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

Applicability evaluation of In-Can Vitrification
- FY2019-2020 Achievement –

Orano ATOX D&D SOLUTIONS Co., Ltd.
(ANADEC)

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This document doesn’t include the information related to the unique technology of the project proponent.

Table of contents

1. Executive summary

From the study performed on the In-Can process, we demonstrate that:

- Fukushima Effluent Treatment Waste (FETW) can be processed with high Waste Loading (WL*) as follows:
  - ✓ ALPS slurry: 25% ~ 40%
  - ✓ Zeolite: over 60%
  - ✓ CST: ~30%
  - ✓ Cs-rich waste (Mix of zeolite, CST and sand): 80%

*In this presentation, WL is expressed in oxide mass unless otherwise specified

- Higher WL can be further studied, without degrading leaching properties
- A containment of 99,96% for Cs and 99,99% for Sr can be achieved
- The vitrified materials have a low leaching rate, similar to international standards glasses of radioactive wastes,
- The canister can be manufactured with appropriate material, a good cost-benefit approach

Based on our site owner & operator experience, we propose two Dem&Melt** units to process Cs-rich waste and Sr-rich waste*** in 14 years.

**Dem&Melt: Industrial demonstrator of the In-Can process. In operation since November 2020.
***ALPS slurry, Kurion-CST, Evaporator concentrates, ALPS TiO_2, ALPS ferrocyanide

2. Background

History of vitrification technology development

La Hague

Several types of vitrification systems have been tested and developed. **AVM**, **AVH**, **CCIM**, **In-Can Melter**...

- 1950's — Choice of Borosilicate Glass
- 1960's — Hot-wall Metallic Induction Melter (PIVER)
- 1970's — Two-step Vitrification Process
- 1978 — UP1 AVM Start-up
- 1980's — CCIM Initial Studies
- 1989 — La Hague R7 Start-up
- 1992 — La Hague T7 Start-up
- 1996 — Mechanical Stirring
- 2001 — CFA Platform Development
- 2004 — PEV+CCIM Industrial Platforms
- 2005 — In-Can Melter process development starts
- 2008 — In-Can Melter process pilot starts
- 2010 — CCIM in R7
- 2016 — "Dem&Melt program" launch
- 2020 — Dem&Melt pilot start

Marcoule

La Hague

2. Background

Features of the In-Can process

<u>In-Can process</u>: Thermal treatment technology with the feature that a CAN containing waste and glass frit is heated by surrounding resistive heater in furnace, and directly used for waste package

- No need to drain the molten glass
- No need for a specific “starter” or “finisher” to start or finish the heating process
- Possible to flexibly control the heating cycle

➔Versatile and robust process for radioactive waste

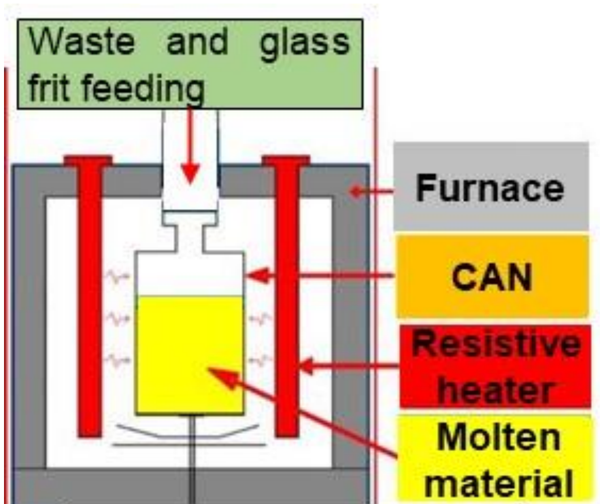


Image of In-Can process

3. Overview of the FY2019-2020 project
Target and approach

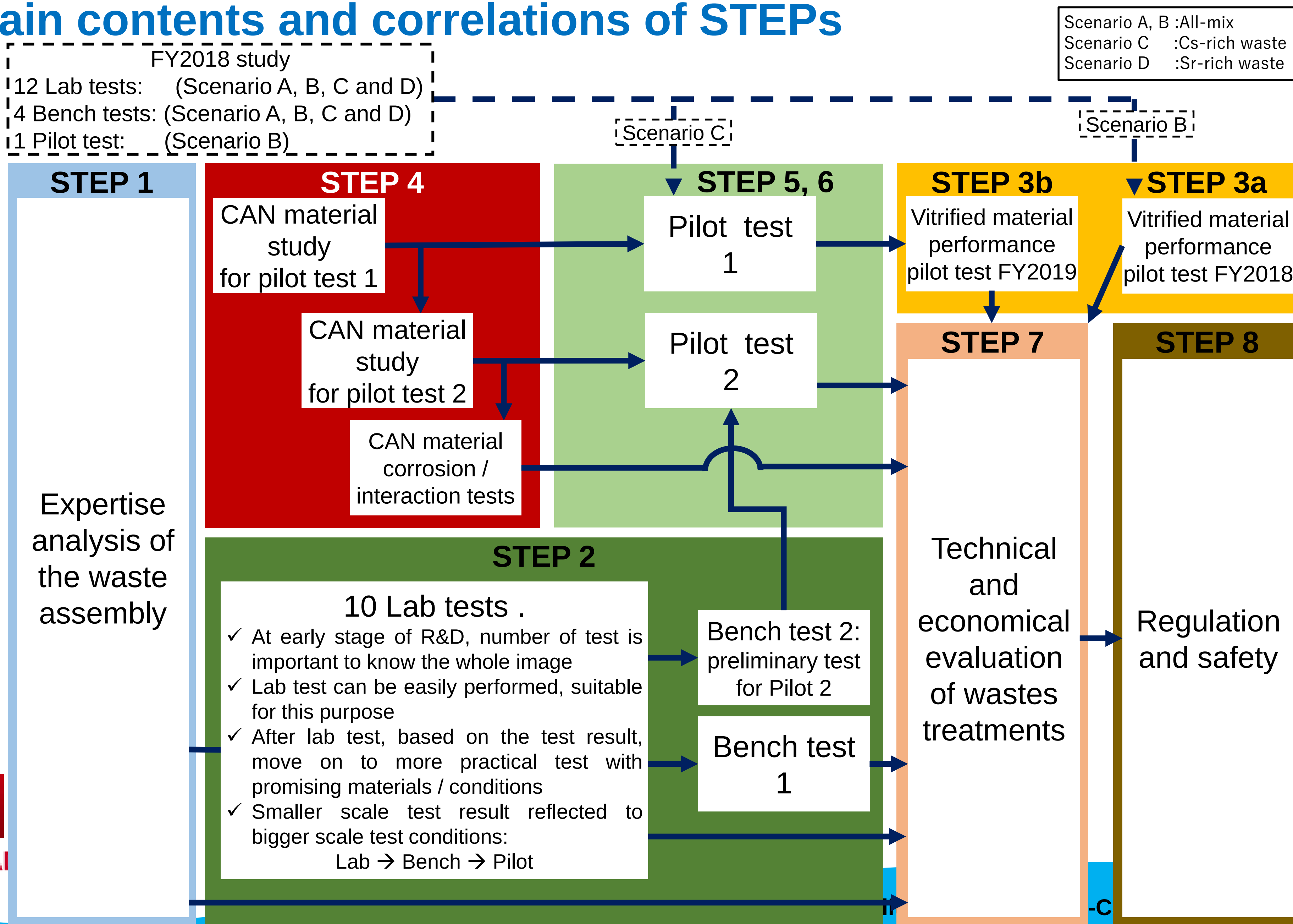
Target: Complete the overall feasibility of the In-Can vitrification by end of FY2020.

STEP-by-STEP approach adopted to achieve the target and to proceed with the project efficiently

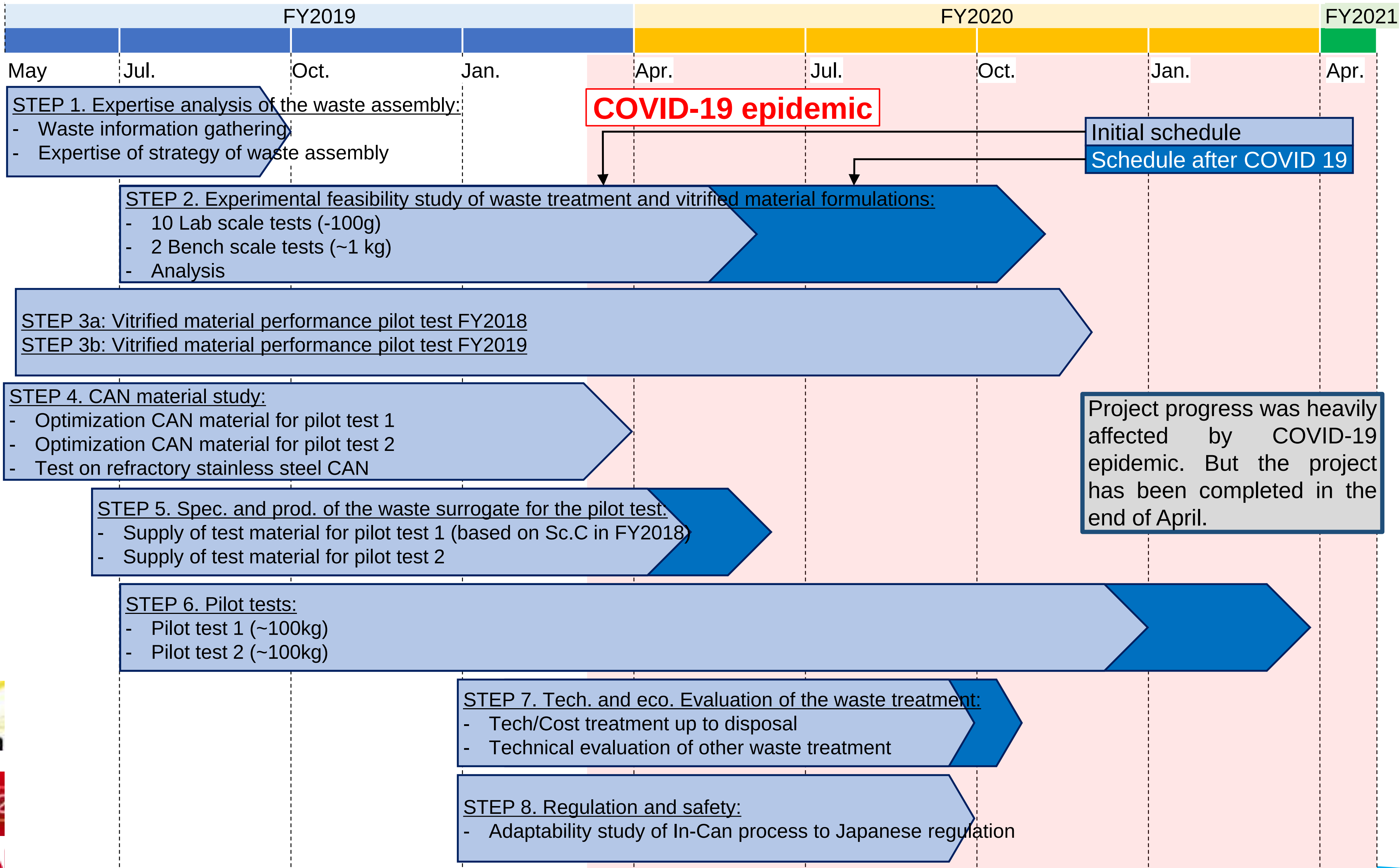
STEP	Items
1	Expertise analysis of the waste assembly - Integration of input data and study of testing condition/strategy to treat waste stream one-by-one
2	Experimental feasibility study of waste treatment and vitrified material formulations - Melting tests on lab/bench scale and analysis of the vitrified material produced
3a, 3b	STEP 3a: Vitrified material performance pilot test FY2018 STEP 3b: Vitrified material performance pilot test FY2019 - Leaching and mechanical tests on the vitrified material produced by pilot tests
4	CAN material study - Theoretical and experimental study of promising CAN material and comparison with Inconel
5	Specification and production of the waste surrogates for the pilot tests
6	Pilot tests - Demonstration of whole process such as production of vitrified material, volatility and feeding system testing
7	Technical and economical evaluation of waste treatments - Study on layout, secondary waste, CAPEX and OPEX and impact of the challenging waste
8	Regulations and safety - Study on adaptability of In-Can vitrification to Japanese regulations

3. Overview of the FY2019-2020 project

Main contents and correlations of STEPs



4. Schedule


FY2019
FY2020
FY2021
May
Jul.
Oct.
Jan.
Apr.
Jul.
Oct.
Jan.
Apr.
COVID-19 epidemic
Initial schedule
Schedule after COVID 19
STEP 1. Expertise analysis of the waste assembly:
- Waste information gathering
- Expertise of strategy of waste assembly
STEP 2. Experimental feasibility study of waste treatment and vitrified material formulations:
- 10 Lab scale tests (-100g)
- 2 Bench scale tests (~1 kg)
- Analysis
STEP 3a: Vitrified material performance pilot test FY2018
STEP 3b: Vitrified material performance pilot test FY2019
STEP 4. CAN material study:
- Optimization CAN material for pilot test 1
- Optimization CAN material for pilot test 2
- Test on refractory stainless steel CAN
STEP 5. Spec. and prod. of the waste surrogate for the pilot test:
- Supply of test material for pilot test 1 (based on Sc.C in FY2018)
- Supply of test material for pilot test 2
STEP 6. Pilot tests:
- Pilot test 1 (~100kg)
- Pilot test 2 (~100kg)
STEP 7. Tech. and eco. Evaluation of the waste treatment:
- Tech/Cost treatment up to disposal
- Technical evaluation of other waste treatment
STEP 8. Regulation and safety:
- Adaptability study of In-Can process to Japanese regulation
Project progress was heavily affected by COVID-19 epidemic. But the project has been completed in the end of April.

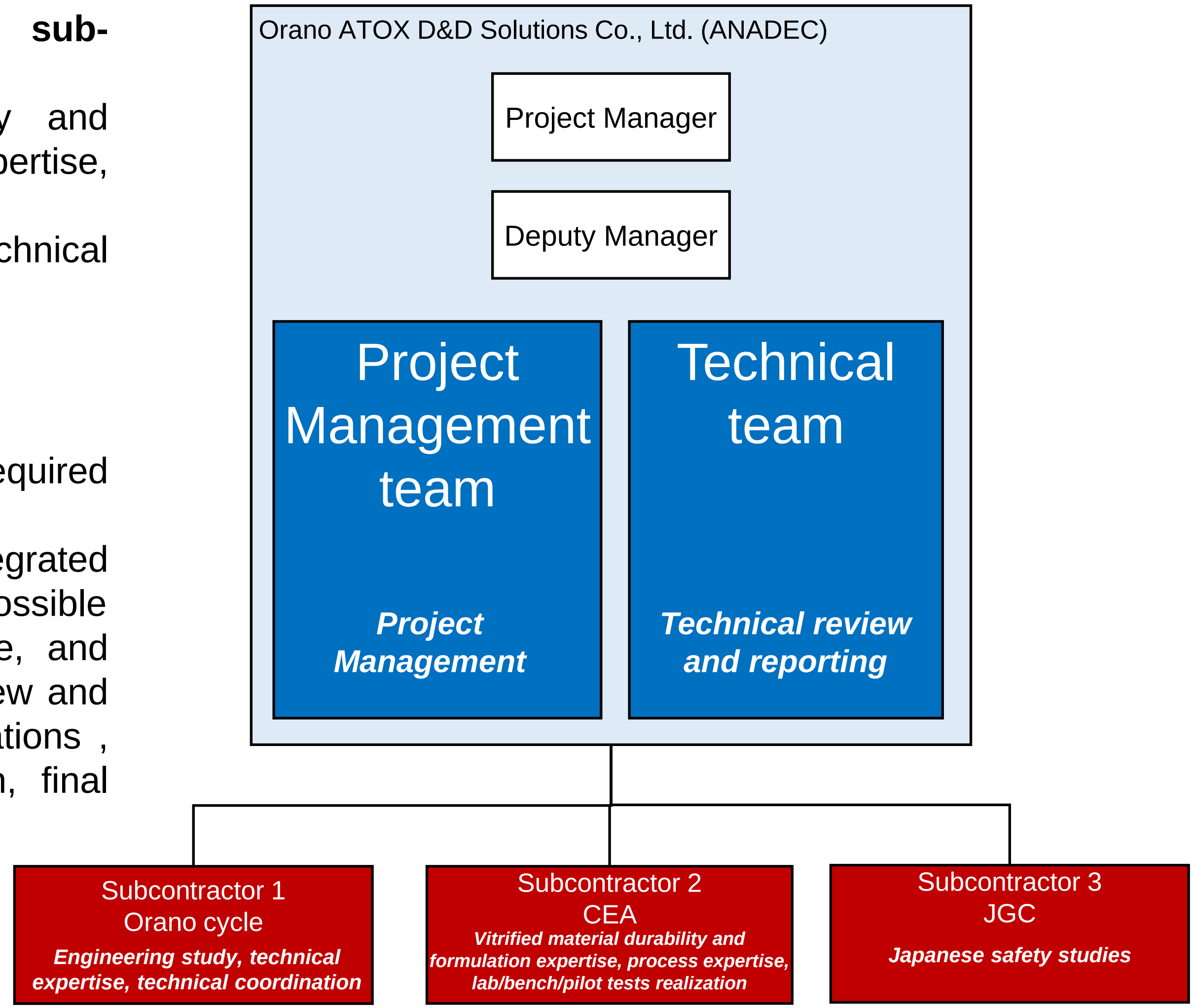
5. Organization chart

Project managed by ANADEC and sub-contracted to:

- **CEA** for vitrified material durability and formulation expertise, process expertise, lab/bench/pilot tests realization
- **Orano** for engineering studies, technical expertise and technical coordination
- **JGC** for Japanese safety studies

ANADEC ensures that:

- All subcontractors have the required information on time
- The requests from its customer are integrated in the project, as much as reasonably possible
- All documents are submitted on time, and compliant with specifications after review and validation by ANADEC (Final presentations , Intermediate report, final presentation, final report)



6. Implementation contents

STEP 1. Expertise of analysis of the waste assembly: treatment strategies

Based on the waste data inventory, FY2018 achievement* and CEA/Orano expertise, strategy of treatment and need of experimental study was defined.

* Please see the following document for details:
The summary results of subsidy program (the First solicitation) for the" Project of Decommissioning and Contaminated Water Management (Research and Development of Processing and Disposal of Solid Waste (Research and development on preceding processing methods and analytical methods))" in the FY2017 Supplementary Budget.

Strategy of treatment

- FY2018:
  Mixture of the different waste to validate the glass formulation between several waste and to optimize the waste loading, the number of the waste packages produced and the process operation/design.

- FY2019-2020:
  One-by-one treatment of each FETW to provide an alternative In-Can treatment methodology for FETW.
  The presence of Chloride and alpha nuclides will be considered

Applicability of both mixing and one-by-one treatment has been studied. → Possible to provide flexible options to treat FETWs in the future developments

6. Implementation contents

STEP 1. Expertise of analysis of the waste assembly: 10 Lab tests

Lab tests
Bench tests
Pilot tests

10 Lab tests selected based on one-by-one treatment strategy:

Aim of tests: Feasibility demonstrations giving the waste loading evaluation, suitable operation temperature, glass additives to be used and CAN material corrosion (to a lesser extent)

Test	Waste stream	Glass additive	WL (wt%)	RN simulation	CAN corrosion
LAB 1	Carbonated ALPS slurry*	Glass frit 1***	~40	• Sr • Ce for α nuclide simulation	Visual observation
LAB 2	Ferric ALPS slurry*	Glass frit 1***	~25	• Sr • Ce for α nuclide simulation	Visual observation
LAB 3	Mixed ALPS slurry Mix 1*, **	Glass frit 1***	~40	• Sr • Ce for α nuclide simulation	Visual observation
LAB 4	Mixed ALPS slurry Mix 2*, **	Glass frit 1***	~40	• Sr • Ce for α nuclide simulation	Visual observation
LAB 5	Zeolites IONSIV® R9160-G	Glass frit 2***	over 60	• Cs • Ce for α nuclide simulation	Visual observation
LAB 6	CST IONSIV® R9120-B	Glass frit 3***	over 30	• Cs and Sr • Ce for α nuclide simulation	Visual observation
LAB 7	Test contents from LAB 7 to LAB 10 are not disclosed because the information related to the unique technology of the project proponent are included.				
LAB 8					
LAB 9					
LAB 10					

*Cl-considered waste used
**Material that ALPS carbonate slurry and ALPS ferric slurry are mixed at different rates.
***3 different glass frits used

6. Implementation contents

STEP 1. Expertise of analysis of the waste assembly: 2 Bench & 2 Pilot tests

Lab tests | Bench tests | Pilot tests

2 Bench tests and 2 Pilot tests selected based on one-by-one treatment strategy:

Bench-scale: Confirm the result of the lab-scale test using small In-Can equipment and the benefit of the upscale process

Pilot-scale: Check the compatibility of the whole process including feeding, Off Gas Treatment System (OGTS), vitrified material elaboration, process parameters with pilot-scale equipment

Test	Waste stream	RN simulation	Note
Bench 1	Test contents of Bench 1 is not disclosed because the information related to the unique technology of the project proponent are included.		
Bench 2	Mix of ALPS slurry Mix 1	• Sr • Ce for α nuclide simulation	• Corresponding to LAB 3 • 75vol% of waste inventory • Cl-considered waste used • Preliminary test for Pilot 2
Pilot 1	Mix of Zeolite, CST and Sand	• Cs and Sr • Ce for α nuclide simulation	• FY2018 Sc. C: Cs-rich waste • CAN corrosion checked
Pilot 2	Mix of ALPS slurry Mix 1	• Sr • Ce for α nuclide simulation	• 75vol% of waste inventory • Cl-considered waste used • CAN corrosion checked

~1kg bench-scale can

~100kg pilot-scale can

Testing parameters updated based on the lab test results

6. Implementation contents

STEP 2. Experimental feasibility study of waste treatment and vitrified material formulations: Executive summary

- **ALPS slurry, zeolite and CST are successfully vitrified (Results are explained in the following pages.)**
  - **ALPS slurry: Feasibility confirmed at about 40% WL**
  - **Zeolites: Feasibility confirmed at over 60% WL**
  - **CST: Feasibility confirmed at over 30% WL**
  - **Feasiblity of ALPS slurry mix vitrification were also confirmed at bench scale.**

The results obtained are promising as applicability demonstration phase

Some items can be still improved:

- **Increase of WL (through optimized additives)**
- **Optimization of treatment temperatures**
- **Vitrification feasibility of minor streams.**

6. Implementation contents

STEP 2. Experimental feasibility study of waste treatment and vitrified material formulations: LAB 1 ~ 4, ALPS slurry tests

No.	LAB 1	LAB 2	LAB 3	LAB 4
Waste	ALPS carbonate slurry	ALPS ferric slurry	Mixed ALPS slurry 1	Mixed ALPS slurry 2
WL	~40	~25	~40	~40
Result	After each test, epoxy resin was filled into the crucible for protection of the vitrified material during cutting. 			

- ✓ Solidified and dense vitrified material in the form of a solid mass obtained
- ✓ The vitrified materials obtained mainly consist in vitreous phase containing RNs and Cl.
- ✓ No major corrosion of the metallic crucible is observed.

▶ ALPS slurry successfully vitrified with the WL of 25 ~ 40%

▶ Higher WL should be reachable with an optimized glass frit adapted to the waste

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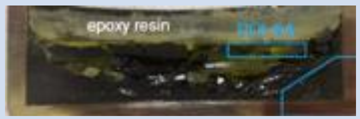
6. Implementation contents

STEP 2. Experimental feasibility study of waste treatment and vitrified material formulations: LAB 5 ~ 6, Zeolite and CST tests

No.	LAB 5	LAB 6
Waste	Zeolite	CST
WL	Over 60	Over 30
Result		

▶ Zeolite and CST successfully vitrified with the WL of over 60 and over 30 wt%, respectively

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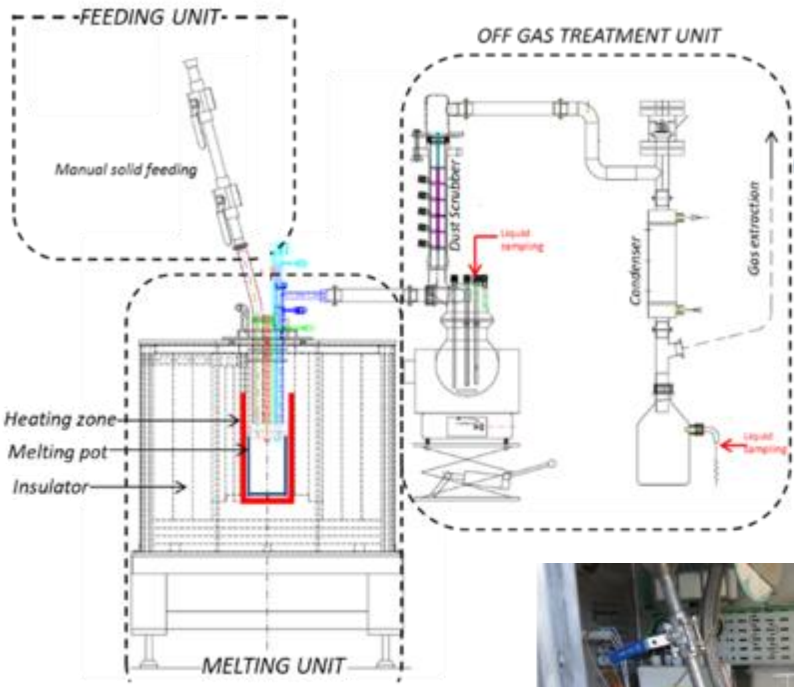
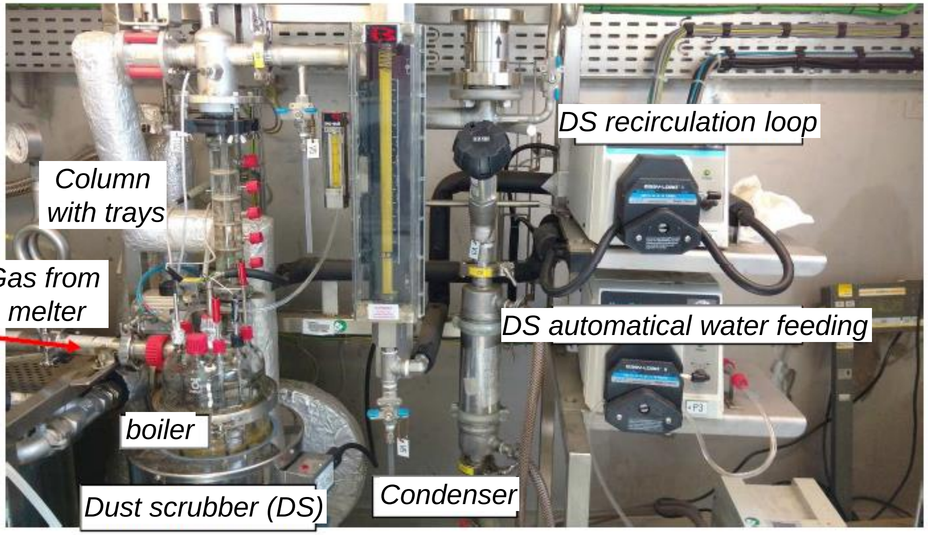
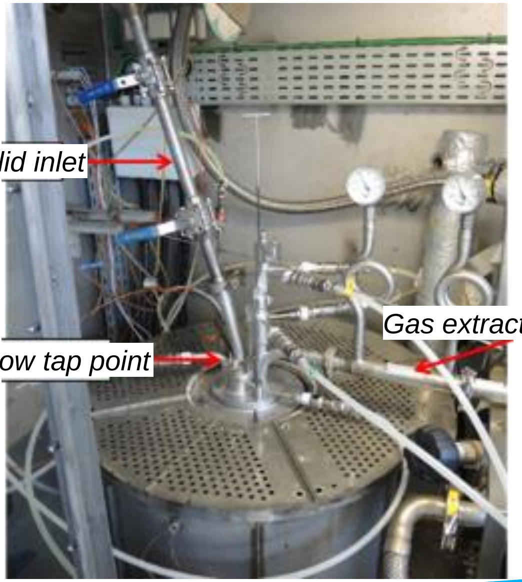
6. Implementation contents

STEP 2. Experimental feasibility study of waste treatment and vitrified material formulations: Bench-scale test equipment







Bench scale test equipment

- Feeding unit (Existing equipment: not used for these tests)
- Melting unit (resistive heating)
- Off-gas treatment unit (dust scrubber and condenser)

6. Implementation contents

STEP 2. Experimental feasibility study of waste treatment and vitrified material formulations: Bench-scale tests conditions

Bench-scale: Confirm and complement the result of the lab-scale test using small In-Can equipment and the benefit of the upscale process

	Bench 2 (ALPS slurries vitrification)
WL	~ 40 %
Mass	slurry dehydrated surrogate + Glass frit 1 ~ 1 kg in total
Appearance of the waste before test	

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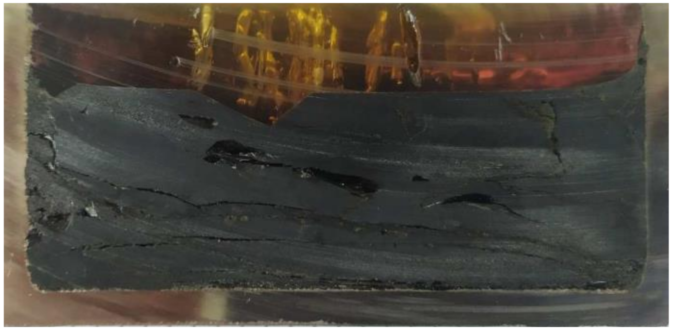
6. Implementation contents

STEP 2. Experimental feasibility study of waste treatment and vitrified material formulations: Bench 2: ALPS slurry vitrification – summary



Vitrified material on Bench 2

Vitrified material on LAB 3

- **Low Sr volatility: < 0.05% (Ce volatility: < D.L.*)**

*Detection limit

- Microstructure analysis revealed that vitrified material with a **homogeneous** appearance obtained.
  - ✓ Very close to the vitrified material on lab-scale test
    - Showing the benefits of the up-scale process
  - ✓ Composed of SiO2, Na_2O, CaO, B_2O_3 and Fe_2O_3, and also contains the majority of Ce and Sr.
  - ✓ Only few crystals are present along the crucible walls and on the vitrified material surface.
- No major corrosion observed by SEM and visual inspections

Success of vitrification of ALPS slurry mix with WL ~40%

- ► **Homogeneous vitrified material**
- ► **High WL (could be optimized through a dedicated glass frit adapted to the waste)**
- ► **Very low volatility: <0.05%**

6. Implementation contents

STEP 3a. Vitrified material performance pilot test FY2018 Summary

- Performance of "Scenario B" (Treatment of the mix of ALPS slurry, zeolite, CST and sand) vitrified material about compression strength and leaching rate has been experimentally analyzed. Results are explained in the following pages.
- The microstructure of the vitrified material is very similar regardless of the location, consisting of a vitreous phase with embedded durable crystals distributed homogeneously.
- Cs is localized in the vitreous phase and Sr is distributed between the crystal phases and the vitreous phase.
- The compressive strength were between 40 and 200 MPa, typical value of borosilicate glasses.
- The leaching test results are typical as borosilicate glasses with a sharp drop of the leaching rate. Cs and Sr leaching rate is very low and Cs is retained in the alteration layer.

► Experimental result revealed that it's possible to produce a dense and durable vitrified material on scenario B with 80% WLox.

► This will enable a significant volume reduction of waste and shortening of the operation period necessary to treat the whole waste inventory.

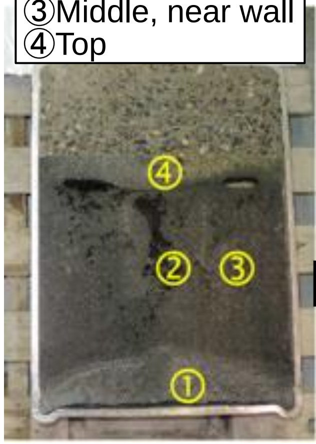
6. Implementation contents

STEP 3a. Vitrified material performance pilot test FY2018

1. Microstructural analysis, 2. Compressive test and 3. Leaching test

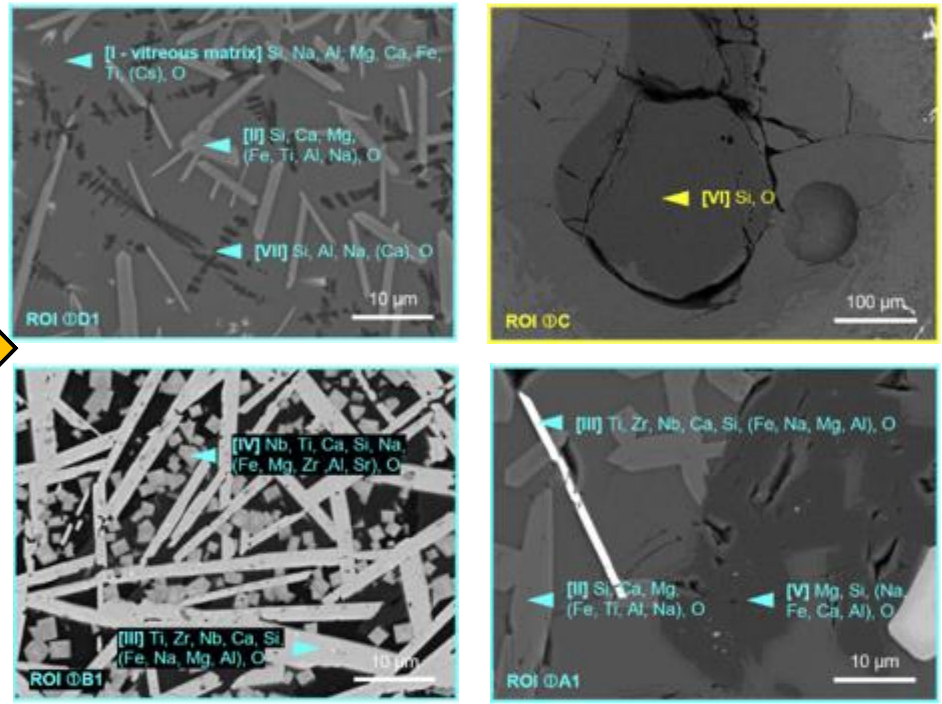
4 samples are analyzed, 6 main chemical natures of phases confirmed

①Bottom
②Middle, center
③Middle, near wall
④Top



FY2018 Sc. B (All waste)
- *ALPS slurries*
- *Zeolites*
- *CST*
- *Sand*

WL = 80%



Examples of SEM images and EDS analyses in region ① (Bottom of the vitrified material)

- **The vitrified material is well densified.**
- **Cs is mostly located in the vitreous phase**.
- Sr is in both vitreous phase and the crystal phases.

Microstructure of the vitrified material obtained is very similar at all location of the vitrified material

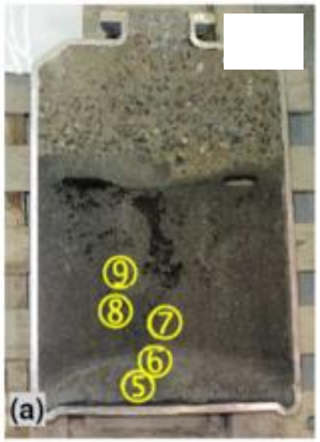
➔The reactivity between the wastes and the glass frit appears to be homogeneous

6. Implementation contents

STEP 3a. Vitrified material performance pilot test FY2018

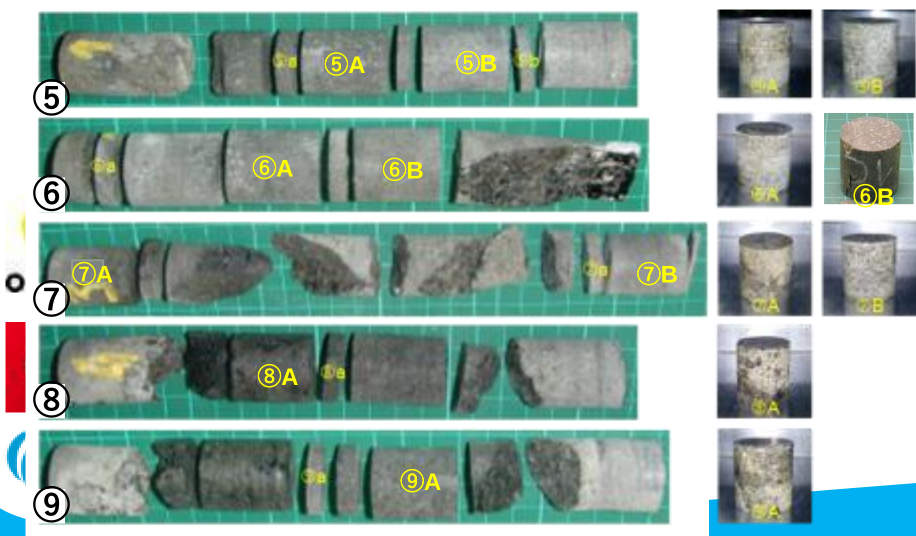
1. Microstructural analysis, 2. Compressive test and 3. Leaching test

Uniaxial compression tests performed on 5 cores, 8 samples



	Compression strength [MPa]	Reference value For B-Si glass* [MPa]
Min	42	22*
Max	200	384**
Ave	101	-

*Ojovan M.I., Lee W.E., 2005. Chapter 17 - Immobilisation of Radioactive Wastes in Glass. In: Ojovan, M.I., Lee, W.E. (Eds.), An Introduction to Nuclear Waste Immobilisation. Elsevier, Oxford, p. 213-249.
**Ashby M.F., 2013. Chapter 15 - Material profiles. In: Ashby, M.F. (Ed.), Materials and the Environment (Second Edition). Butterworth-Heinemann, Boston, p. 459-595.



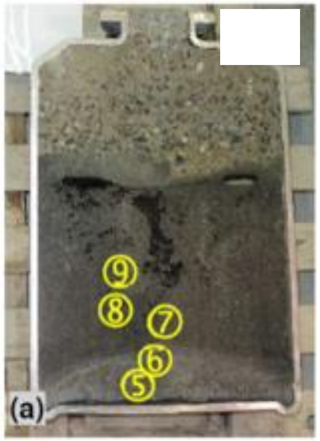
Mechanical strength of the vitrified material was the same order of magnitude as borosilicate glass.

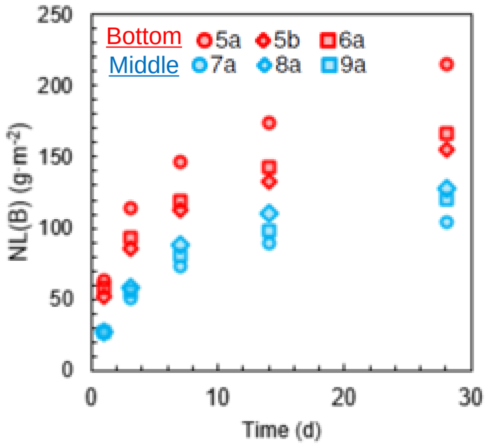
6. Implementation contents

STEP 3a. Vitrified material performance pilot test FY2018

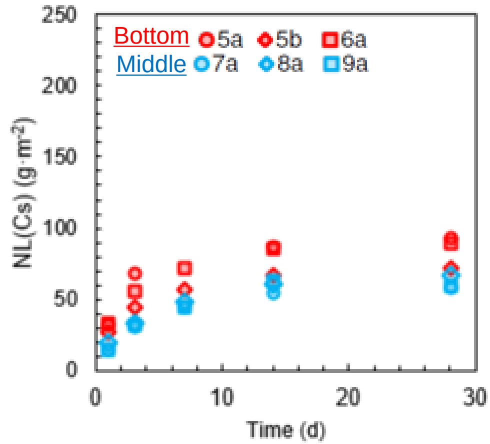
1. Microstructural analysis, 2. Compressive test and 3. Leaching test

Leaching tests (adapted from MCC-1) performed on 6 samples (taken from 5 cores)





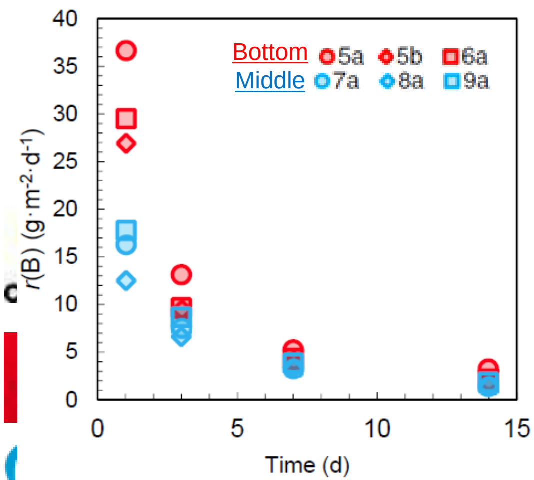
Normalized mass loss of B: NL(B)



Normalized mass loss of Cs: NL(Cs)

- NL(B) curve exhibited the typical trend of borosilicate glasses.
- NL(Cs) can be calculated and compared to NL(B) because B is located in the vitreous phase and, according to the microstructure analysis, Cs was also mainly located in the vitreous phase.

➔ Cs was partially retained in the alteration layer



Evolution of leaching rate of B

▶Very good leaching performances

▶leaching rate is 1.5 times lower than the EA glass

▶Leaching test results are typical as borosilicate glasses with a sharp drop of the leaching rate.

▶The Cs and Sr leaching rate is very low and Cs is retained in the alteration layer

6. Implementation contents
STEP 4. CAN material study

For cost optimization, we selected several materials for possible CAN material from preliminary study and CEA/Orano feedback and experience. The quantity of material is directly linked to material properties.

- Following topics were implemented in this STEP.
  - CAN material study for Pilot 1
  - CAN material study for Pilot 2
  - CAN material corrosion / interaction test
- The most economical balance between material intrinsic cost and quantity of the material per CAN is researched through the study above.

6. Implementation contents

STEP 5 & 6. Pilot test 1: Summary of result

Pilot 1: Vitrification of Cs-rich waste (Zeolite, CST and Sand, FY2018 Sc. C)

Parameter	Result
Mass of production	103kg of vitrified material with Cs, Sr, Ce produced
Volatility	Cs: 0.04%, Sr: 0.01%
CAN	No corrosion observed
WL	~ 75%
Leaching rate	Same order of magnitude as R7T7 glass
Compression strength	Same order of magnitude as the standard concrete and typical HL vitrified material

- ✓ **Test successfully performed with High WL**
- ✓ **Low volatility: Cs: 0.04%, Sr: 0.01%**
- ✓ **Very good performances on chemical durability viewpoint. Leaching rate with the same order of magnitude as French R7T7 reference glass for high-level waste (~0.2g/m^2/d): Result of STEP 3b**

6. Implementation contents

STEP 5 & 6. Pilot test 2: Summary of result

Pilot 2: ALPS slurry mix vitrification (Carbonate 5 : Ferric 1)

Parameter	Result
Mass of production	72kg of vitrified material with Sr, Ce
Volatility	Sr: < $4*10^{-3}$ %, Ce: < D.L.
CAN	No corrosion observed
WL	~ 40%

- ✓ **High WL**
- ✓ **Extremely low volatility of Sr: < $4*10^{-3}$%**
- ✓ **From visual observation, the vitrified material appears homogeneous.**

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6. Implementation contents

STEP 7. Technical and economical evaluation of waste treatments

- ❑ Engineering study and cost evaluation* performed assuming the installation of In-Can vitrification technology to Fukushima Daiichi NPS

*The implementation contents of cost evaluation is not disclosed.

► 2 compact vitrification units designed (2 furnaces in each unit):

- Cs rich waste ➔ Dem&Melt unit with remotely-controlled operation and maintenance
- Sr rich waste ➔ Dem&Melt unit with contact maintenance

➔ **This strategy would allow optimizing costs and duration for waste treatment**

Cs-rich waste: Waste with high Cs activity

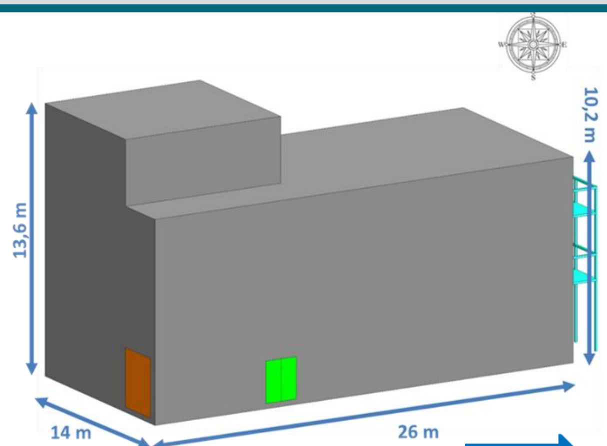
Sr-rich waste: Waste with less Cs activity and high Sr activity

► CANs to be produced** and duration estimate (depending on strategy):

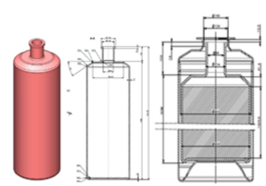
- Cs rich waste ➔ Between 4000 and 4800 CANs to be produced and between 11 and 13 years of operation
- Sr rich waste ➔ Between 4500 and 5000 CANs to be produced and between 13 and 14 years of operation

**Calculated based on WL tested so far and on the size of Dem&Melt unit etc.

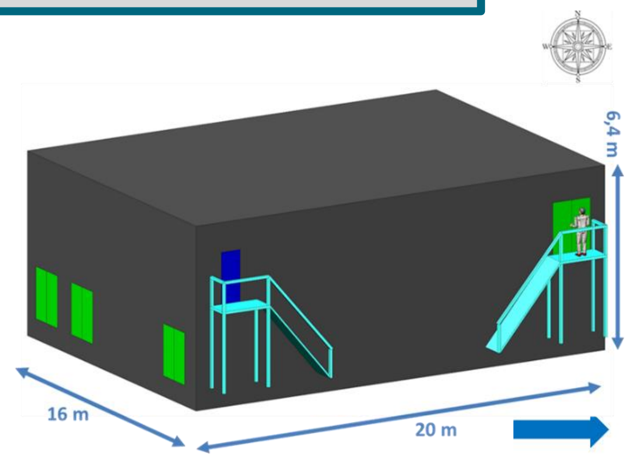
Dem&Melt units design benefits from mature and proven technologies (from up stream functions to down stream functions) – Over 40 years of HA operation at La Hague and Marcoule.



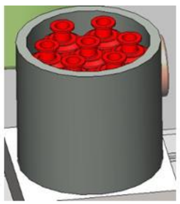
Cs rich waste unit



CAN evacuated through UC



Sr rich waste unit



CAN evacuated through large cylindrical shielded container

6. Implementation contents

STEP 8. Regulation and safety: Introduction

Applicability of Dem&Melt In-Can vitrification facility to Japanese safety requirements for installation to 1F was studied:

Method：

1. Based on the laws and regulations referred to in the design of low-level radioactive waste treatment facilities, items that should be considered in the safety design of Dem&Melt In-Can Melter facilities are extracted from the laws and guidelines below.
   - Laws and regulations for Nuclear Facilities in General
   - Laws and regulations specific to Fukushima Daiichi Nuclear Power Station
   - Guidelines set forth by the Nuclear Regulation Authority
   - Implementation Plan prepared by TEPCO
   - (Major non-nuclear laws that may be relevant for the construction of nuclear facilities)
2. Key terms in the statute that are relevant to safety design are summarized. And then, the applicability and classification are studied.

It was confirmed that there was no problem that was difficult to be solved assuming the items to be described in the implementation plan.
Dem&Melt In-Can Melter facility is capable of being designed, constructed and installed meeting the safety requirements in the Japanese regulations.

7. Summary and future prospect

Conclusion of the project

Target of FY2019-2020 study:

- **Complete the overall feasibility of the In-Can technology by end of FY2020**.

- 1F waste can be processed with high WL as follows:
  - ✓ ALPS slurry: 25% ~ 40%
  - ✓ Zeolite: over 60%
  - ✓ CST: ~30%
  - ✓ Cs-rich waste (Mix of zeolite, CST and sand): 80%
- On pilot 1:
  - ✓ Very low volatility achieved: 0.04% for Cs, 0.01% for Sr
  - ✓ The vitrified material obtained has good leaching resistance, similar to international standards.
- On pilot 2, almost 100% of Sr contained in the CAN
- Two facilities were conceptually designed to process all wastes in 14 years for a reasonable initial cost, low maintenance, and relatively small amount of secondary wastes.
- Dem&Melt facilities are capable of meeting the safety requirements of the Japanese regulations

7. Summary and future prospect

Further study after this project

From the results obtained by this project, it was found that studies shown below can further improve the applicability of In-Can technology.

1. Full-scale test
   - To evaluate and demonstrate the applicability of the technology at Full-scale with high WL with upgraded feeding system, based on all achievements obtained so far.
   - Target waste is considered to be dewatered ALPS slurry with high WL
2. CAN corrosion-resistance
   - Study to conclude the best CAN material, from both technical and economical viewpoint, in accordance with FETW specific features such as high Cl content.

Applicability of In-Can technology would be demonstrated more precisely by these studies.