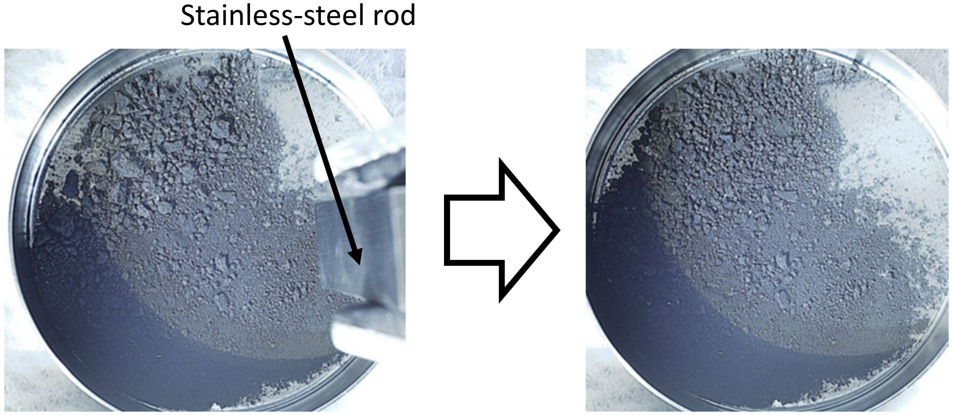
- The cubic crystal Fe_3O_4 peak and tetragonal crystal ZrO_2 peak were examined.
- A very weak peak assumed to be a cubic crystal UO_2 peak was seen (refer to enlarged portion of chart).
- There is a peak shift on the low angle side of the tetragonal crystal ZrO_2 that suggests a solid solution of other elements.



Crystal structure	Observed peaks	Standard X-ray diffraction pattern No.
Tetragonal crystal ZrO_2	■	01-070-7360
Cubic crystal Fe_3O_4	●	01-076-7159
Cubic crystal UO_2	▲	01-071-6417

[Reference] Specimen ① Composition analysis results（ICP-MS＋SEM-EDS）

- Specimen preparation
  - Plate-shaped clumps were sampled after coarsely grinding specimens A and B.
  - The remaining portions were ground and mixed by pushing them several times with a stainless-steel rod.
  - Specimens A and B were determined to be equivalent and mixed together to prepare a uniform powder.



Specimen preparation (uniform powder mixture)

- ICP-MS＋SEM-EDS（Bulk）
  - 109.5 mg of the specimen were dissolved in aqua regia and hydrofluoric acid
    - Undissolved residue: 6.4 mg
    - Dissolution rate: Approx. 94%
    - Overall composition = Solution composition(ICP-MS)＋ Undissolved residue composition (SEM-EDS)

- Semi-quantitative analysis using SEM-EDS (Specimen surface)
  - The uniform powder was sampled using adhesive tape and analysis of the elements was performed excluding C and O contained in the adhesive tape.
  - The specimen was sampled using an In plate that does not contain C and O, and the remaining quantity was analyzed with a focus on Fe, which remained in large quantities, without being impacted by peaks from C, O or In.

[Reference] Specimen ① Surface composition analysis of the entire specimen (ICP-MS＋SEM-EDS analysis results from the uniform powder)

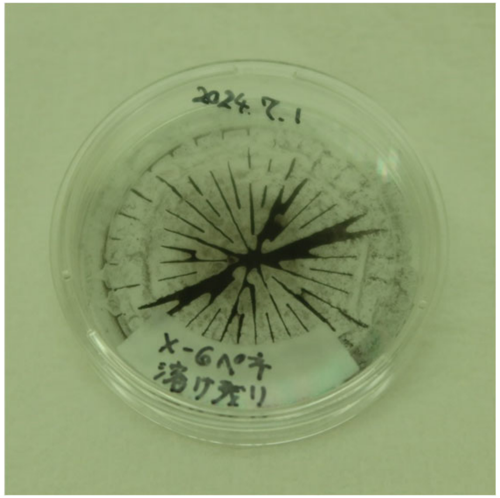
- The uniform powder (109.5mg) was dissolved in aqua regia and hydrofluoric acid.
- The undissolved residue was filtered and the solution was separated from the undissolved residue (6.4mg).
- The dissolution rate ((Dissolution sample quantity - Undissolved residue quantity) / Dissolution sample quantity) was approximately 94%.
- The solution and undissolved residue were subjected to composition analysis using ICP-MS and SEM-EDS, respectively.
- Compositional elements (Fe, Cr, Ni, etc.) were mixed in with elements originating from the fuel (U, Zr).
- The amount of uranium detected was 38.8mg.

Element	ICP－MS+SEM-EDS Specimen composition (at%)			
B	<	1.5		
Na	<	1.4		
Mg	<	1.3		
Al		0.16	±	0.04
Si	<	1.1		
Ca		0.025	±	0.003
Ti	<	0.2		
Cr		2.7	±	0.1
Mn		0.18	±	0.02
Fe		12.9	±	0.7
Ni		2.12	±	0.03
Cu	<	0.2		
Zn	<	0.5		
Zr		7.3	±	0.1
Mo		0.079	±	0.001
Ba	<	0.1		
Pb		0.06	±	0.01
U		6.4	±	0.1
O		68		

※ Only U-238 was quantified (U-235, etc. not included)

※ Values followed by "±" indicate uncertainty (coverage factor k=1)

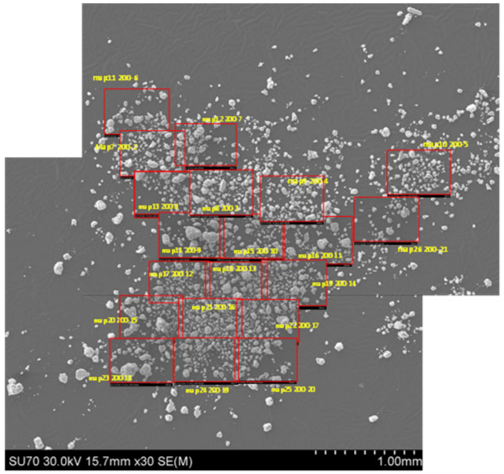
Solution
(Liquid color: light yellow)



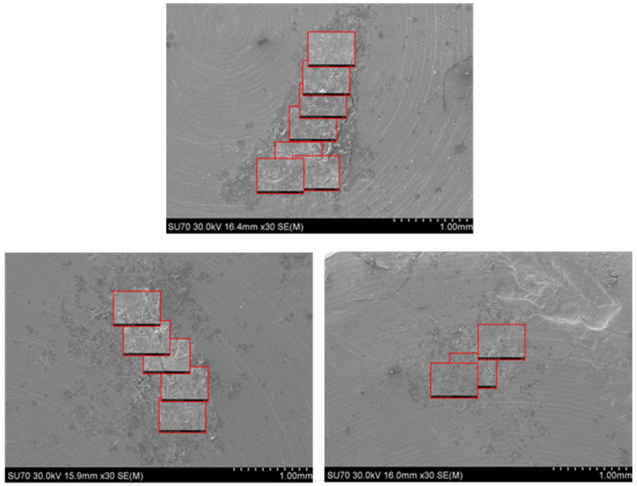
Undissolved residue
(Amount of residue: 0.0064g)

[Reference] Specimen ① Surface composition analysis of the entire specimen (SEM-EDS analysis position of the uniform powder)

- Uniform powder was sampled using adhesive tape from 20 locations and an In plate from 15 locations, and surface analysis was performed.
- C was not detected, and the molten cable covering was assessed to contribute little to the deposits inside the X-6 penetration.
- Approximately 38at% is Fe, the main element, and a total of approximately 45at% elements originating from structural materials, etc.
- U content rate is approximately 2at%, and a total of approximately 7at% of the elements originate from fuel.



Uniform powder (on adhesive tape)



Uniform powder (on In plate)

Surface composition analysis results of the entire specimen using SEM-EDS at%

	C	O	Mg	Al	Si	S	U	Ti	Cr	Fe	Ni	Zr
Average	n.d.	46.0	0.1	0.1	1.7	0.2	2.1	0.2	2.4	37.8	4.4	5.0
σ	0.0	1.0	0.2	0.2	0.3	0.2	0.3	1.0	0.2	1.1	0.2	0.6

- σ indicates the discrepancy in analysis results between each region (Standard deviation for 15 regions of C, O, and 20 regions of other elements).
- The average value from 15 regions was used for C, O in the In plate specimen, and the average from 20 regions on the adhesive tape were used for the values for other elements and normalized so the total for the entire specimen came to 100at%.
- In plate specimen results were corrected so that the Fe average was not remarkable when integrating the results.

[Reference] Specimen ① Uniform powder composition analysis results and surface composition analysis results comparison

- A comparison of the five main metal elements (U, Fe, Zr, Cr, Ni) was made using the ICP-MS+SEM-EDS element composition analysis results and the SEM-EDS powder surface composition analysis results.
- It is assumed that the ICP-MS+SEM-EDS results obtained from dissolving and analyzing the specimen present the data for the entire specimen (bulk), while the SEM-EDS results, which measure the specimen as a powder, show the data for the specimen surface.
- Fe is abundant on the surface of the uniform powder, suggesting that U and Zr are abundant on the inside.
  - It is possible that Fe vapor deposits adhered to the surface layer of particles several 10~100µm in size containing U and Zr and accumulated into the abundant deposits.
- The U/Fe ratio is approx. 50at% in bulk and approx. 5at% on the surface.
  - This is relatively high in the X-6 penetration deposit contact investigation device smear (2~4at%).

Main element bulk concentration (ICP-MS) and surface concentration (SEM-EDS) comparison

Element	O	U	Fe	Zr	Cr	Ni
ICP-MS+SEM-EDS(bulk) (at%)	68	6.4	12.9	7.3	2.7	2.1
SEM-EDS(surface) (at%)	47	2	39	5	2	4

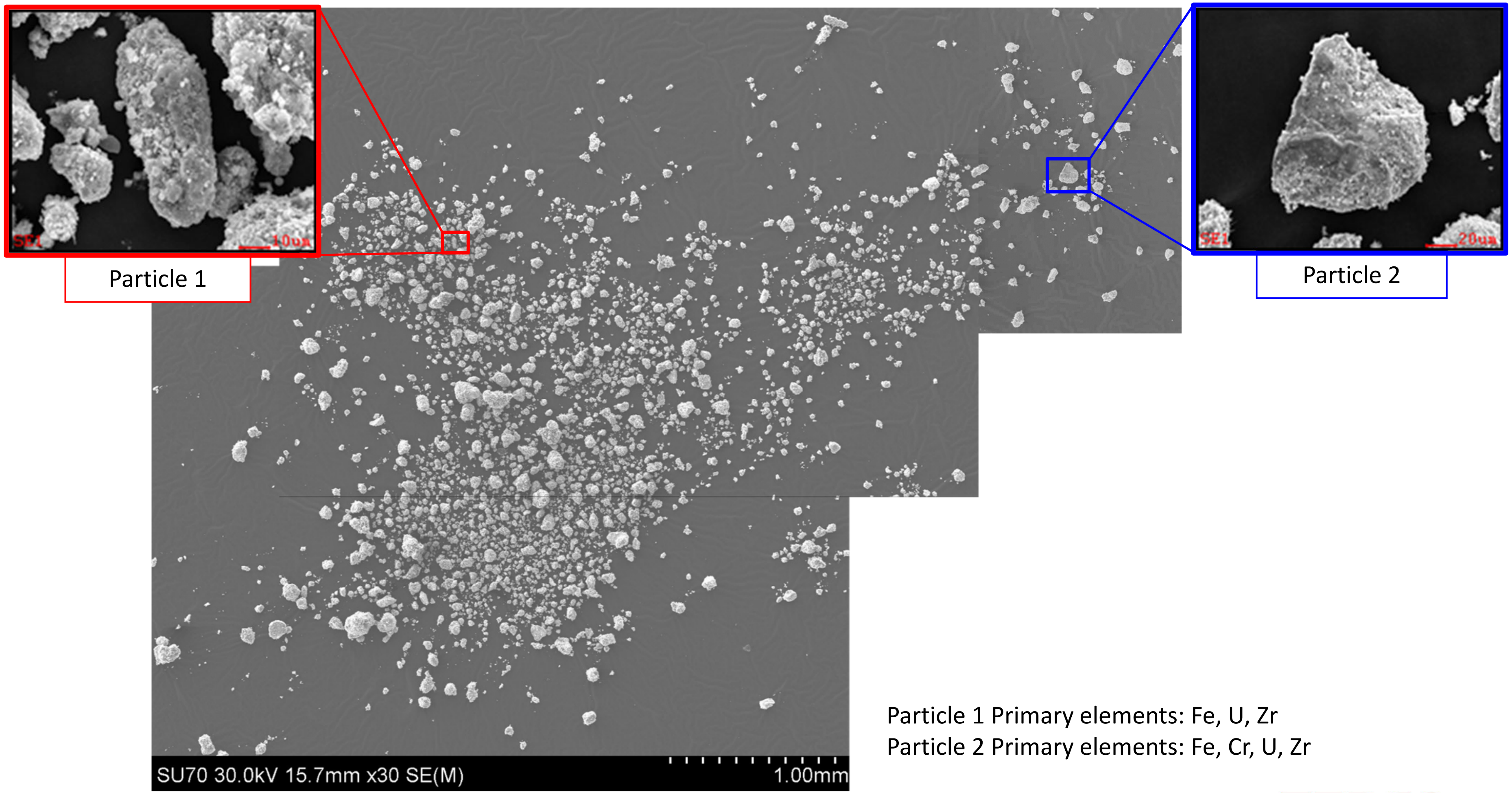
- The concentrations of the primary six elements from compositional analysis and surface analysis were extracted and normalized at 100at%
- O Values are for reference (ICP-MS O quantity is assumed to account for the difference in the amount of detected elements and minuscule amount of residue, and the amount of the specimen provided for analysis. The SEM-EDS O quantity contains a large amount of uncertainty.)

Primary radioactive nuclide ratio for U mass

Nuclide	Am-241	Eu-154	Eu-155	Cs-134	Cs-137	Co-60	Sb-125
Radioactivity ratio for U mass (Bq/ng-U)	7.92E-02	6.97E-02	2.15E-02	2.28E-04	1.64E-02	1.34E-02	6.80E-03

[Reference] Specimen ① External appearance of uniform powder （2PEN2301-2） and TEM particle of interest

- Particles several 10~100µm in size, most particles are Fe, U and Zr.
- From the uniform powder, TEM-EDS specimens were made from particle 1, which has Fe, U, and Zr as the primary elements, and particle 2 which has Fe, Cr, U, and Zr as the primary elements.



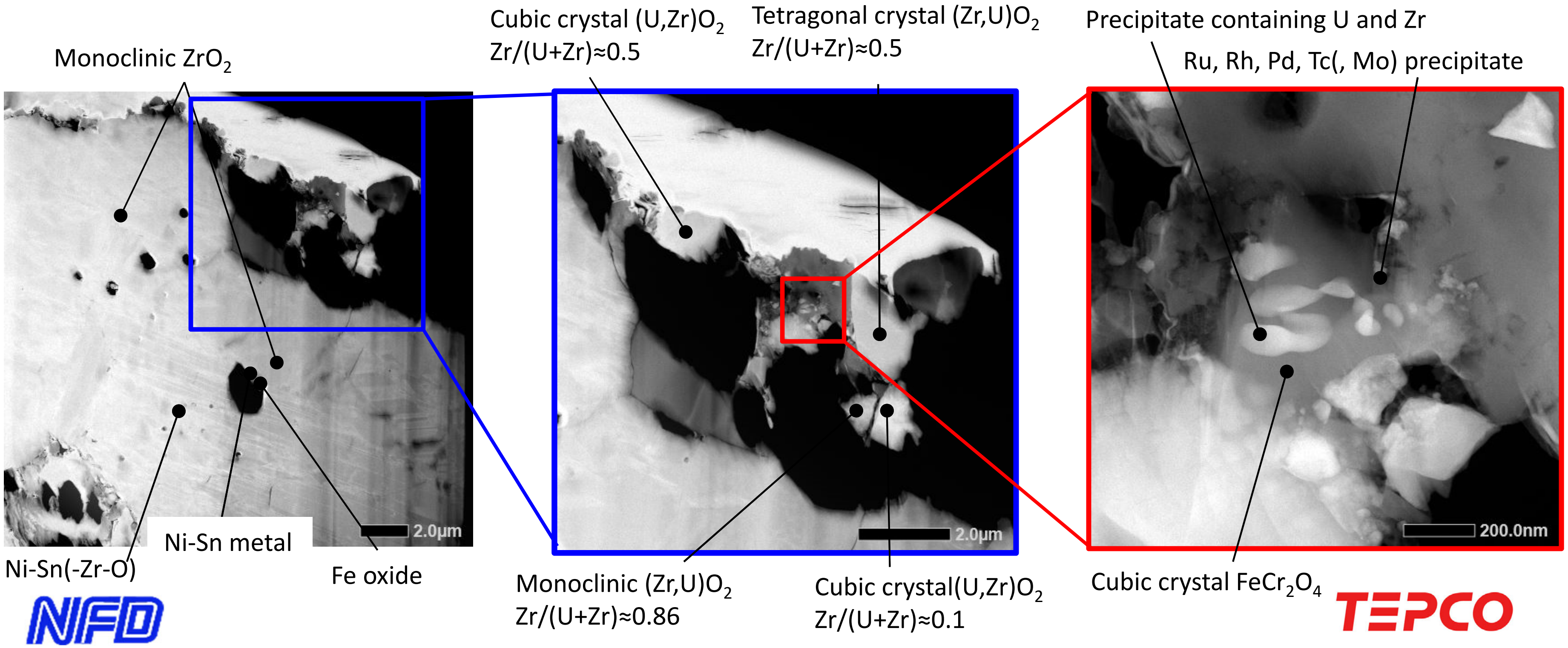
SEM image of particles of interest

Particle 1 Primary elements: Fe, U, Zr
Particle 2 Primary elements: Fe, Cr, U, Zr

[Reference] Specimen ① TEM-EDS results（Uniform powder particle 1　Region 01）

- Tiny Fe oxide particles and metal Ni or Sn precipitate are present inside the large monoclinic ZrO_2 that do not contain U.
- The blue box shows adhesion of multiple types of tiny particles.
- In the red box tiny particles containing U and Zr are scattered within the cubic crystal $FeCr_2O_4$, suggesting that as tiny particles precipitated from the Fe-Cr-U-Zr-O molten material, cubic crystal $FeCr_2O_4$ coagulated.
- Particles comprised of Ru-Rh-Pd-Tc(-Mo) are present.

Assessment
- Since U is not contained, it is assumed that other tiny particles adhered themselves to the solidified molten zircaloy mass.
- It is hypothesized that the adhered particles were quickly cooled from temperature of approximately 1800°C.

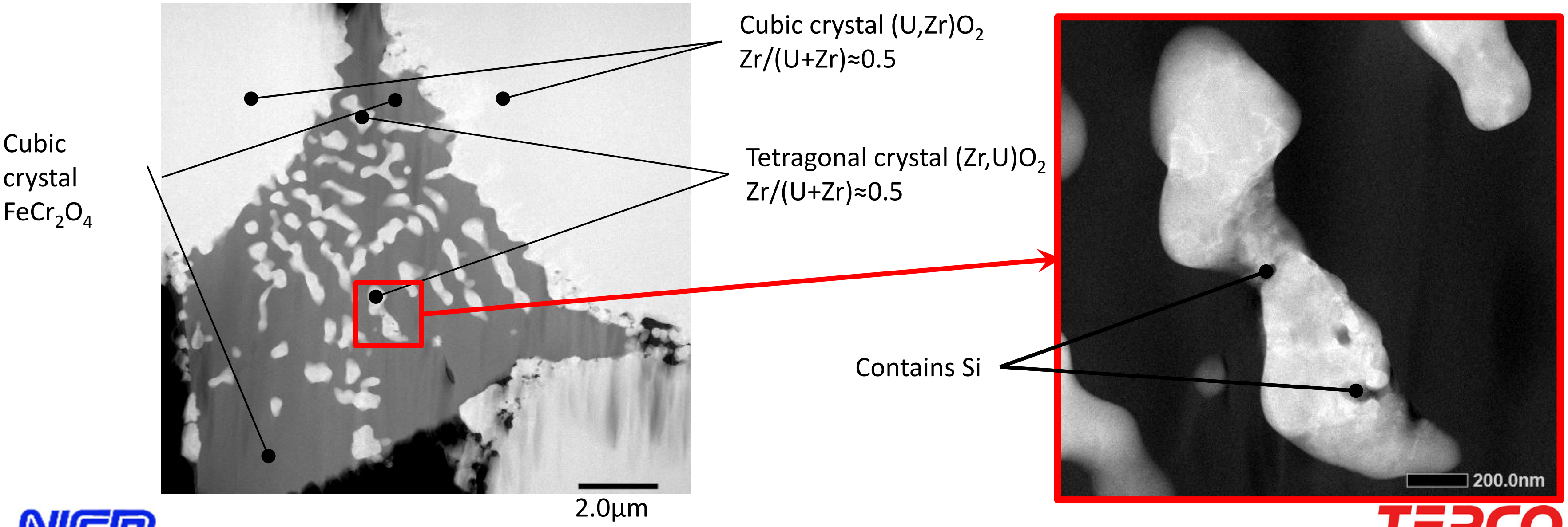


[Reference] Specimen ① TEM-EDS results（Uniform powder particle 2　Region 05）

- Cubic crystal $FeCr_2O_4$ that contain miniscule precipitate of Tetragonal crystal (Zr, U) O_2 (high temperature stable phase) are present in between the large cubic crystal $(U,Zr)O_2$ (high temperature stable phase) precipitate that does not have smooth precipitate boundaries.
- Tiny Si precipitate (red box) can be seen if you enlarge the boundary of the tetragonal crystal $(Zr,U)O_2$l.

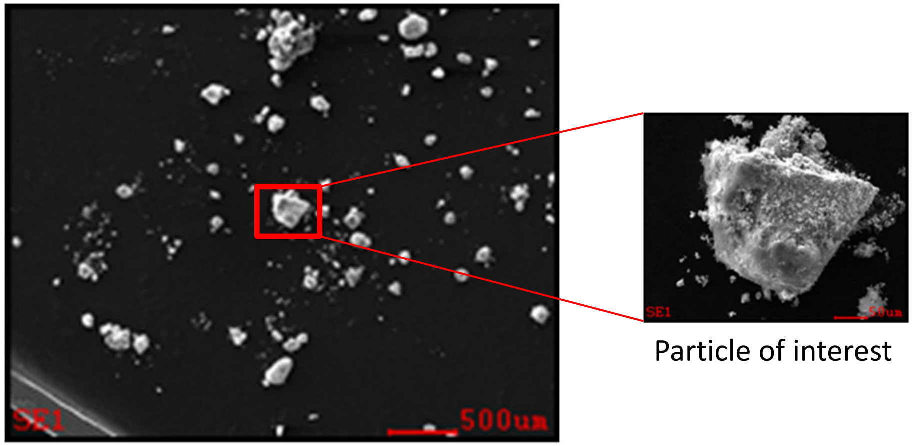
Assessment

- ➢ Fuel reacted with structural materials to form molten U-Zr-Fe-Cr-O (above 1,900°C, composition dependent) that coagulated.
- ➢ It is assumed that the Si is from the tie plate, structural materials, or the sealant used on the inner surface of the suppression chamber.
- ➢ Tiny cubic precipitate $(U,Zr)O_2$ crystals were formed during the cooling process.
- ➢ ①, ② were formed by the agglomeration of tiny precipitate after is passed though the liquid phase.
- ➢ We speculated that tetragonal crystal $(Zr,U)O_2$ formed right before the $FeCr_2O_4$ phase coagulated prior to achieving sufficient equilibrium to form smooth boundaries.



[Reference] Specimen ① External appearance of specimen sampled from the yellow singularity on the plate-shaped specimen (A-1 surface)

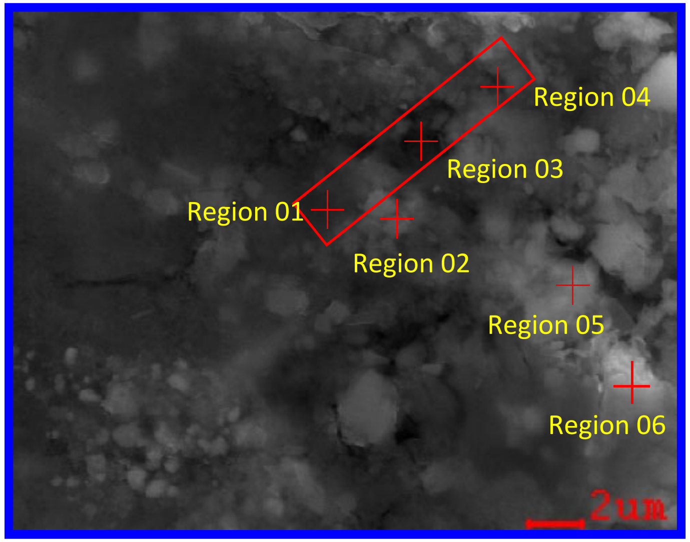
- A specimen was sampled from the yellow surface singularity on the plate-shaped specimen that was sampled prior to grinding the specimen into a uniform mixture, and particles showing the distribution of Ni concentration were focused on.
- A TEM-EDS specimen that transcends different regions of different concentrations around the region of a high concentration of Ni (Region 03) was prepared (red box in the SEM image on the right).



Yellow singularity on A-1 surface

Particle of interest

SEM image of plate-shaped specimen



Enlarged surface of particle of interest

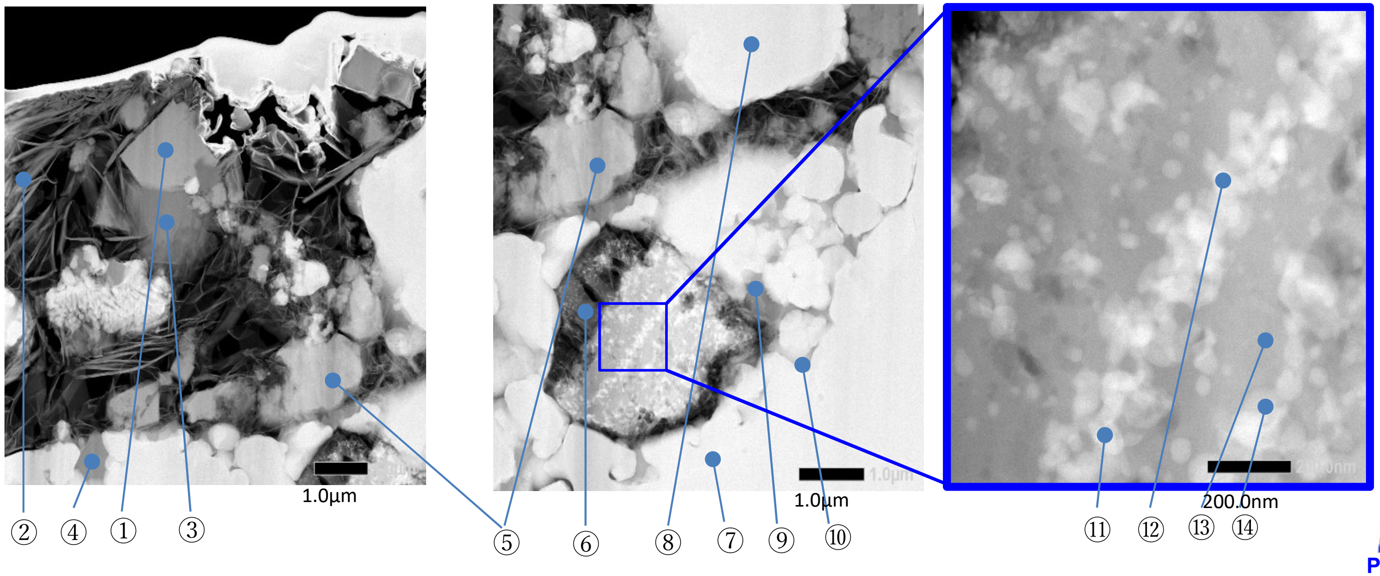
[Reference] Specimen ① TEM-EDS results（Yellow singularity on A-1 surface Region 03）

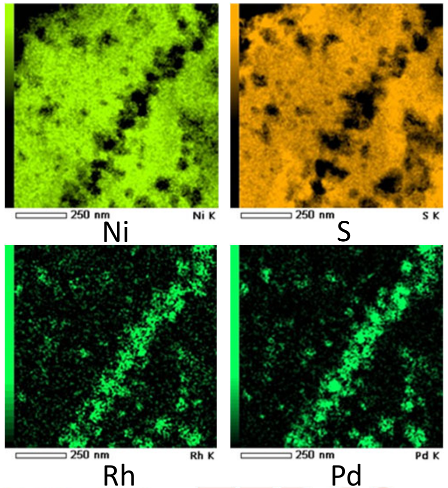
- Agglomeration of tiny particles with various compositions and crystalline structures.
- The particles shown in the blue box in the center are Ru, Rh, Pd precipitate in Ni_3S_2 (right photos ⑪~⑫）.

Assessment

- It is assumed that these are deposits of tiny particles formed through different processes.
- Assumed formation process of Ni_3S_2 particles that contain Ru, Rh, Pd precipitate: Alloys containing Ni come in contact with the cladding tubes in a reductive atmosphere. Ni infiltrates the Zr and turns to a liquid, while the Zr reacts with UO_2 and becomes a U-Zr liquid thereby forming Ni-Zr-U alloy. In conjunction with this, the metal FP inside the pellets (Ru, Rh, Pd) is taken in.
- It is assumed that Ni_3S_2 forms through the reaction with S in the seawater, etc., and metal FP precipitates in conjunction with cooling. At approximately 800°C, the Ni_3S_2 portion coagulates.

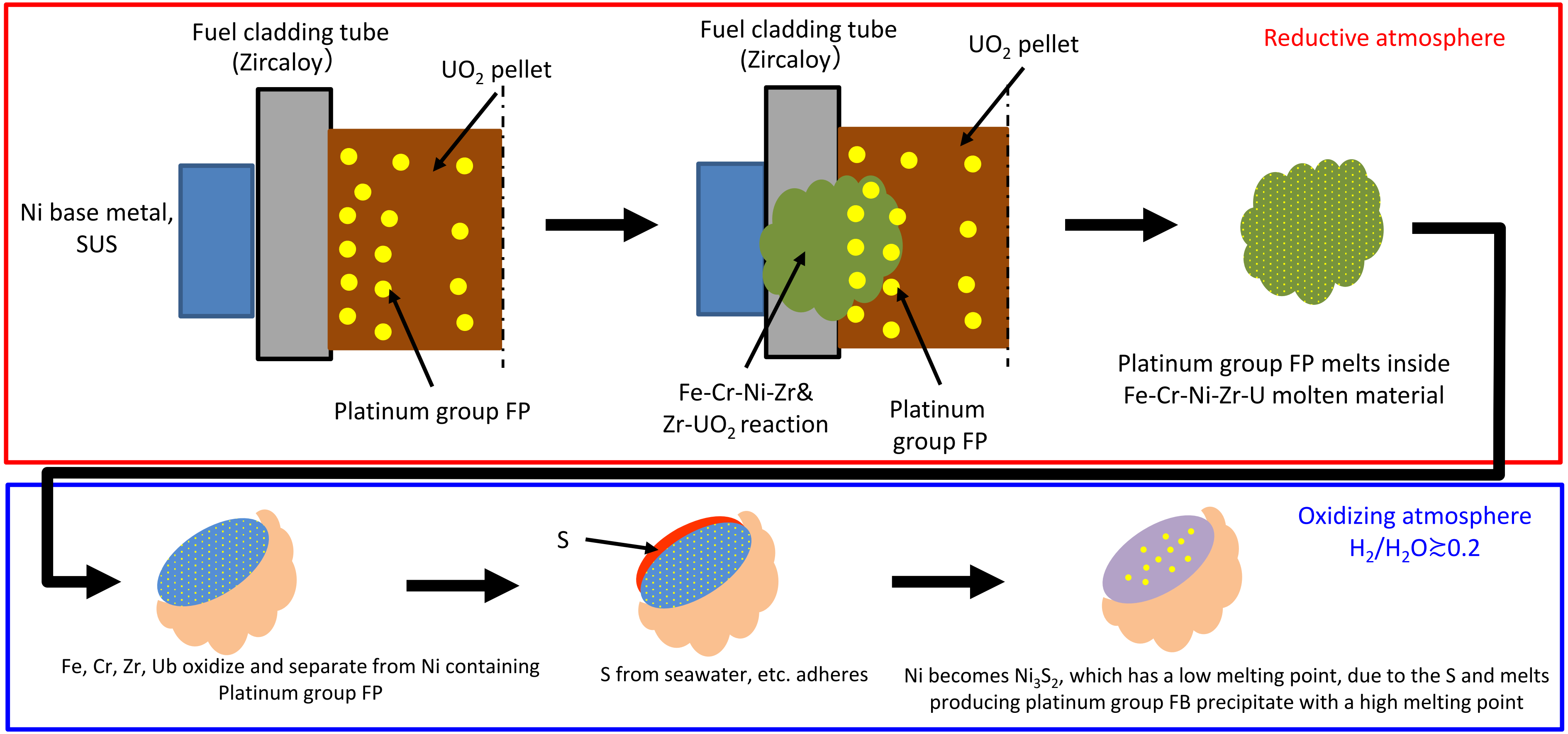
Position	Chemical form	Position	Chemical form	Position	Chemical form	Position	Chemical form
①	Cubic crystal Fe_3O_4(contains Ni)	②	Cubic crystal (Fe,Ni)O	③	$FeSiO_3$	④	Cubic crystal $FeCr_2O_4$
⑥	Ni-Fe-O compound	⑦	Cubic crystal $(Zr,U)O_2$	⑧	Tetragonal crystal $(Zr,U)O_2$	⑫	Peritectic Ni_3S_2 (Ru,Rh,Pd)





[Reference] Specimen ① Assumed formation process of Ni_3S_2 particles containing Ru,Rh,Pd

- Alloys containing Ni, such as SUS and Inconel, produce a eutectic reaction when they come in contact with alloys containing zirconium and melt.
- Meanwhile, when zircaloy and UO_2 come in contact and temperatures exceed 1200° C, a U-Zr liquid is formed that contains metal FP thereby forming molten Ni-Zr-U-metal FP.
- When the H_2/H_2O ratio exceeds approximately 1, Zr oxidizes but the Ni and S do not thereby forming ZrO_2 and separating from Ni.
- Ni reacts with S to form Ni_3S_2, which has a low melting point, and metal FP precipitates in conjunction with cooling.



Fe, Cr, Zr, Ub oxidize and separate from Ni containing Platinum group FP

S from seawater, etc. adheres

Ni becomes Ni_3S_2, which has a low melting point, due to the S and melts producing platinum group FB precipitate with a high melting point

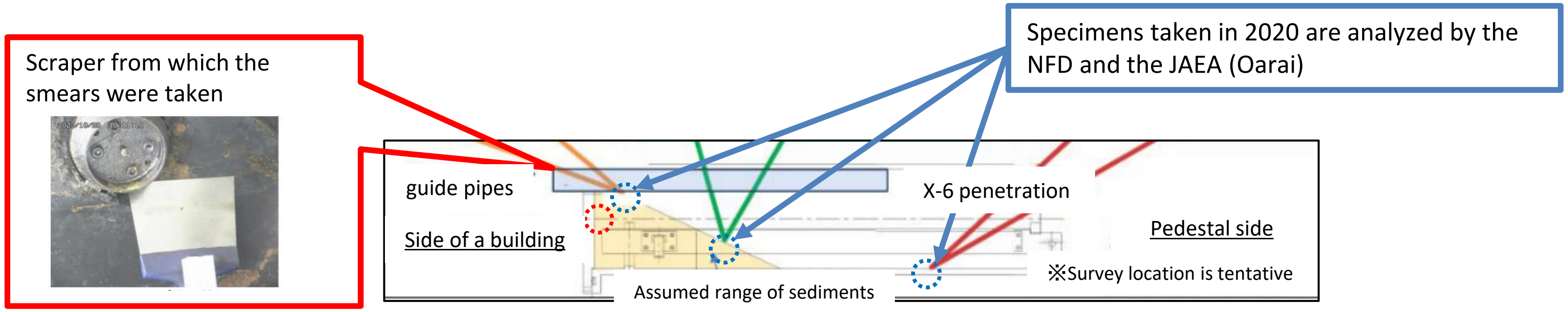
[Reference] Specimen ① Conclusions

Radio chemical analysis, ICP-MS, XRD, SEM-EDS, and TEM-EDS were performed on the deposit fragment that fell onto waste paper towel when the Unit 2 X-6 penetration flange was opened to ascertain details about the attributes of the deposit fragment.

- Radioactive concentrations of the deposits showed small percentages of Cs-134 and Cs-137, which are volatile nuclear fission products, and large percentages of Am-241 and Eu-154.
- The main elements of the deposits originate from structures made of Fe, Cr, and Ni, and are mixed with elements originating from the combustion of U and Zr. C was not detected. Furthermore, the deposits comprise tiny iron oxide particles less than 1~3µm in size and particles ranging in size from several 10~several hundred µm that contain U.
- ICP-MS and SEM-EDS composition analysis of the undissolved residue measured 38.8mg of uranium in the sample that was provided for analysis.
- Almost none of the elements from the melted cable covering remain in the deposits.
- U in particles containing U: Zr ratio and crystal structure seem stable at high temperatures so we believe they were quickly cooled from high temperatures.
- When the molten material (or molten-solidified material) fell from the RPV into the PCV, some of the particles from this substance remained in the air and migrated into the X-6 penetration suggesting the possibility that a large amount of the deposits formed as tiny iron oxide particles were supplied in this manner over a long period of time.

[Reference] Specimen ② Overview/analysis flow

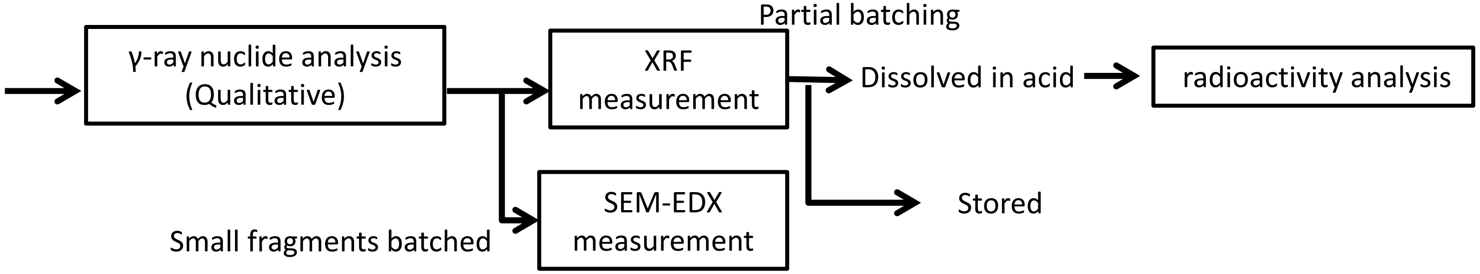
- When the unit 2 X-6 penetration hatch was opened, smears were taken from a scraper run over the back of the hatch at nine points and analyzed at JAEA building 1.
- After the smears were subjected to surface dose measurements, γ-ray nuclide analysis, XRF and SEM-EDS element analysis, they were dissolved in acid and subjected to radiochemical analysis.



Scraper from which the smears were taken

Specimens taken in 2020 are analyzed by the NFD and the JAEA (Oarai)

Positional relationship of the material attached to the smear filter paper inside the X-6 penetration



Smear specimen analysis flow

[Reference] Specimen ② Smear surface dose rate

- Surface dose rate was high for smears with a lot of black grime. And, βγ (70 µm dose rate) tended to be higher than γ (1cm dose equivalent rate).

External appearance of smears

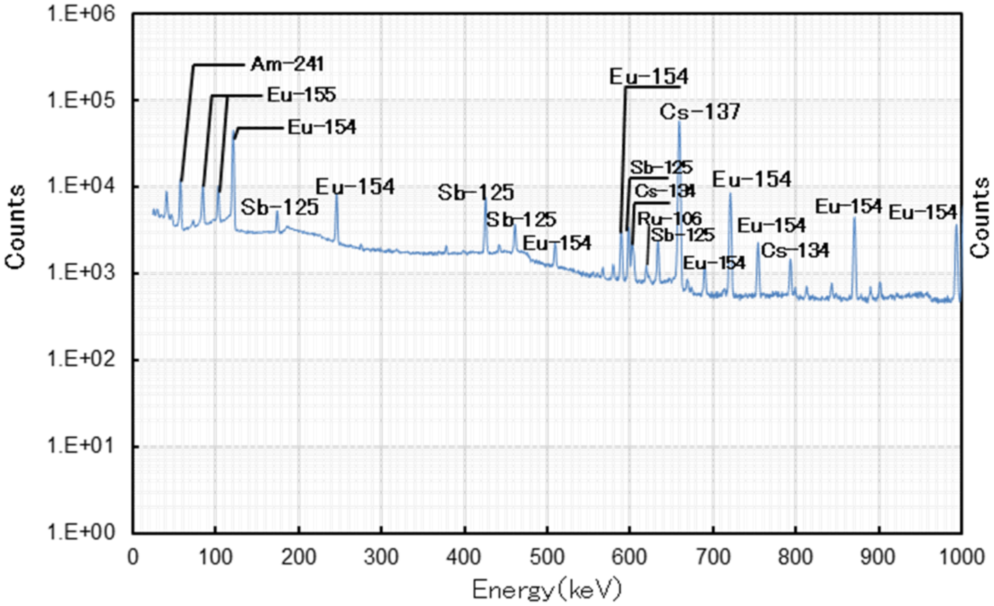
Smear dose rate

Specimen (JAEA)	γ [µSv/h]	βγ [µSv/h]
23P-1	180	3,000
23P-2	60	790
23P-3	190	3,500
23P-4	9	170
23P-5	4	73
23P-6	3	40
23P-7	2	40
23P-8	7	110
23P-9	1	20

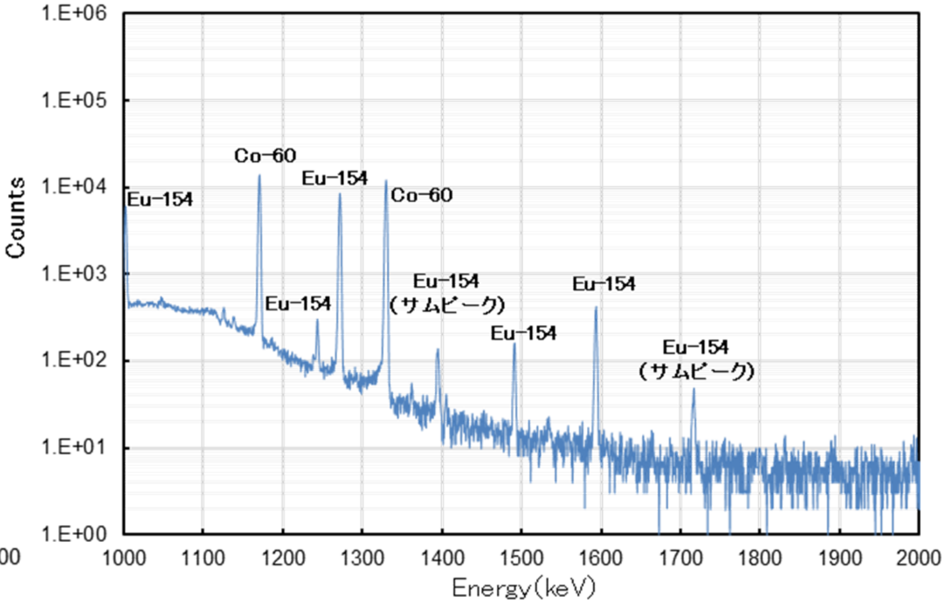
Measured using an ionization box survey meter outside the plastic bag. BG (γ, βγ) ：0.00 µSv/h

[Reference] Specimen ② γ-ray nuclide analysis results

- γ-ray nuclide analysis detected Co-60, Sb-125, Cs-134, Cs-137, Eu-154, Eu-155, and Am-241. The amount of radioactivity was not quantitatively assessed because smear sampling efficiency and a smear amount were not quantified.
- Since the γ-ray nuclides detected in the smears of the nine samples were equivalent, subsequent analysis was conducted for 23P-2, which has a relatively low dose rate for the reducing worker exposure, among 23P-1 to 23P-3, which had clear adherent black grime.



Smear（23P-2）γ-ray spectrum（0 ～ 1,000 keV）

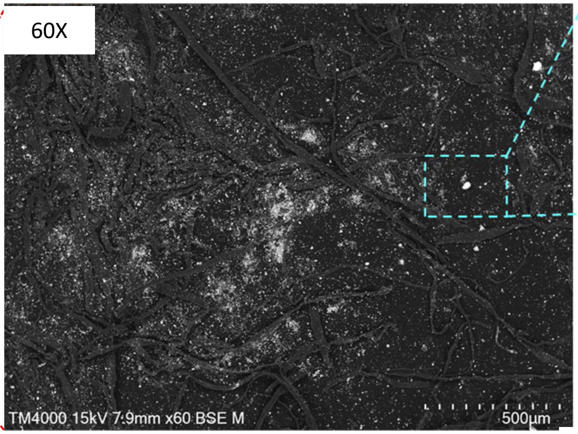


Smear（23P-2）γ-ray spectrum（1,000 ～ 2,000 keV）

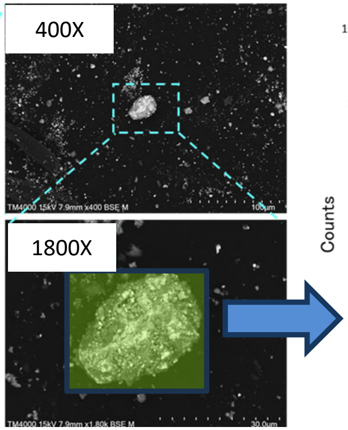
[Reference] Specimen ② XRF, SEM-EDS results

- A quantitative element analysis using XRF and SEM-EDS was conducted for specimen 23P-2.

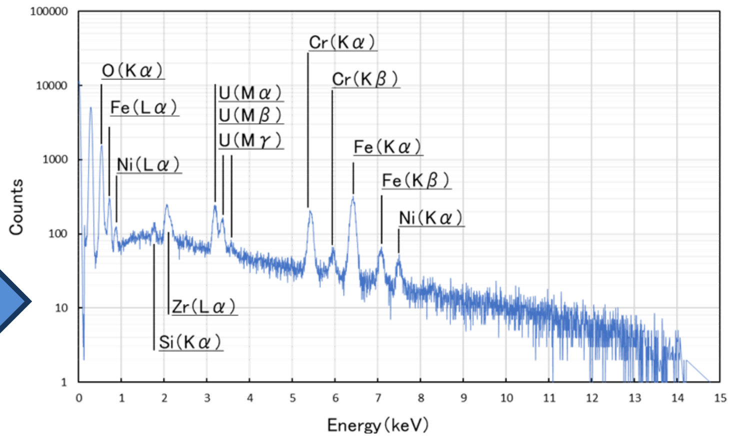
Smear



SEM image



EDS running area
(29.25μm×31.5μm)



EDS spectrum

Smear SEM-EDS and XRF element analysis results

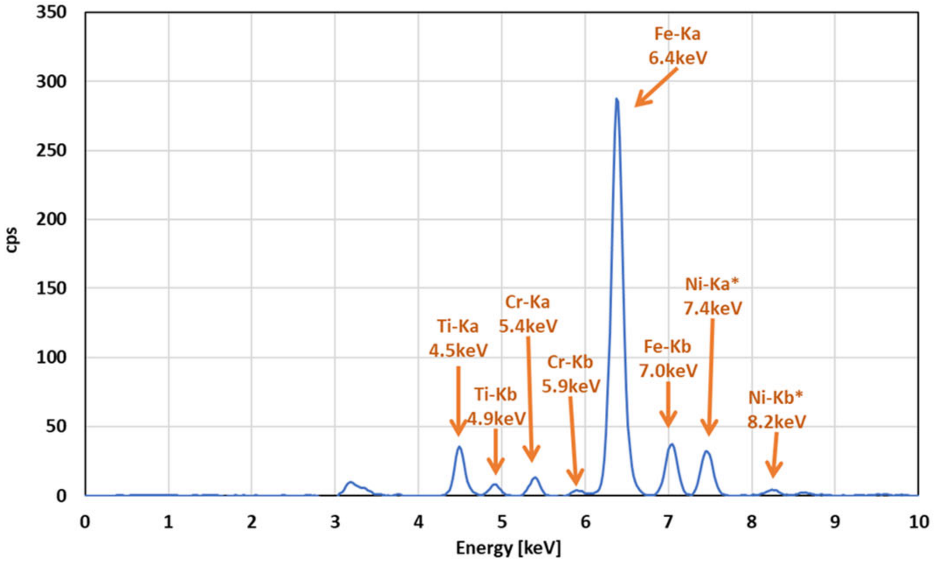
Analysis method	O	Na	Mg	Al	Si	S	Cl	Ca	Ti
SEM-EDS	○			(○) ※	○			(○) ※	
XRF	Not applicable	Not applicable	Not applicable	Not applicable					○

Analysis method	Cr	Fe	Ni	Cu	Zn	Zr	Mo	Sn	Pb	U
SEM-EDS	○	○	○			○				○
XRF	○	○	○			○				○

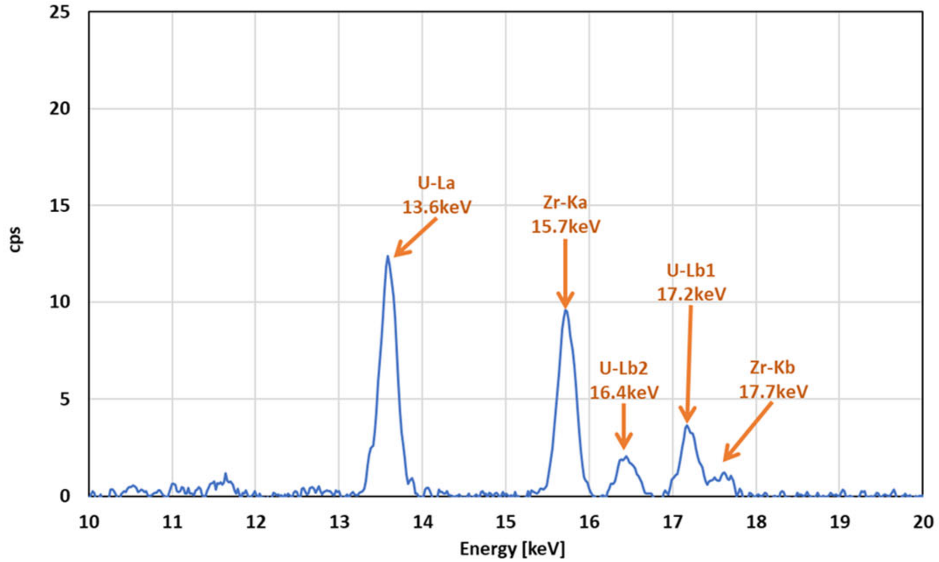
※Peak was observed, but the signal strength was lower than other Element

[Reference] Specimen ② XRF results

- A qualitative element analysis using XRF was conducted for specimen 23P-2.
- From 0~10 keV, the main peaks was from Fe, but Ti, Cr, and Ni were also detected. It is assumed that Fe, Cr, and Ni originated from core internal structures.
- From 10~20 keV U and Zr were detected, so it is assumed that the U originated from the fuel and the Zr originated from the cladding tubes.



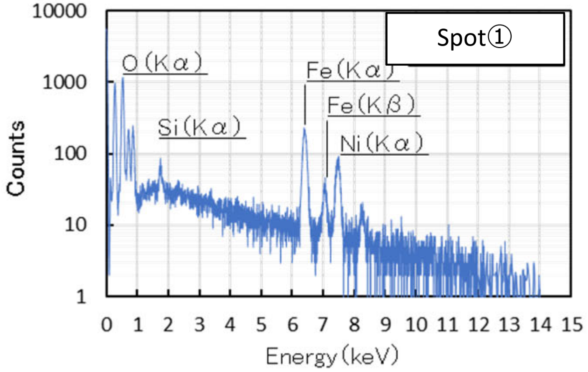
0 ~10 keV XRF spectrum

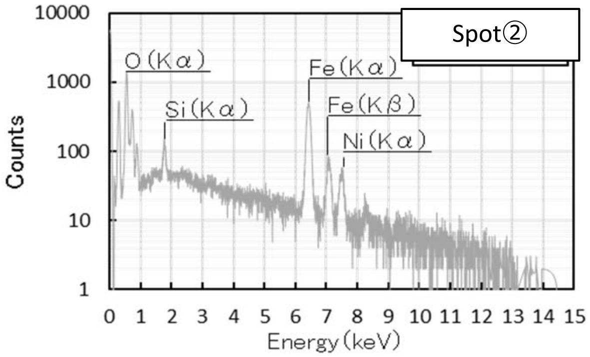


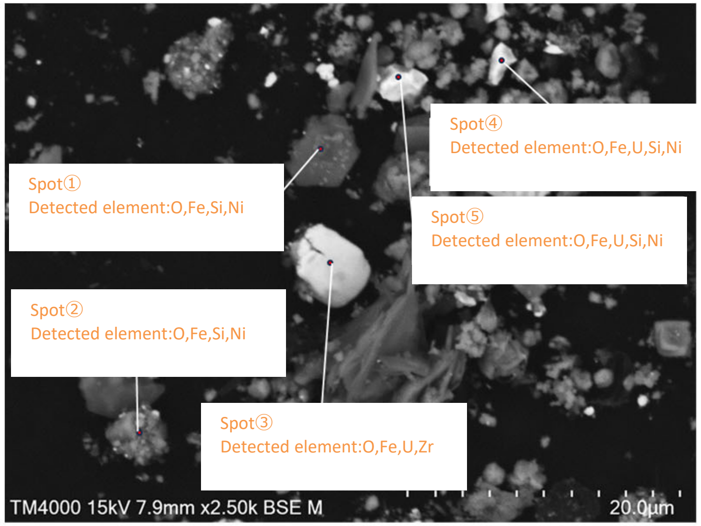
10～20 keV XRF spectrum

[Reference] Specimen ② SEM-EDS results

- O, Fe, and U were commonly found from the SEM-EDS analysis of the smears, and Zr, Cr, Ni, and Si were detected at sporadic locations.







Spot①
Detected element:O,Fe,Si,Ni

Spot②
Detected element:O,Fe,Si,Ni

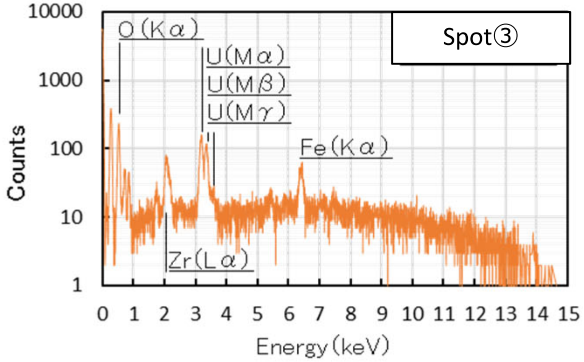
Spot③
Detected element:O,Fe,U,Zr

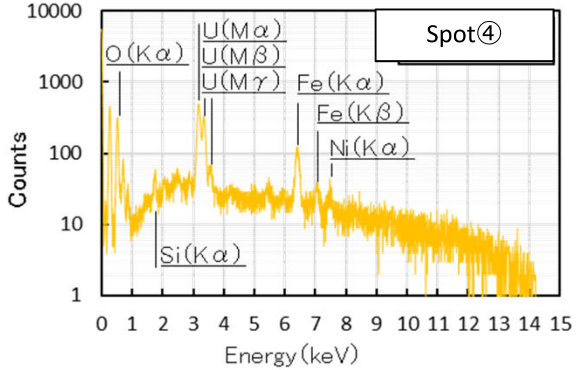
Spot④
Detected element:O,Fe,U,Si,Ni

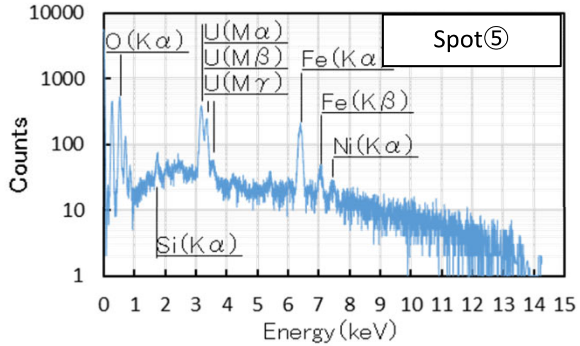
Spot⑤
Detected element:O,Fe,U,Si,Ni

Resolution : 1,048×786 [pix]
1pixel size : 47.6 [nm]
Image size : 50×37 [μm]

SEM image and EDX measurement results

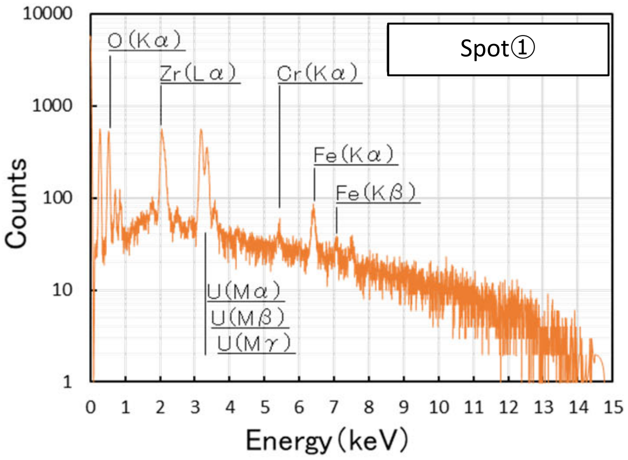


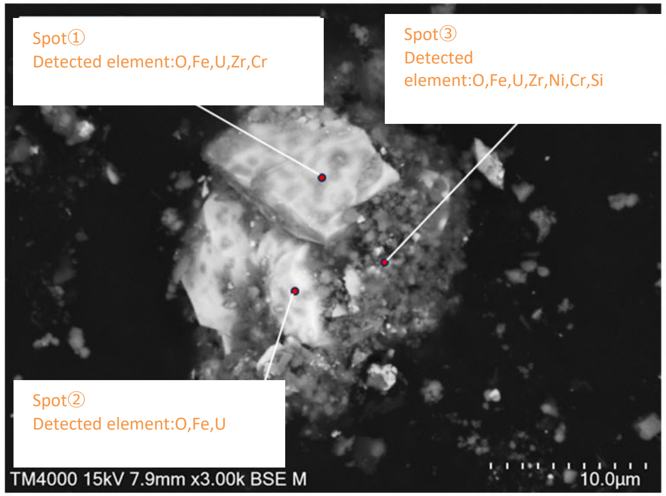


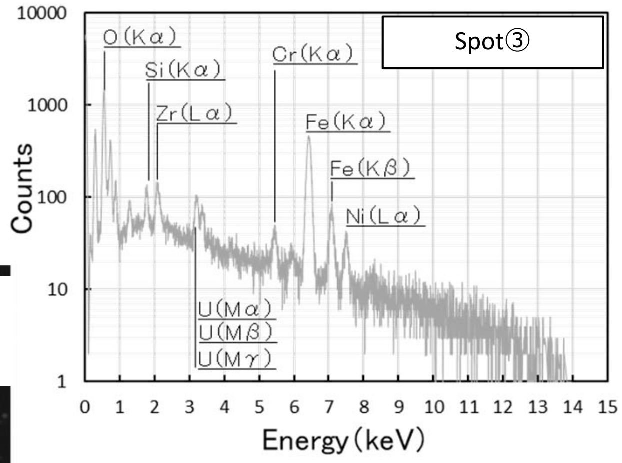


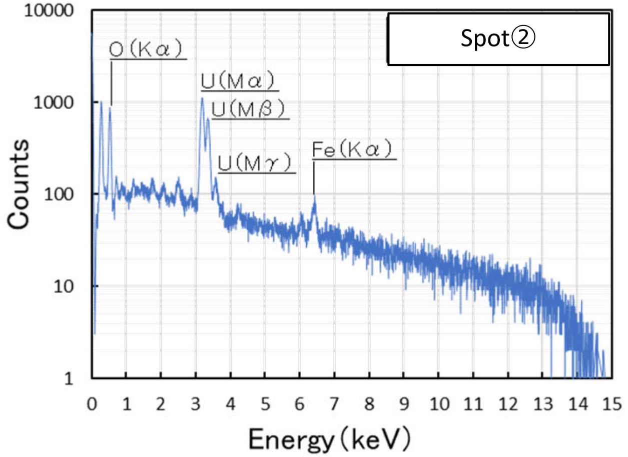
[Reference] Specimen ② SEM-EDS results

- Mainly O, Fe, and U were detected in other particles adhered to the same smear.









Resolution : 1,048×786 [pix]
1pixel size : 39.7 [nm]
Image size : 42×31 [µm]

SEM image and EDX measurement results

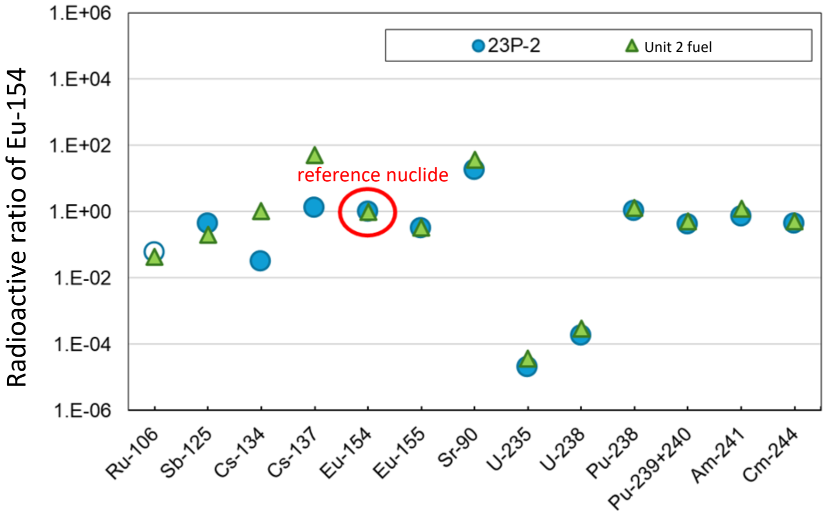
[Reference] Specimen ② Radioactive analysis results

- The smear was dissolved in acid and subjected to radioactive analysis that quantified the amount of radioactivity for each nuclide as shown in the chart below.
- The radioactivity ratio of Eu-154 for Cs-134 and Cs-137 in the 23P-2 specimen was lower than the Unit 2 fuel composition.

Radioactive analysis results

Specimen	Radioactivity amount[Bq/Specimen]			
	^{60}Co (Approx. 5.3 years)	^{137}Cs (Approx. 30 years)	^{106}Ru (Approx. 1 year)	^{125}Sb (Approx. 2.8 years)
23P-2	2.97×10^{2}	5.65×10^{2}	$<2.58\times10^{1}$	1.83×10^{2}
	^{134}Cs (Approx. 2.1 years)	^{154}Eu (Approx. 8.6 years)	^{155}Eu (Approx. 4.8 years)	^{90}Sr (Approx. 29 years)
	1.35×10^{1}	4.27×10^{2}	1.32×10^{2}	7.60×10^{3}
	^{235}U (7.0×10^{8} years)	^{238}U (Approx. 4.5×10^{9} years)	^{238}Pu (Approx. 88 years)	$^{239+240}$Pu (Approx. 6.6×10^{3} years)
	8.70×10^{-3}	7.61×10^{-2}	4.36×10^{2}	1.73×10^{2}
	^{241}Am (Approx. 4.3×10^{2} years)	^{244}Cm (Approx. 18 years)		
	3.00×10^{2}	1.88×10^{2}		

*Evaluated Nuclear Structure Data File（ENSDF） referred to for half-life data （https://www.nndc.bnl.gov/ensdf/）



Radioactivity ratio of Eu-154

*Since Ru-106 was not detected, the radioactivity ratio was plotted based on calculations of the lower detection limit.

[Reference] Specimen ② Conclusions

When the unit 2 X-6 penetration hatch was opened, smears were taken from a scraper run over the back of the hatch and brought to JAEA building 1 where the smears were subjected to surface dose measurements, γ-ray nuclide analysis, XRF and SEM-EDS element analysis, and then dissolved in acid and subjected to radiochemical analysis.

- Surface dose rate was high for smears with a lot of black grime. And, βγ tended to be higher than γ .
- γ-ray nuclide analysis detected Co-60, Sb-125, Cs-134, Cs-137, Eu-154, Eu-155, and Am-241.
- A qualitative element analysis using XRF detected Fe, but Ti, Cr, and Ni. It is assumed that Fe, Cr, and Ni originated from core internal structures. U and Zr were also detected, so it is assumed that the those originated from the fuel and the cladding tubes.
- O, Fe, and U were commonly found from the SEM-EDS analysis of the smears, and Zr, Cr, Ni, and Si were detected at sporadic locations.
- Radioactive analysis detected Cs-134, Cs-137, Co-60, Sr-90, Pu-238, Pu-239+240, U-235, U-238, Am-241, and Cm-244. And, aside from Co-60, Cs-134, and Cs-137, the radioactivity ratio of U-238 was close to the Unit 2 fuel composition.

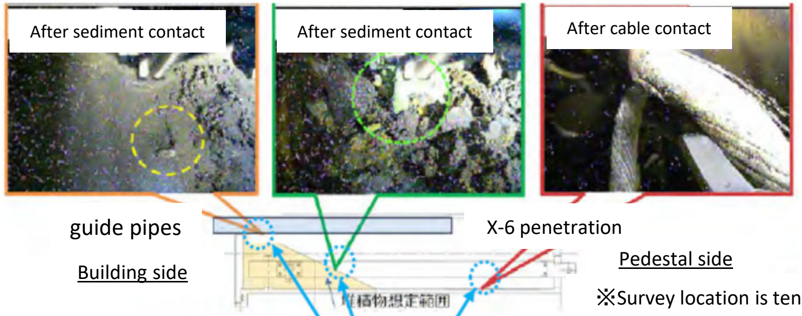
[Reference] Specimen ③ Analysis results from the smear taken from the investigation device used to contact deposits inside the X-6 penetration

- Tiny iron oxide particles were present around the (U, Zr)O_2 particles that were approx. 20µm wide.
- There was a large distribution of elements originating from steel mixed in with particles originating from fuel elements, structural materials, paint, and instrument materials, etc., and the U/Fe ratio was approximately 2~4at%.

Analysis sample

Material adhered to the X-6 penetration investigation device

◆Three types of smears were sampled from the material adhered to the end of the investigation device used for the contact investigation of deposits inside the X-6 penetration [4] and used as analysis samples.
※Refer to the diagram on the bottom right for smear sampling locations

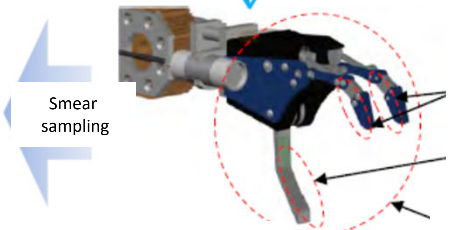


※Survey location is tentative

X-6 penetration internal deposit contact investigation
(Additional information provided in reference document [4])

※The diameters of the smear papers are all approximately 5cm

External appearance of samples of the adhered material that was sampled (photographed when received at the analysis facility)



End of investigation device (use to contact the surface of deposits)

Inside of two fingers → Adhered material 1
Inside of one finger → Adhered material 2
Entire hand → Adhered material 3

(Reference) Doses of sampled smears:
γ : 0.006～0.008mSv
β : 3.0～5.0mSv

※From Document 3-1 from the 41st Meeting of Deliberate Accident Analysis for the TEPCO Fukushima Daiichi Nuclear Power Station