sumglass 2023

International Perspectives on Glass Waste Form Development for Low and Intermediate Level Radioactive Waste

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- Wooyong Um, Pohang University of Science and Technology, Korea; PNNL

- Scope
- Introduction

- Asia
  - Republic of Korea
  - China
  - India
  - Japan
- Europe
  - France
  - UK
- North America
  - Canada
  - US

- Comparison
- Conclusions

Scope of this review

- **Low-level waste**
  - LILW
    - LLW
    - ILW
  - LAW

- Some potential LILW waste forms
  - **Vitrified**
  - Cements
  - Geopolymers
  - Bitumen
  - Etc.

HLW

High Level Waste

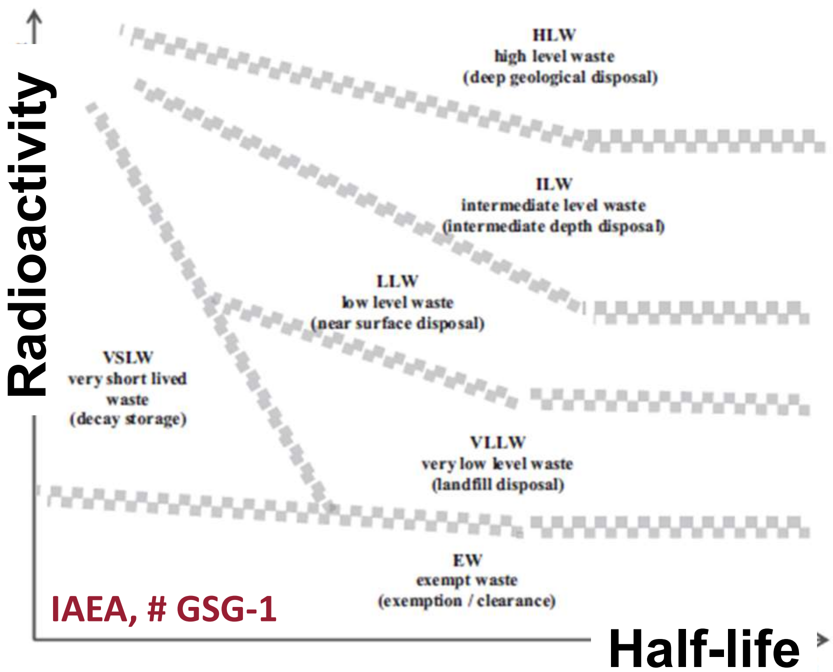
ILW

Intermediate Level Waste

LLW

Low Level Waste

Radioactive waste classification



IAEA, # GSG-1

- LLW = "suitable for near surface disposal"
- Boundary between LLW and ILW is not generally definable only by radioactivity
- Each country must decide their own classification

Table 1 Classification of radioactive wastes in Japan [modified after ANRE (2021) and Irie (2002)].

Type of waste				Example of waste	Disposal method
Waste from nuclear fuel cycle facilities	Waste from nuclear power plants (NPPs)	Waste below clearance level (treatable as non-radioactive material)		Most waste from decommissioning NPPs, etc.	Recycling/disposal as non-radioactive material
		Low-level radioactive waste (LLW)	Very low-level radioactive waste (LLW-L3)	Concrete, metal, etc.	Trench disposal (near-surface disposal without EBS)
			Relatively low-level radioactive waste (LLW-L2)	Solidified liquid waste, spent equipment, consumables, etc.	Disposal in concrete vault (near-surface disposal with EBS)
			Relatively high-level radioactive waste (LLW-L1)	Control rod, core-internals, solidified liquid waste, etc.	Intermediate depth disposal (over 70 m) with EBS
			Relatively large volume of long half-lifetime nuclides	Solidified fuel assembly parts, etc.	Geological disposal (over 300 m)
		High-level radioactive waste (HLW)		Vitrified waste	

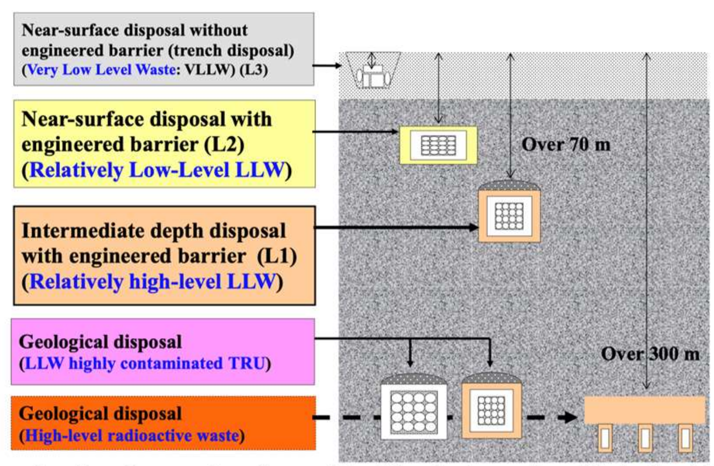


Fig. 1 Types of radioactive wastes disposal facilities in Japan [modified after ANRE (2021)].

- Nakarai, Kenichiro, et al. "Low-Level Radioactive Waste Disposal in Japan and Role of Cementitious Materials." Journal of Advanced Concrete Technology 20, 359 (2022)

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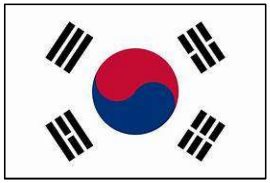
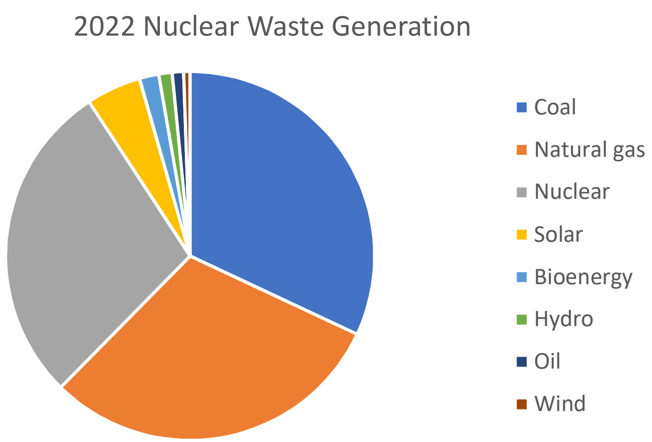
LLW Context in Republic of Korea

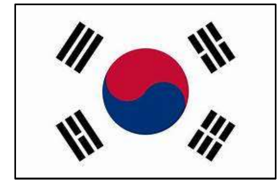


- Extensive nuclear industry
  - 24.5 GWe, 28% of electricity generation
  - Pressurized Water Reactors (PWRs)
  - Current policy is for growth in nuclear energy
- Various LLW generated from civilian energy program
  - "Dry active waste" Contaminated packaging, clothing, paper
  - Ion-exchange resins
  - Zeolite and other inorganic filters
  - Miscellaneous minor waste streams
- **Korea Hydro & Nuclear Power Co. (KHNP)** manages nuclear power generation and waste responsibility
- Vitrification active at Ulchin Vitrification Facility (UVF)
- LLW disposed at **Wolsong** Low- and Intermediate-Level Radioactive Waste Disposal Facility



- International Atomic Energy Agency. *Korea, Republic of -2023 - Country Nuclear Power Profiles*.
- Park, Jin-Beak, et al. "Wolsong Low- and Intermediate-Level Radioactive Waste Disposal Center: Progress and Challenges." *Nuclear Engineering and Technology*, vol. 41, no. 4, May 2009, pp. 477–92.
- Won-Gyo Jung. *Experience on the Commercial Operation of Ulchin Vitrification Facility*. ISOE ASian ALARA Symposium.

Glass Types

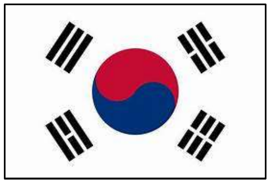


- Sodium alumino-boro-silicate glasses
  - DG-2 is the primary glass made today (DG-2 3x weight of SG and AG8W1)
  - Radionuclide targets: Co, Cs, and Sr
  - Li_2O a significant additive
- Compositions reportedly chosen primarily due to lessons from US – Hanford and aqueous durability
- Glass frit mixed with waste
- Up to 70:1 reduction in waste volume (dry active waste)
  - Most combusts

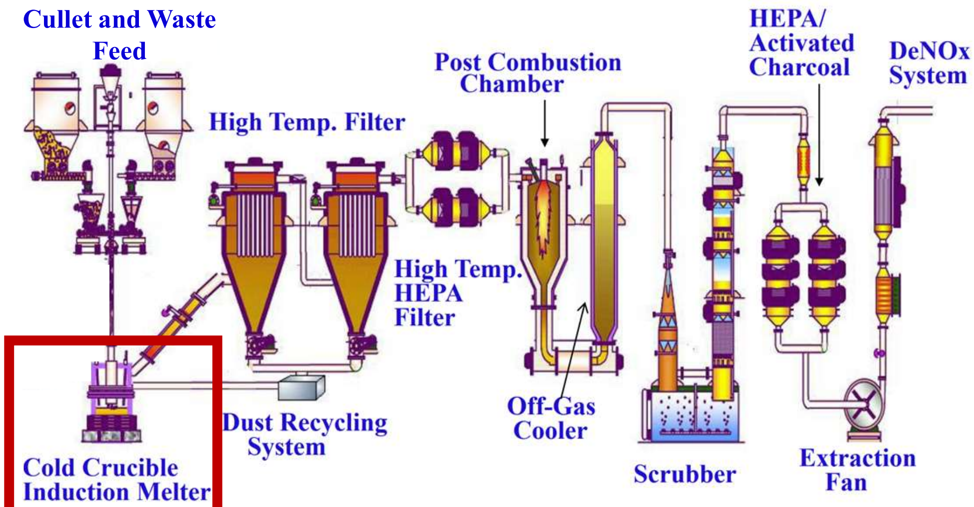
	Glass ID	DG-2	SG	AG8W1	KEV-A PVC	KEV-A Borate	ISG-1
Details	Waste streams	Dry active waste	Ion-exchange resins	Mixed LLW wastes	Polyvinyl chloride	Liquid borate	Reference
	Melter type	CCIM	CCIM	CCIM	-	-	-
	Current use	Yes - UVF	Yes - UVF	Yes - UVF	Proposed	Proposed	-
	Reference	Kim 2018, Jung 2006	Kim 2018, Jung 2006	Kim 2018, Jung 2006	Choi 2000	Choi 2000	Kasper 2019
Properties	Operational T (°C)	1150	1150	1150	1110	1110	1300
	Waste loading (wt%)	25	40	40	50	<15	-
	Viscosity at T (poise)	10	4	67	20	30	6
	Conductivity at T (S/cm)	0.46	0.40	0.31	-	-	-
	PCT 7d, total NL (g/m^2)	2	3	2	2	24	1
Composition (wt%)	SiO_2	41.2	37.5	43.1	35.1	47.6	56.4
	Al_2O_3	7.1	7.4	12.3	3.6	4.2	6.4
	B_2O_3	11.3	10.6	10.0	7.5	25.7	17.3
	Total alkali oxide	19.8	16.9	24.6	11.6	19.5	13.0
	Total alkali earth oxide	14.4	20.4	2.3	24.9	0.4	5.0
	Transition metal oxide	4.9	6.0	8.4	17.1	2.6	2.1
	Other	1.4	0.0	0.1	0.3	0.0	0.0

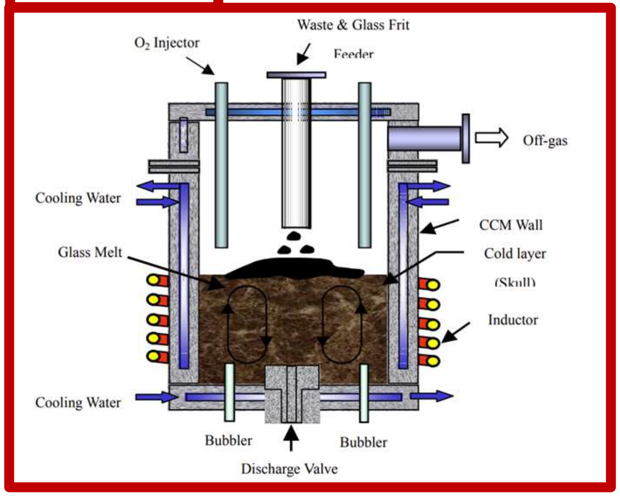
- Kim, Deuk Man, et al. *Glass Composition for Vitrifying Flammable Waste Products*. US Patent 9988297, June 2018.
- Kim, Miae, et al. "Leaching Behaviors and Mechanisms of Vitrified Forms for the Low-Level Radioactive Solid Wastes." *Journal of Hazardous Materials*, vol. 384, Feb. 2020, p. 121296.
- Jung, Hyun-Su, et al. "Characterization of Glass Melts Containing Simulated Low and Intermediate Level Radioactive Waste." *Journal of the Korean Ceramic Society*, vol. 43, no. 3, 3, Mar. 2006, pp. 148–51.
- Choi, Kwansik, et al. "Utilizing the KEP-A Glass Frit to Vitrify Low-Level Radioactive Waste from Korean NPPs." *Waste Management*, vol. 20, no. 7, Nov. 2000, pp. 575–80.
- Kim, Miae, et al. "Leaching Behaviors and Mechanisms of Vitrified Forms for the Low-Level Radioactive Solid Wastes." *Journal of Hazardous Materials*, vol. 384, Feb. 2020, p. 121296.

Vitrification Technologies



- Ulchin Vitrification Facility (UVF) currently vitrifying LLW waste (DAW)
  - Commissioned 2009, 30 y design life
  - Nuclear Environmental Technology Institute (NETEC), a division of Korea Hydro & Nuclear Power Co. (KHNP)
- Cold Crucible Induction Melter
  - Shredded waste fed with cullet
  - ~20 kg waste/hr
  - 100-200 kW, 250-270 kHz
  - Reductive environment from organics burn off
- High performance off-gas system
  - 25 regulated contaminates, 9 below limit, 16 not detected
- Future vitrification systems planned, including for PVC, liquid waste, and inorganic (often zeolite) filters

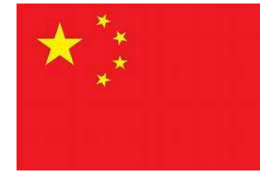




- Cheon-Woo Kim, et al. *Vitrification of Simulated LILW Using Induction Cold Crucible Melter Technology*. Waste Management. 2006.
- Won-Gyo Jung. *Experience on the Commercial Operation of Ulchin Vitrification Facility*. ISOE ASian ALARA Symposium. Sept 2012.

Sheffield Hallam University
Knowledge Applied

Case study: China

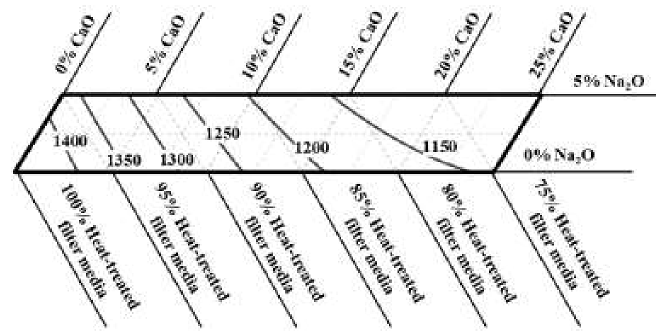


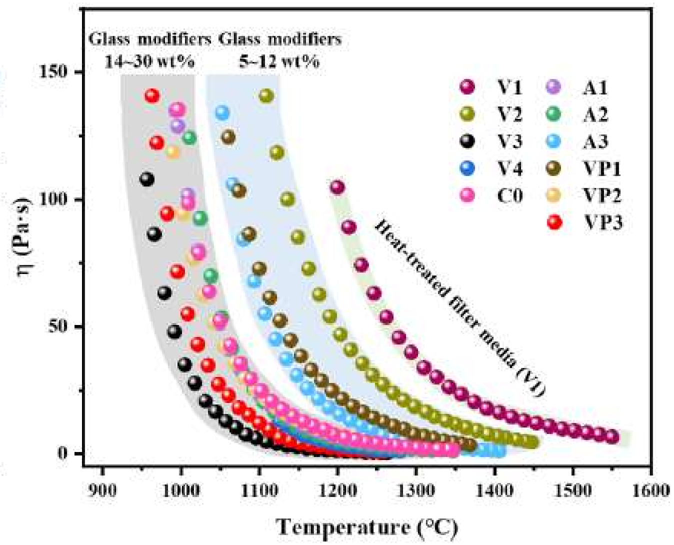
Chinese **LILW solids** are immobilised with:

- Cement
- Bitumen
- Composite polymers
- However, China developed thermal plasma technology since 2009 to decontaminate dry wastes for safety and volume reduction
- Organic matter gasified/incinerated by a thermal plasma torch, with high volume reduction
  - Inorganic residual ashes are melted with glass additives below 1300°C in a melter
  - Homogenized melt is discharged into a steel canister to form a stable glass waste form
- Waste HEPA filters (> 2000 / year) are currently cemented but concerns over durability prompted search for alternatives

Chemical composition of the simulated filter media after heat treatment at 1000 °C obtained from XRF (for Si analysis) and ICP-OES studies.

Oxide	Composition (wt%)
SiO_2	57.19
B_2O_3	5.56
Al_2O_3	6.44
Na_2O	6.89
K_2O	5.96
CaO	11.62
BaO	3.60
ZnO	2.74
SUM	100.00





- G. Fang *et al.*, Vitrification of nuclear-contaminated HEPA filter media: A study on the viscosity-component correlation and the volatilization of simulated radionuclides, *J. Non-Cryst. Solids* 619 (2023) 122568.
- L. Peng, Investigation of thermal plasma melting of typical intermediate and low level radioactive wastes from nuclear power plant, *Materials China* 35 (2016) 504-508.

Sheffield Hallam University
Knowledge Applied

Case study: India

Indian LILW solids are immobilised with:

- Cement
- Bitumen
- Composite polymers

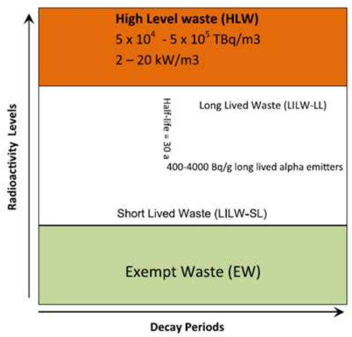
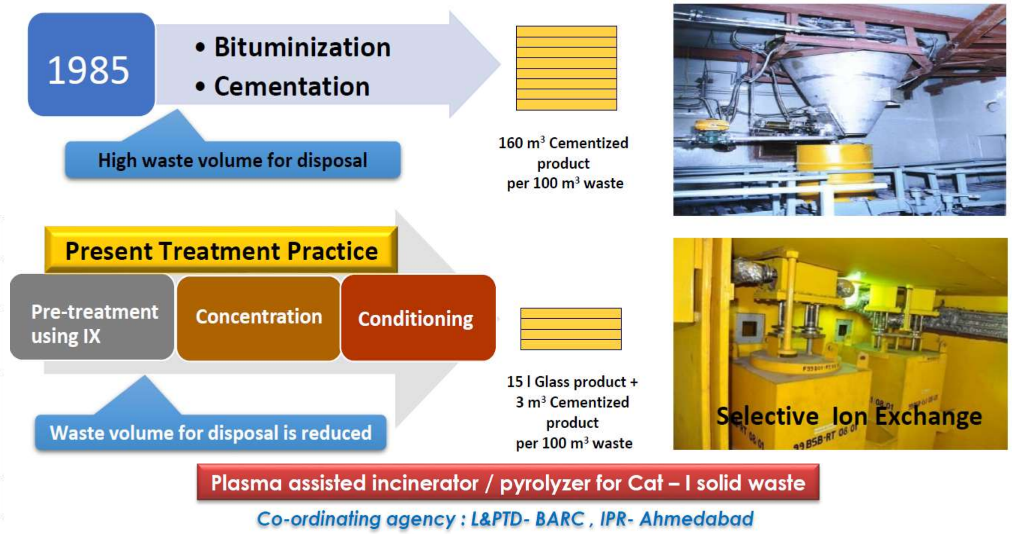


TABLE IV. INCINERATOR FACILITIES IN OPERATION IN SOME MEMBER STATES

Country	Facility/ Site	In-service date	Capacity	Notes
Austria	Seibersdorf Research Center	1983	40 kg/h solid	
Belgium	CILVA, Belgoprocess	1995	80 kg/h solid 50 kg/h liquid	Solids, liquids and ion exchange resins
Canada	Ontario Power Generation, Western Waste Management Facility	2002	2 t/d solid 45 l/h liquid (license limit)	Continuous feed, starved air system.
India	BARC Kalpakkam	1990's	50 kg/h solid	Organic solids without Cl and S



Incinerators in operation since 1970's at:

- Trombay
- Kalpakkam

- Combustible waste incinerated at 800-1100˚C
- Off-gas treatment by HEPA filters
- 10x to 50x volume reduction
- Ash is cemented for storage and disposal

✓ Conventional incinerator only caters to cellulosic wastes (VRF= 30-50)

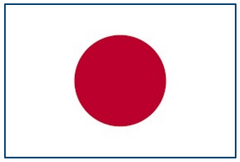
✓ Plasma based system will cater to all Rubber/Plastic/ Cellulosic waste (VRF – 30)

✓ 500 kg of inactive mixed waste processed successfully

✓ 500 kg of actual radioactive cellulosic waste processed successfully (upto 5 mR/hr)

- C. P. Kaushik, Fuel cycle perspective – Indian Context, GCNEP-IAEA Theme Meeting "Strategies and Opportunities for Management of Spent Fuel from Power Reactors in the Longer Timeframe", GCNEP, Bahadurgarh, India (2019).
- S. Kumar et al., Integrated radioactive waste management from NPP, research reactor and back end of nuclear fuel cycle – an Indian experience, *Technologies for the Management of Radioactive Waste from Nuclear Power Plants and Back End Nuclear Fuel Cycle Activities* (2001) 19, IAEA-CSP--6/C.
- P. K. Wattal, Indian programme on radioactive waste management, *Sadhana* 38 (2013) 849–857; IAEA, Application of thermal technologies for processing of radioactive waste (2006) IAEA-TECDOC-1527.

Case study: Japan



- LLW is generated through:
  - Nuclear power plants
  - Spent fuel reprocessing facilities
  - Mixed-Oxide (MOX) fuel-processing facilities
  - Nuclear accidents
- Fukushima Daiichi Nuclear Power Station (FDNPS) decommissioning and fallout radiological waste
  - Unique waste streams, e.g., rubble, cut trees, and secondary wastes
  - Effluent from the Advanced Liquid Processing System (ALPS) for contaminated water treatment from the FDNPS accident present unique challenges
- Waste forms
  - Incineration, compression, and cement waste forms
  - Vitrification technology has yet to be fully adopted
- Japan has begun development of its own vitrification technology
  - Fused Glass Solidification (FGS) technology
  - In-Container Vitrification (ICV)
  - Cold Crucible Induction Melter (CCIM) technology
- Advantages over cementation
  - ¼ reduction of LLW volume
  - Increase in composition flexibility

Current condition of 1F site: Fukushima Daiichi

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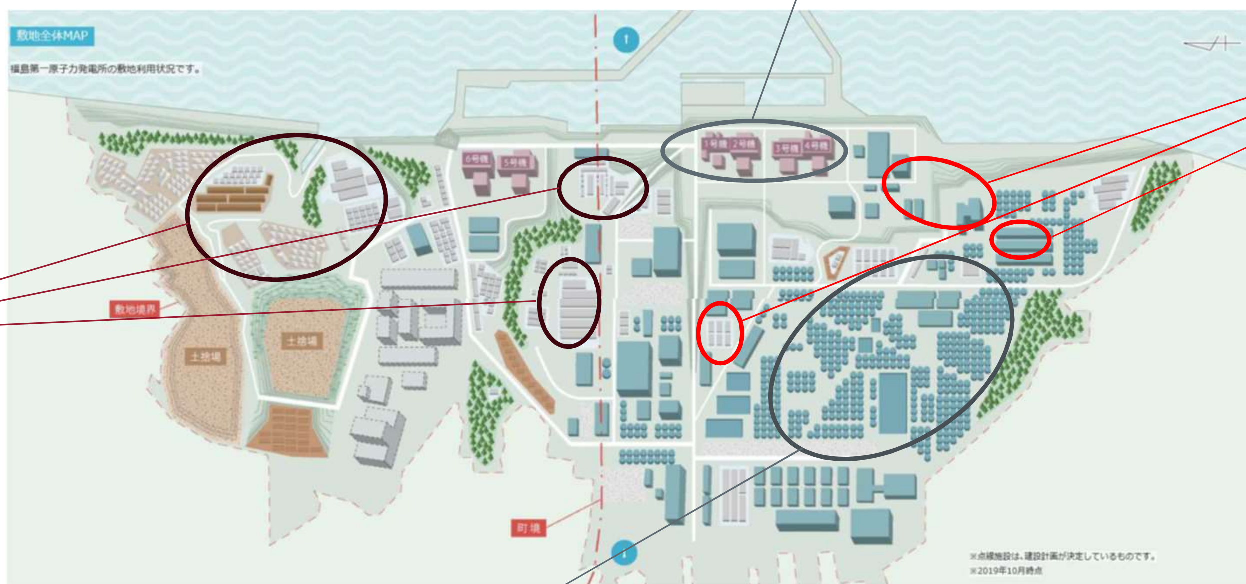
Spent fuels (unit 1,2)
Fuel debris (unit 1,2,3)

➡ Recovery program is under way.



Solid wastes (soil, wood, concrete, metal, etc.)
540,000 m^3

Secondary wastes from contaminated water treatment system
- Cs absorbent vessel --- 1,289
- ALPS HIC --- 4,212
- ALPS vessel --- 90

High-integrity container (HIC)

ALPS=Advanced Liquid Processing System

Decontaminated (treated by ALPS) water tanks
1,330,000 m^3

➡ Release to the sea (started from 24-Aug-2023)

As of 3-Aug-2023

- HP of TEPCO; https://www.tepco.co.jp/decommission/information/committee/roadmap_progress/pdf/2023/d230831_09-j.pdf

Contaminated Water Treatment System

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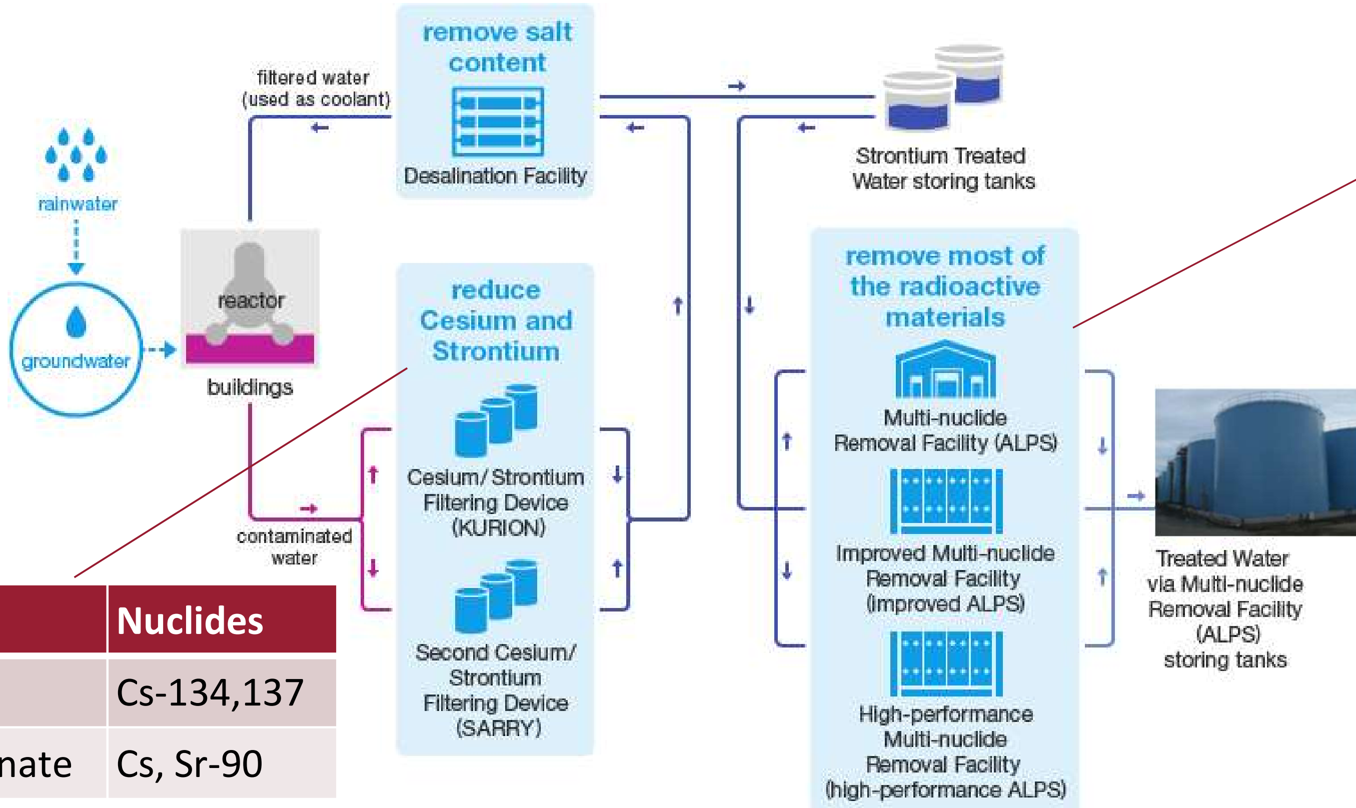

Media	Nuclides
Zeolite	Cs-134,137
Silicotitanate	Cs, Sr-90

Media	Nuclides
Carbonate slurry	Sr-90
Iron co-precipitated slurry	α-nuclides Sr-90
Activated carbon	Colloids I-129
Titanate absorbent	Sr-90
Ferrocyanide absorbent	Cs-134,137
TiO_2	Sb-125
Resins	Co-60, Ru-106

- HP of TEPCO.
- Hijikata, Textbook "Nuclear Fuel Cycle" (in Japanese), Capter9-2 (2015). http://www.aesj.or.jp/~recycle/nfctxt/nfctxt.html

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Secondary wastes from contaminated water treatment

	Carbonate slurry	Iron co-precip. slurry		silicotitanate	Decontamination device sludge (AREVA)	
Wastes	**CS**	**IS**	**Zeolites**	**ST**	**ARS**	**Others**
Component	$CaCO_3$: 50% $Mg(OH)_2$: 40% Na_2CO_3: 10%	FeO(OH)	SiO_2 Al_2O_3 Na_2O	SiO_2 TiO_2	$BaSO_4$ $Ni_2[Fe(CN)_6]$ Sand polymer	Titanate Absorbent Active carbon Resin etc.
Water content (wt%)	80	80	?	?	80	
Nuclides	Sr-90, Cs-137	Sr-90	Cs-134,137, I-129	Cs-134,137, Sr-90	Sr-90 Cs-134,137	
Volume (m^3)	7200	1200	1000	510	600	
Container	High integrity container (HIC)	HIC	Bessel	Bessel	Steel container	

(As of Jul. 2020, estimated)

- HP of Management Office for the Project of Decommissioning, Contaminated Water and Treated Water Management; https://en.dccc-program.jp/3952

Basic treatment concept for 1F waste

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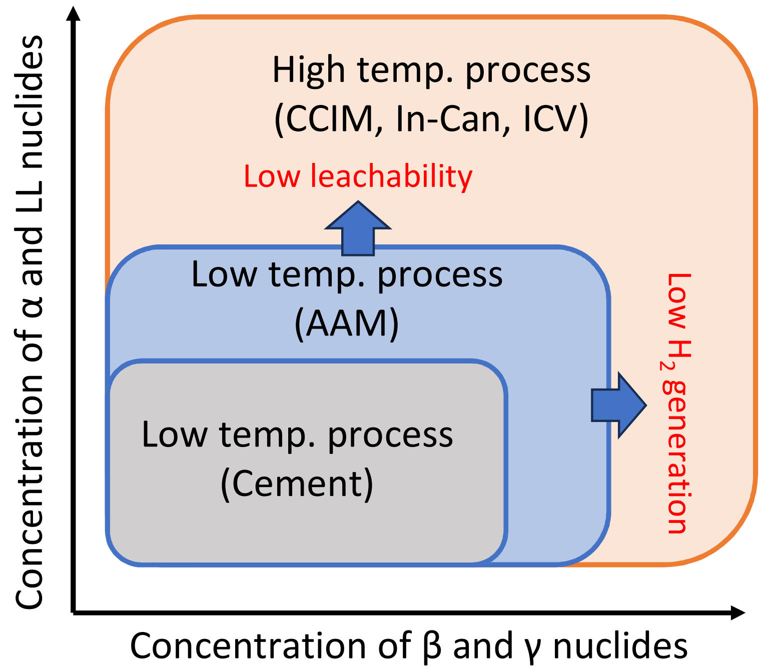
In order to treat a large amounts of wastes, easy, reliable, fast, affordable, method is required.

- ✓ Cement form has a priority.
- ✓ If cement is not available due to leachability, hydrogen generation, etc., then AAM (Alkali Activated Material = Geopolymer) will be adopted.
- ✓ If AAM is not available, glass will be considered. Fast and flexible (adoptable for may wastes) process will be selected.



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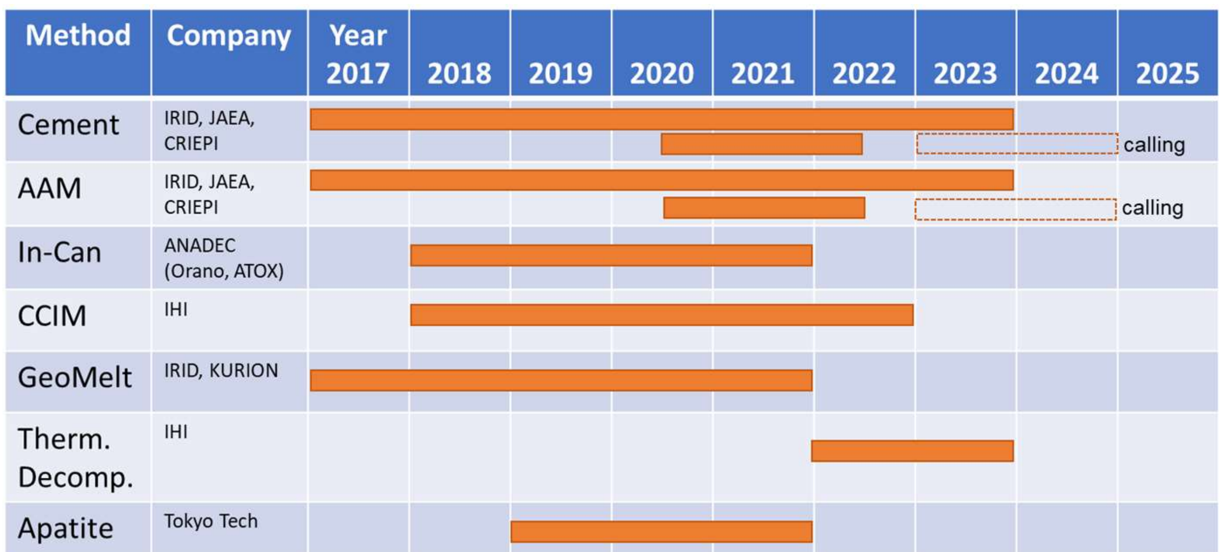
Development of treatment methods

1. Cement form — (low temperature method)
2. AAM — (low temperature method)
3. In-Can melting — (High temperature method)
4. CCIM — (High temperature method)
5. GeoMelt — (High temperature method)
6. Thermal Decomposition — (Middle temperature method)
7. Apatite form — (Middle temperature method)



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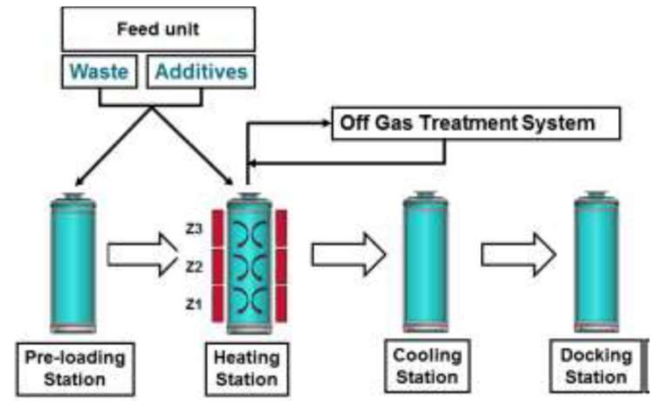
In-Can melting

In-Can melting method: waste and additives are loaded in a container and the container is heated by a furnace.

- ✓ Step by step tests from lab- (~100 g), bench- (~1 kg), pilot-(~100 kg) to industrial scale (~300 kg) were implemented.
- ✓ High waste loadings of 80% for all waste mixing assembly and 50% for ALPS slurry were achieved.
- ✓ Volatilities of Cs and Sr were 0.5 and 0.1 wt%, respectively during pilot scale tests.



DEM&MELT In-Can Vitrification Process

Dem&Melt full-scale demonstrator

Waste form obtained from test with Dem&Melt (51 wt% WL)

- Didierlaurent et al., Proc. WM2020, 20034, Phoenix, Arizona (2020).
- HP of Management Office for the Project of Decommissioning, Contaminated Water and Treated Water Management; https://en.dccc-program.jp/4521

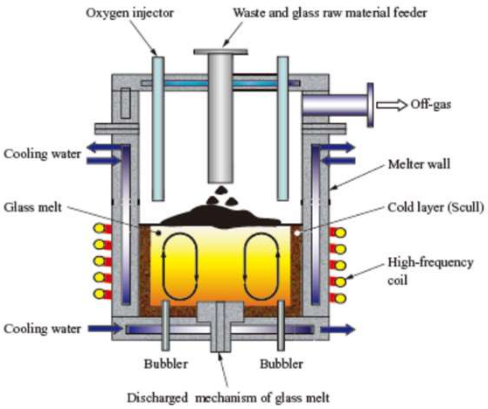
CCIM

Wastes and additives in cold crucible induction melter is heated by high-frequency induction coil and the melter wall is protected by water-cooled scull layer.

- ✓ To avoid Cs volatilization, glass formulation that can melt under 1100˚C was surveyed.
- ✓ Engineering scale vitrification test (~300 kg) was conducted (at KHNP, South Korea).
- ✓ Organic absorbent could also be combusted in CCIM.
- ✓ Engineering system to convey and feed the carbonate slurry (CS) and/or its squeezed lump was developed.

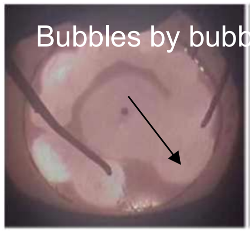
Glass examples from lab-scale tests

CS	IS	Zeolite	ST
			
WL=20%	35	62	25



Appearance of CCIM
(Source: KHNP's brochure)

300 kg scale test



Molten surface

Glass draining

- Oniki et al., IHI Engineering Review, 53(1) (2020).
- HP of Management Office for the Project of Decommissioning, Contaminated Water and Treated Water Management; https://en.dccc-program.jp/3952
- HP of TEPCO: https://www.tepco.co.jp/decommission/information/committee/roadmap_progress/2022-j.html

GeoMelt

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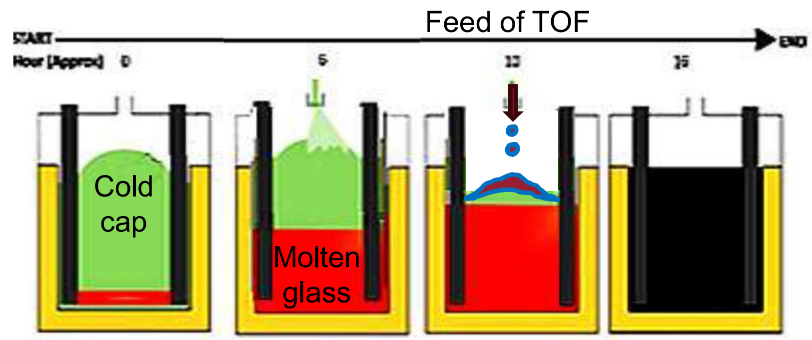
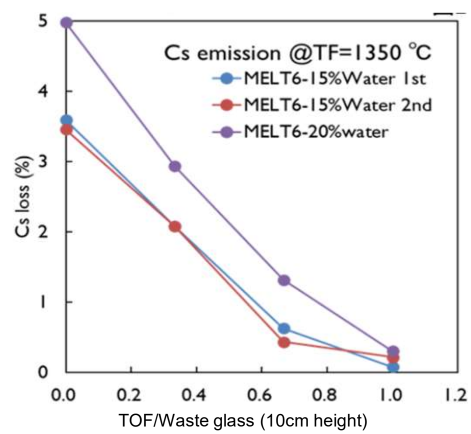
GeoMelt® ICV™ is a joule-heated melter technology which uses a refractory-lined single-use container combining the melter and disposal container.

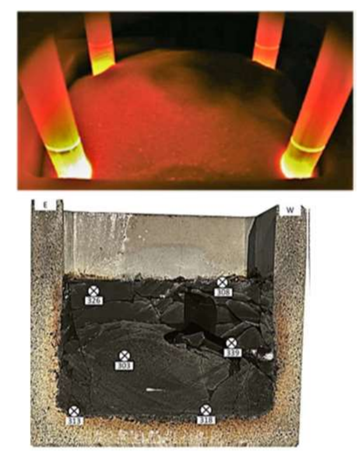
- ✓ To avoid Cs volatilization, manner of top-off frit (TOF) addition was improved
- ✓ Engineering scale vitrification tests (~240 kg in 43*43*43 cm^3 container) were conducted
- ✓ WL was nearly 80% for zeolite+CS+IS co-melting of which CS was 25%.
- ✓ Cs retention in glass was more than 90% for most of the cases. Volatilized Cs was almost completely captured by sintered metal filter.



Operation scheme of GeoMelt



TOF addition vs Cs loss



Melter inside during heating and vitrified product

- Finucane, et al., Proc. WM2020, 20212, Phoenix, Arizona (2020).
- HP of Management Office for the Project of Decommissioning, Contaminated Water and Treated Water Management; https://en.dccc-program.jp/4626
- HP of TEPCO: https://www.tepco.co.jp/decommission/information/committee/roadmap_progress/2022-j.html

- Scope
- Introduction

- Asia
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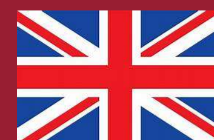
  - France
  - UK



- North America
  - Canada
  - US

- Comparison
- Conclusions

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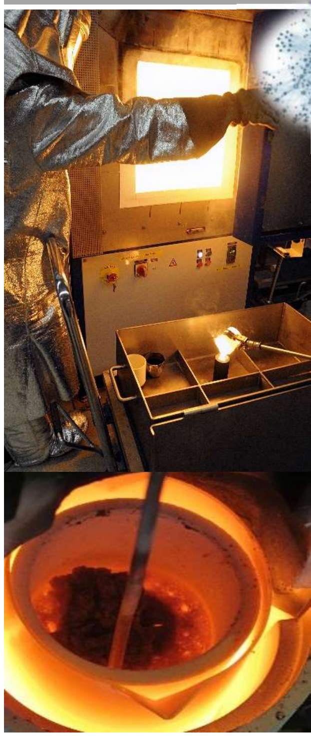
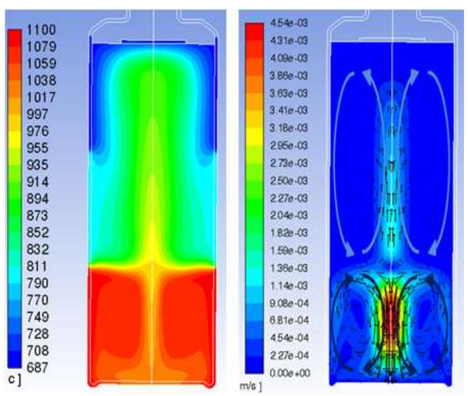
French LILW vitrification : R&D from lab scale to industrial prototypes

	Lab scale		Mock up and modelling				Technologies development		
TRL	1	2	3	4	5	6	7	8	9





R&D investigated for LLW/ILW wastes arising from dismantling operations

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DEM&MELT technology

cea · orano

Vitrification of Cs-impregnated zeolite

cea · orano

Vitrification of Fukushima Daiichi ALPS slurries

cea · orano · ECM

Vitrification of co-precipated sulfate slurries

LLW/ILW Waste

- Solid LLW-ILW deposits
- Adsorbents zeolites Silicotitanate sand
- Liquid fission products (Legacy waste)
- Sludges/ Slurries from co-precipitation process
- Ashes from incineration process

PIVIC

Process for Incineration and Vitrification In Can

cea · orano · ANDRA

In-Can Incineration and Vitrification Processing

H2020 PREDIS (PRE-DISposal management of radioactive waste Project

cea · HORIZON 2020

Molten glass coating for ashes conditioning

In-Can Vitrification of ALPS Slurries from Fukushima Daiichi Effluent Treatment using DEM&MELT Technology (i)

See Aliénor Vernay poster on Monday

Study of ALPS (Advanced Liquid Processing System: Multi Radionuclides Removal) slurries

- A large amount of water treatment secondary waste have been stored on Fukushima Daiichi Nuclear Power Station site
- ~80%vol. of water treatment secondary waste are sludge and slurry
- ALPS system generates two types of co-precipitation slurries ➔ **Iron hydroxide slurry** and **Calcium carbonate/magnesium hydroxide slurry**

➔ Goal of the French study was to confirm the feasibility of vitrification of ALPS slurries treated as a mixture (5 carbonated : 1 ferric) using the DEM&MELT In Can Technology

Ferric slurry

\+

Carbonated slurry

→

Mixed slurries

\+

Glass frit

Dry composition (wt.%)	Surrogate slurry Mix (5 carbonated:1 ferric)
$CaCO_3$	47.30
$Mg(OH)_2$	29.47
Na_2CO_3	3.52
SiO_2	2.98
$SrCO_3$	**1.90**
$FeO(OH).H_2O$	**11.97**
Al_2O_3	0.94
$Co(OH)_2$	0.50
$Ti(OH)_2$	0.45
$Zn(OH)_2$	0.38
$Ca(OH)_2$	0.32
Cl	**0.26**

(WL_{ox}: mass ratio of slurries in oxide form in final wasteform): 40 %

Thermal treatment + optimized conditions

→

1100°C

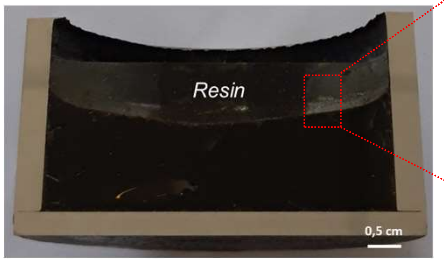
• Verney, Michel, EPJ Nuclear Sci. Technol. 8, 33 (2022)

In-Can Vitrification of ALPS Slurries from Fukushima Daiichi Effluent Treatment using DEM&MELT Technology (ii)

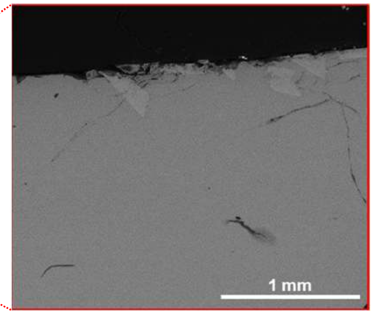
cea orano

See Aliénor Vernay poster on Monday

Lab Scale



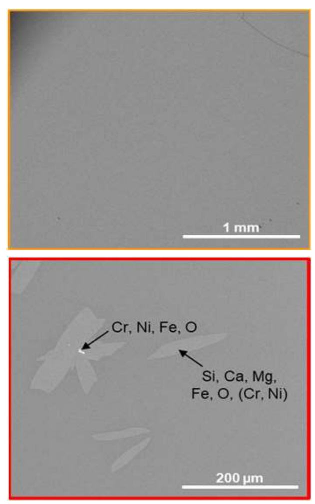
Final wasteform WL_{oxide} 40%



SEM microscopy: homogeneous glass Si, Na, Ca, O, Mg, Fe, Sr, (Al, Cl, Ti, Co)

Full Scale prototype DEM&MELT

2 can: 280 kg of glass



SEM analysis

- ➔ Good homogeneity of the glass melt was ensured at lab scale and with the DEM&MELT In-Can vitrification process
- ➔ Few crystals dispersed in the glass matrix: could be favoured by Cr and Ni from the can and a slower cooling temperature
- ➔ Leaching test (MCC-1 type: 28 days, 90°C in pure water, S/V of 2 m^{-1}) are typical as borosilicate glasses with a sharp drop of the alteration rate

Feasibility of the vitrification of ALPS slurries (40-42% waste loading) validated at full-scale with the In Can process DEM&MELT

This study was performed through funding from the Japanese Ministry of Economy, Trade and Industry as The Subsidy Program /Project of "Decommissioning and Contaminated Water Management"

- Verney, Michel, EPJ Nuclear Sci. Technol. 8, 33 (2022)

In-Can vitrification of spent mineral sorbents using DEM&MELT technology

See Caroline Michel poster on Monday

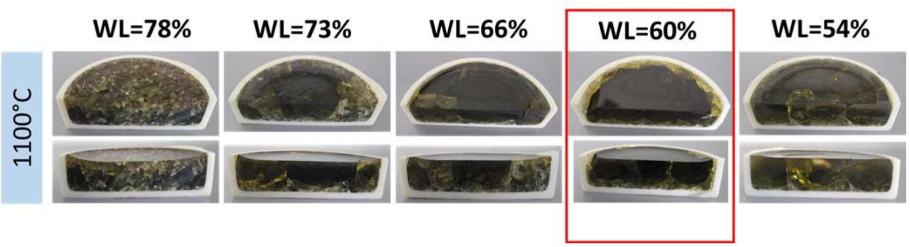
Goal : Conditionning Cs-impregnated zeolite coming from decontamination effluent treatment in a borosilicate glass

➔ Validate the feasibility at laboratory scale and full scale prototype DEM&MELT

Validation at lab scale

- Ranges for waste loading
- Operating temperature
- Mixture strategy
- Melted material
- Viscosity < 200 dps
- Microstructure

Oxides (w.%)	Zeolite
Al_2O_3	17
CaO	5,5
Fe_2O_3	3
K_2O	4.5
MgO	1.25
SiO_2	51.5
Others	17.25
TOTAL	100



Vitrication on full scale prototype DEM&MELT

- A full CAN of homogeneous glass was obtained
- Final WL was 59 % of zeolite (60% targeted)
- Several zeolite feeding rate were tested [6-20] kg/h

Half-cut CAN
263 kg of final glass
WL = 59,1% of zeolite

Vitrification of waste arising from dismantling operations using DEM&MELT technology

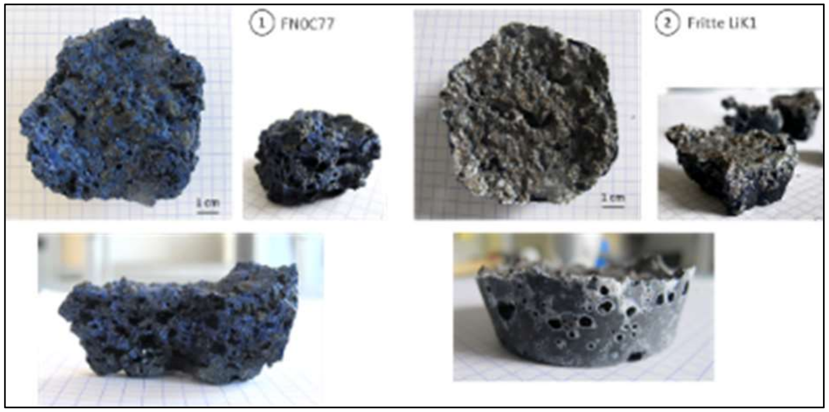
See Aliénor Vernay poster on Monday

PROVIDENCE project (BPI France relance 2030)
Partners: Orano, CEA and ECMT
Objective: Optimize the DEM&MELT process to demonstrate its ability to treat and condition a large inventory of radioactive wastes
Case study: **Sulfated STE2** (Effluent Treatment Plant UP2-400 La Hague) co-precipitation sludge
Challenge: Formulate a low-temperature coating matrix to limit volatilization of certain elements (Cs, S)

Recent results:

- Development of glass frits with sufficiently low viscosity between 750 and 800°C
- **Definition of implementation conditions for process-scale waste treatment ($WL_{800°C}$ of 40 %, T=800°C)**

Perspective
DEM&MELT process trial scheduled for the second half of 2023



100 g samples of slurry/glass coatings made with the 2 frits studied (LiK1 and FNOC77), obtained by treatment at 800°C in a muffle furnace

Molten glass coating for ashes conditioning

See Hélène Nonnet poster on Monday

H2020 PREDIS Pre-disposal management of radioactive waste Project

European Union's Horizon 2020 research and innovation program under grant agreement No 945098 (2020-2024)

Partners: 27 European partner

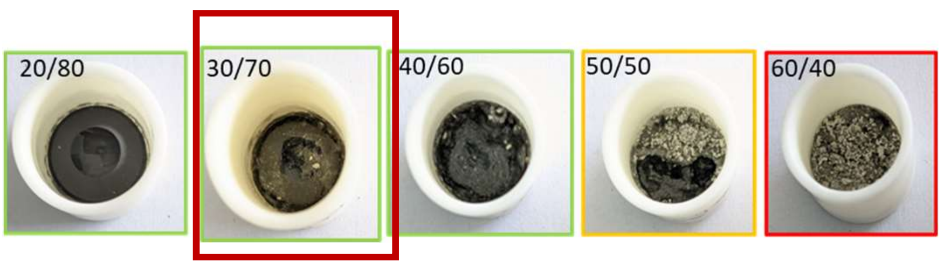
Objective : WP6 is dedicated to the development/conditioning of organic solid waste

Case study: **Ashes**

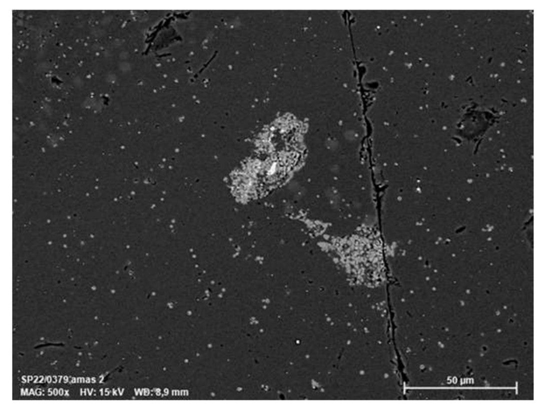
Challenge: Immobilization of waste in a glass matrix at low temperature

➔ *Investigation of several glass formulations to maximize the waste load incorporation of ashes* (calcium-zinc aluminosilicate rich material with a very low level of residual carbon) *coming from the incineration inside a glassy matrix*

➔*Utilisation of molten glass coating, shaped at low temperature, for the safe and efficient immobilization of loose simulant radioactive ashes*



Waste loading ashes/glass screening tests



SEM microstructure glass matrix 30/70

In-Can Incineration and Vitrification Processing of Plutonium contaminated mixed organic/metallic waste

See 2 posters : J. Agullo & A. Quintas posters on Monday

PIVIC project (French government program “Programme d’Investissements d’Avenir”)

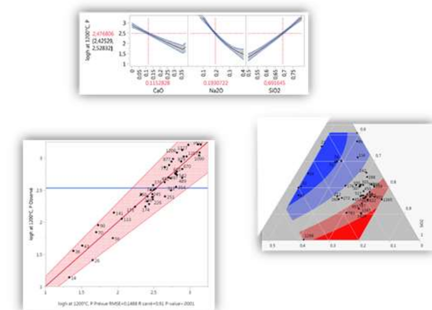
Partners: Orano, CEA and Andra

Objective: Develop a Process for Incineration and Vitrification In Can for mixed medium-level technological waste contaminated with uranium and plutonium.

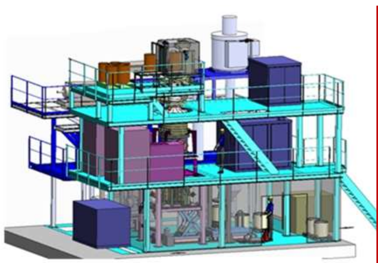
Case study: Variable mixtures of organic, metallic and mineral materials

Challenge: Provide a proof of concept

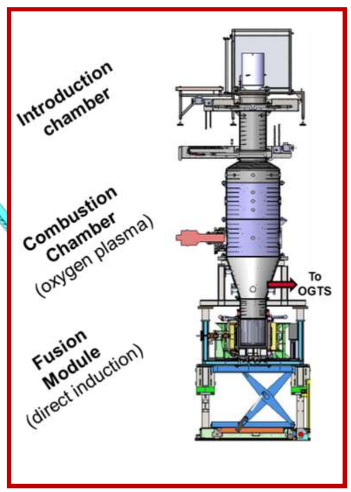
Development of a statistical approach applied to take into account waste composition uncertainties



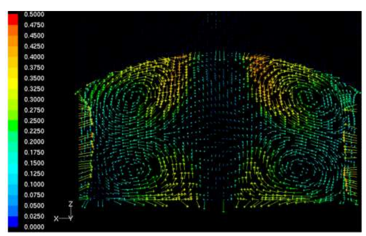
Platform development



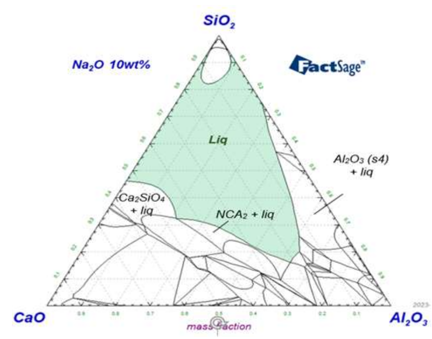
Process optimization



Computer simulation



Thermodynamic calculation



See Damien Perret presentation on Tuesday

LILW in the United Kingdom

Sheffield Hallam University
Knowledge Applied

(Potentially) thermally-treatable UK ILW includes:

- Pond sludges
- Plutonium-Contaminated Material (PCM) wastes
- Sand / clinoptilolite wastes
- Spent Ion Exchange (IEX) media wastes
- Magnox sludge wastes
- Contaminated asbestos wastes
- Miscellaneous beta/gamma solid wastes

Table 3: **Total wastes at 1 April 2022 and estimated for future arisings**

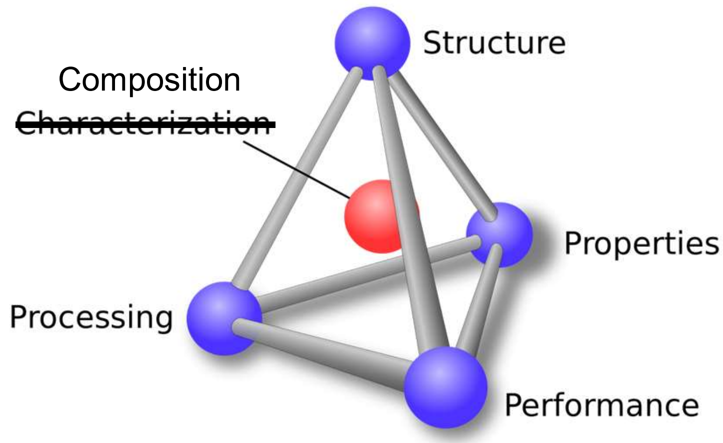
Waste category	Reported volume (m^3)	Reported mass (tonnes)	Packaged volume (m^3)	Number of packages
HLW [1]	1,670	3,500	1,470	7,520
ILW	249,000	310,000	496,000	282,000
LLW	1,580,000 [2]	2,000,000	1,340,000	19,900 [3]
VLLW	2,750,000 [4]	2,800,000	2,610,000	See Note 5
Total	**4,580,000**	**5,100,000**	**4,450,000**	**310,000**

Figure 1: **Major waste producing sites and waste disposal facilities**

- Nuclear Decommissioning Authority, 2022 UK Radioactive Waste Inventory, https://www.gov.uk/government/publications/uk-radioactive-waste-and-material-inventory-2022

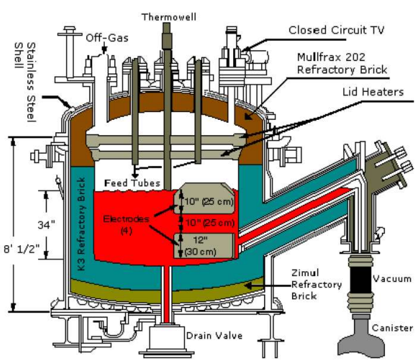
Waste compositions, Technologies

- Pond sludges
  - SiO_2, Fe_2O_3, MgO, Al_2O_3, CaO, ZnO, UO_2, PuO_2, organics
- ***Plutonium-Contaminated Material (PCM) wastes***
  - ***Steel, Cu, Pb, PVC, masonry, glass, PuO_2***
- Sand / clinoptilolite wastes
  - SiO_2, $M_{3\text{-}6}(Si_{30}Al_6)O_{72}.20H_2O$ (M = Ca, Na, K), Cs, Sr
- ***Spent Ion Exchange (IEX) media-bearing wastes***
  - ***Organic resins, radionuclides, process contaminants***
- Magnox sludge wastes
  - $Mg(OH)_2$, Mg, U, Pu, Cs, Sr, I
- Contaminated asbestos wastes
  - $Mg_3Si_2O_5(OH)_4$, concrete, masonry

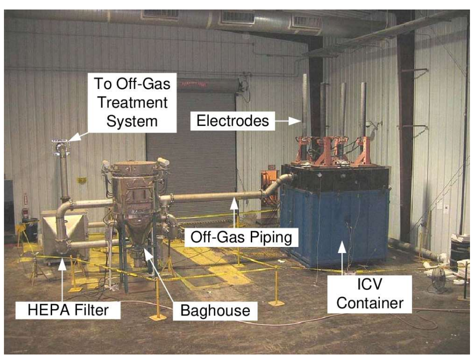


Technology Options Considered / Trialled Include...

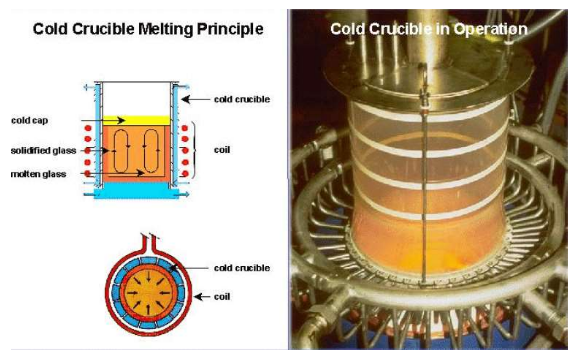
JH-CM



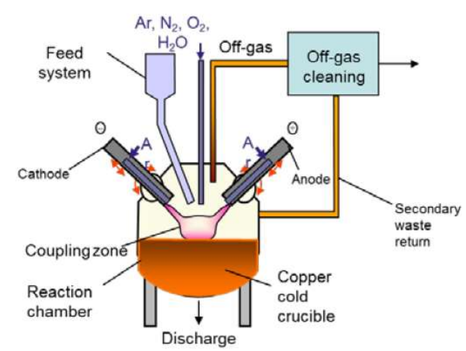
JH-ICV



CCIM



Plasma

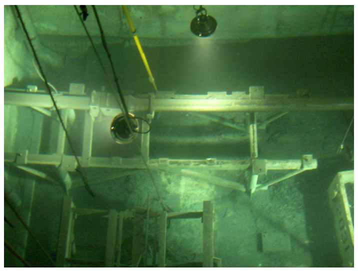


- National Nuclear Laboratory, Thermal Processes for Immobilising Intermediate Level Wastes: Position Paper (2019), www.nnl.co.uk/wp-content/uploads/2019/01/thermal-treatment-position-paper-final-web.pdf

Sheffield Hallam University
Knowledge Applied

UK IEX resin-bearing mixed waste vitrification

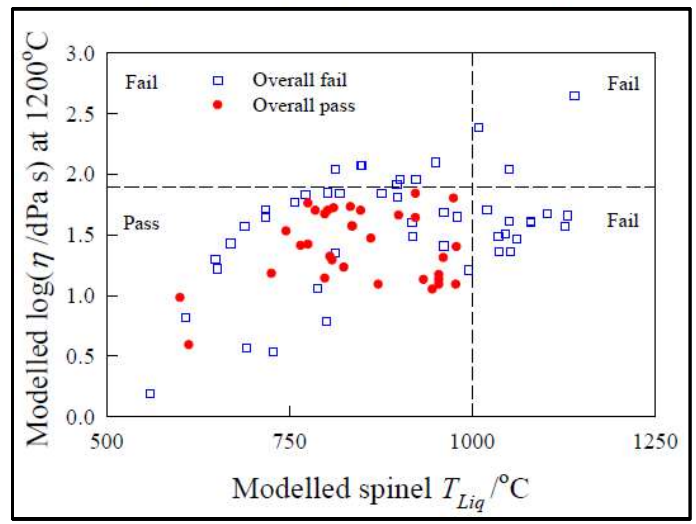
- Hinkley Point ‘A’ Site Decommissioning project, 2008-2012



- Maximise ^{137}Cs and ^{106}Ru retention in the product
- Product with a homogeneous distribution of phases
- Viscosity within acceptable range for pouring
- Target upper melting temperature of 1200°C
- Minimal use of additives
- Leach rate < 10^{-3} gcm^{-2}d^{-1} for Cs, Sr, Na at pH 10·5, T = 50°C, t = 28d
- Outcomes:
  - Glass formulation selection criteria defined
  - >80 glass compositions surveyed
  - Down-selected against criteria
  - Lab-scale trials undertaken
  - Results interpreted
  - Candidate glass formulations defined

Table 2(d). Glass compositions G31-G40 and their measured/modelled physical properties; for details of the properties listed and models used see main text

Sample Code (This Study)	*G31*	*G32*	*G33*	*G34*	*G35*	*G36*	*G37*	*G38*	*G39*	*G40*
Sample Name	EM-38	EM-46	Sample #1	Sample #2	Glass 6	Glass 11	Glass 12	1385 mins	200-38-R	650-38-RR
Reference	96	96	26	26	69	69	69	70	97	97
SiO_2/wt%	42·426	38·283	48·1	47·6	49	39·882	43·323	53·67	38·018	37·315
B_2O_3/wt%	8·842	14·431	8·34	8·19	10·579	9·235	8·991	7·8	13·971	14·558
Al_2O_3/wt%	3·225	6·11			3·285	2·679	2·186	3·07	6·289	8·305
$Fe_{22}O_3$/wt%	19·054	16·675	15·69	16·59	4·962	18·707	18·375	12·57	16·928	15·936
MgO/wt%					0·01	0·01	0·01	1·56		
CaO/wt%	13·769	12·372	11·413	11·636	9·145	13·841	13·893	1·24	9·904	9·931
BaO/wt%										
Li_2O/wt%								4·8		
Na_2O/wt%	7·46	9·237	15·4249	14·9778	20·515	10·253	10·437	6·76	8·931	9·668
K_2O/wt%								2·76		
ZnO/wt%										
ZrO_2/wt%										
PbO/wt%										
TiO_2/wt%										
MnO_2/wt%								2·8		
NiO/wt%			0·519	0·52				1·21		
P_2O_5/wt%										
Cr_2O_3/wt%	0·116	0·115	0·5	0·481						
Sum/wt%	94·892	97·223	99·9869	99·9948	97·496	94·607	97·215	98·24	94·041	95·713
T_{melt}/°C										
Measured T (log(η/dPas)=2)/°C										
Measured T (log(η/dPas)=3)/°C										
Measured log(η/dPas)@T/°C										
Measured T_{Liq}/°C										
Modelled Spinel T_{Liq}/°C										
Temperature/°C										
900										
950										
1000										
1050										
1100										
1150										
1200										
PCT pH										
PCT - Si/ppm										
PCT - B/ppm										
PCT - Na/ppm										
Normalised PCT - Si, g/m^2										
Normalised PCT - B, g/m^2										
Normalised PCT - Na, g/m^2										
Normalised PCT - Li, g/m^2										
Modelled PCT B g/m^2										
Modelled PCT Li g/m^2										
Modelled PCT Na g/m^2										
ΔG_{hyd}/J mol^{-1}										
Σ(FS)										
Selection – Overall Pass/Fail?										



- P. A. Bingham et al., Vitrification of UK intermediate level radioactive wastes arising from site decommissioning Part I, *Glass Technology* 53 (2012) 83-100; Part II, *Glass Technology* 54 (2013) 1-19.

Sheffield Hallam University
Knowledge Applied

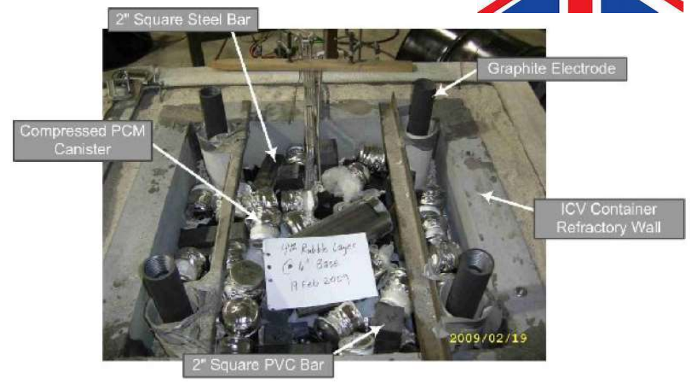
UK PCM wastes: thermal treatment

- Series of projects over past 20+ years

Component (Wt%)	PVC	Masonry	Metal	Mixed	Glass frit
SiO_2	37.93 ±0.36	54.85 ±0.44	69.87 ±0.50	54.23 ±0.44	70.77 ±0.50
MgO	0.85 ±0.06	0.86 ±0.06	1.17 ±0.06	0.93 ±0.06	1.50 ±0.08
Al_2O_3	16.51 ±0.24	11.70 ±0.20	7.60 ±0.11	9.29 ±0.18	1.57 ±0.08
CaO	5.46 ±0.14	7.07 ±0.11	7.43 ±0.11	6.90 ±0.15	10.16 ±0.20
Na_2O	6.02 ±0.15	6.81 ±0.10	7.72 ±0.17	6.53 ±0.15	13.27 ±0.14
Fe_2O_3	30.38 ±0.33	17.65 ±0.26	0.82 ±0.06	18.13 ±0.26	0.36 ±0.03
Cr_2O_3	0.12 ±0.02	0.13 ±0.02	1.48 ±0.07	1.77 ± 0.07	0.24 ±0.02
CeO_2	0.42 ± 0.05	0.33 ± 0.03	0.60 ± 0.05	0.43 ± 0.05	-
Sum	99.31 ±0.60	99.53 ±0.60	98.59 ±0.60	99.09 ±0.60	98.89 ±0.60

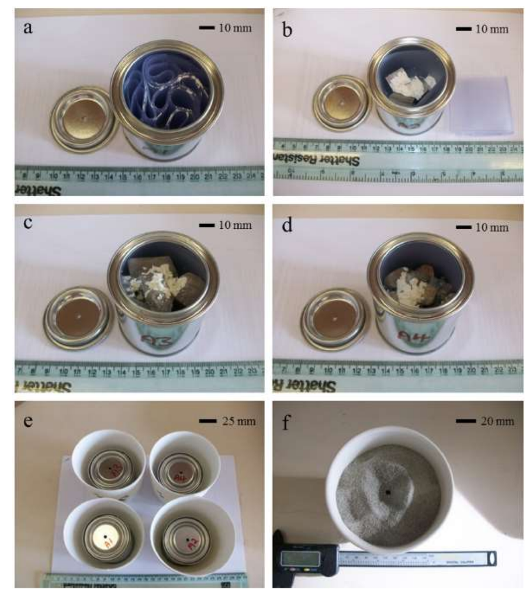
Composition of Calumite Ground Granulated Blast-furnace Slag (GGBS).

Component	Weight %
SiO_2	35.7
Al_2O_3	13.2
Na_2O	0.2
K_2O	0.4
MgO	8.8
CaO	39.7
Fe_2O_3	0.3
MnO	0.5
TiO_2	0.5
SO_3	0.8



Waste Type	PVC Waste	Metal Waste	Masonry Waste	Mixed Waste
Mild Steel (wt%)	44.44	20.00	30.00	30.00
PVC (wt%)	55.56	10.00	10.00	10.00
Metal items (wt%)	0	70.00	0	15.00
Masonry items (wt%)	0	0	60.00	40.00
Glass (wt%)	0	0	0	5.00
Total	100.00	100.00	100.00	100.00

Table 1: Representative PCM waste simulants



- Glass-forming additives considered include:
- Soda-lime-silica (SL) waste glass
- Ground, granulated blast furnace slag (GGBFS)
- “Local soils”

- N. C. Hyatt et al., Thermal treatment of simulant Pu contaminated materials from the Sellafield site by vitrification in a blast-furnace slag, *J. Nucl. Mat.* 444 (2014) 186-199
- L. Boast et al., Thermal treatment of plutonium contaminated material (PCM) waste, *MRS Advances* (2017) 735-740
- K. Witwer et al., Thermal treatment of UK intermediate and low level radioactive waste: a demonstration of the GeoMelt process towards treatment of Sellafield waste, *Proc. WmSym* (2010) 10507

- Scope
- Introduction

- Asia
  - Republic of Korea
  - China
  - India
  - Japan
- Europe
  - France
  - UK
- North America
  - Canada
  - US

- Comparison
- Conclusions

Case study: Canada

- LILW = all radioactive waste except: used nuclear fuel, some medical isotope production waste, uranium mining/milling waste
  - 90% produced by Atomic Energy of Canada Limited (AECL) and Ontario Power Generation (OPG)
- LLW: Subclass VLLW, VSLLW
  - E.g., contaminated equipment from power plant operation
  - “Ongoing” (generators responsible) vs “Historic” (Canadian govt responsible) waste
- ILW
  - E.g., refurbishment waste, ion exchange resins, some radiation therapy sources
- Managed onsite in special facility or transferred for fee to, e.g. Chalk River Laboratories (Canadian Nuclear Laboratories)
- Waste owners meet through CANDU Owners Group (COG) Radioactive Waste Leadership Forum
- **First tentative to use glass as nuclear wasteform was investigated in Canada in the 1950s (Lutze 1988)**

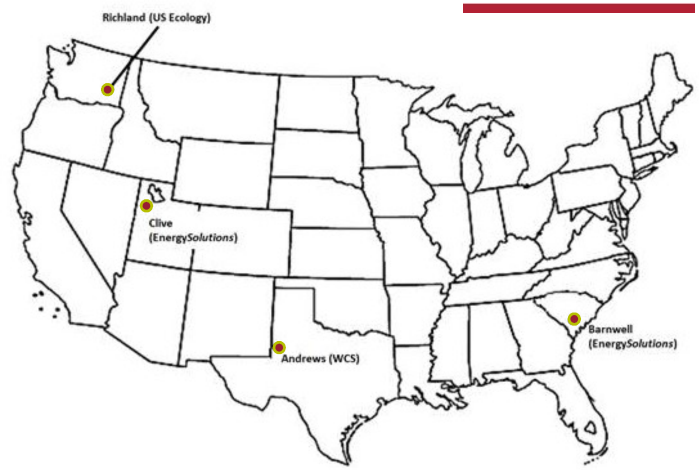
- https://nuclearsafety.gc.ca/eng/waste/low-and-intermediate-waste/index.cfm
- Lutze, *Radioactive waste forms for the future* (1988)

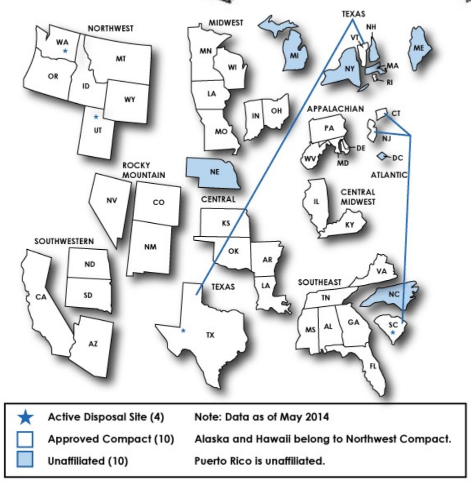
LLW legal status in the USA

- Typically consists of: contaminated protective shoe covers and clothing, wiping rags, mops, filters, reactor water treatment residues, equipment and tools, medical tubes, swabs, injection needles, syringes, and laboratory animal carcasses and tissues
- Nuclear Regulatory Commission (NRC) – commercial only: class A (lowest risk), B, C, >C (highest risk) based on concentration, half-life, and specific radionuclides
- Department of Energy (DOE): HLW, LLW, Waste Incidental to Reprocessing (e.g. Hanford LAW now)
- Low Level Radioactive Waste Policy Act of 1980 (amended 1985) established that each state was responsible for disposing LLRW generated within its boundaries (i.e., on-site); states *may* enter compacts with their neighbor states under Congressional authorization; disposal facility licensed by individual state

2022 Volume and Activity by Disposal Facility

Disposal Facility	Volume (ft^3)	Activity (Curies)**	Compacts	Class
Andrews County, TX	31,287	116,524	Texas & others w/ permission	A/B/C
Barnwell, SC	7,032	29,749	Atlantic	A/B/C
Clive, UT	2,259,959	6,969	All regions	A
Richland, WA	26,682	1,049	Northwest & Rocky Mountain	A/B/C
TOTAL	**2,324,960**	**154,291**		





State compacts

https://www.nrc.gov/waste/llw-disposal/licensing/compacts.html

- https://www.nrc.gov/materials/toolboxes/llrw-waste.html
- https://en.wikipedia.org/wiki/Low-level_radioactive_waste_policy_of_the_United_States

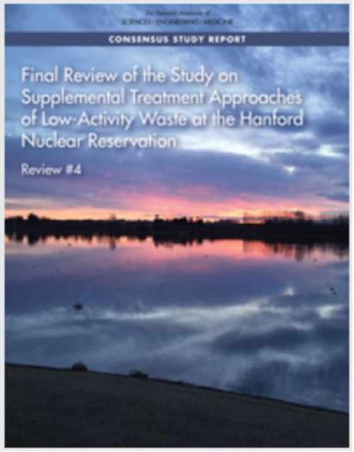
Different $trategies for different $ites

	HLW	LAW	SW
West Valley	Borosilicate glass	Grout	Grout or direct disposal
Savannah River	Borosilicate glass (DWPF)	Grout - Saltstone (SWPF)	Recycle to process
Idaho	Calcine -> HIP? Glass? Or?	Grout (e.g. incinerator fly ash)	
Hanford	Borosilicate glass	Borosilicate glass #	“grout” Castone or direct disposal

Waste classification reviewed (2019) by US National Academy of Sciences committee

- HLW was “waste incidental to reprocessing” (therefore ALL Hanford waste was HLW)
- Now reclassify according to HAZARD; LAW is now WIR but not HLW
- Some SRS grout disposed at commercial LLW facility in Texas

- # significant debate on “good as glass” from the Tri-party agreement (WA Dept. of Ecology, US Environmental Project Agency, US Dept. of Energy)
- **National Academies** studies and public forums 2018-20; “Committee on Supplemental Treatment of Low-Activity Waste at the Hanford Nuclear Reservation”
- Glass vs. Cement vs. Fluidized Bed Steam Reformer (FBSR); cost vs. performance

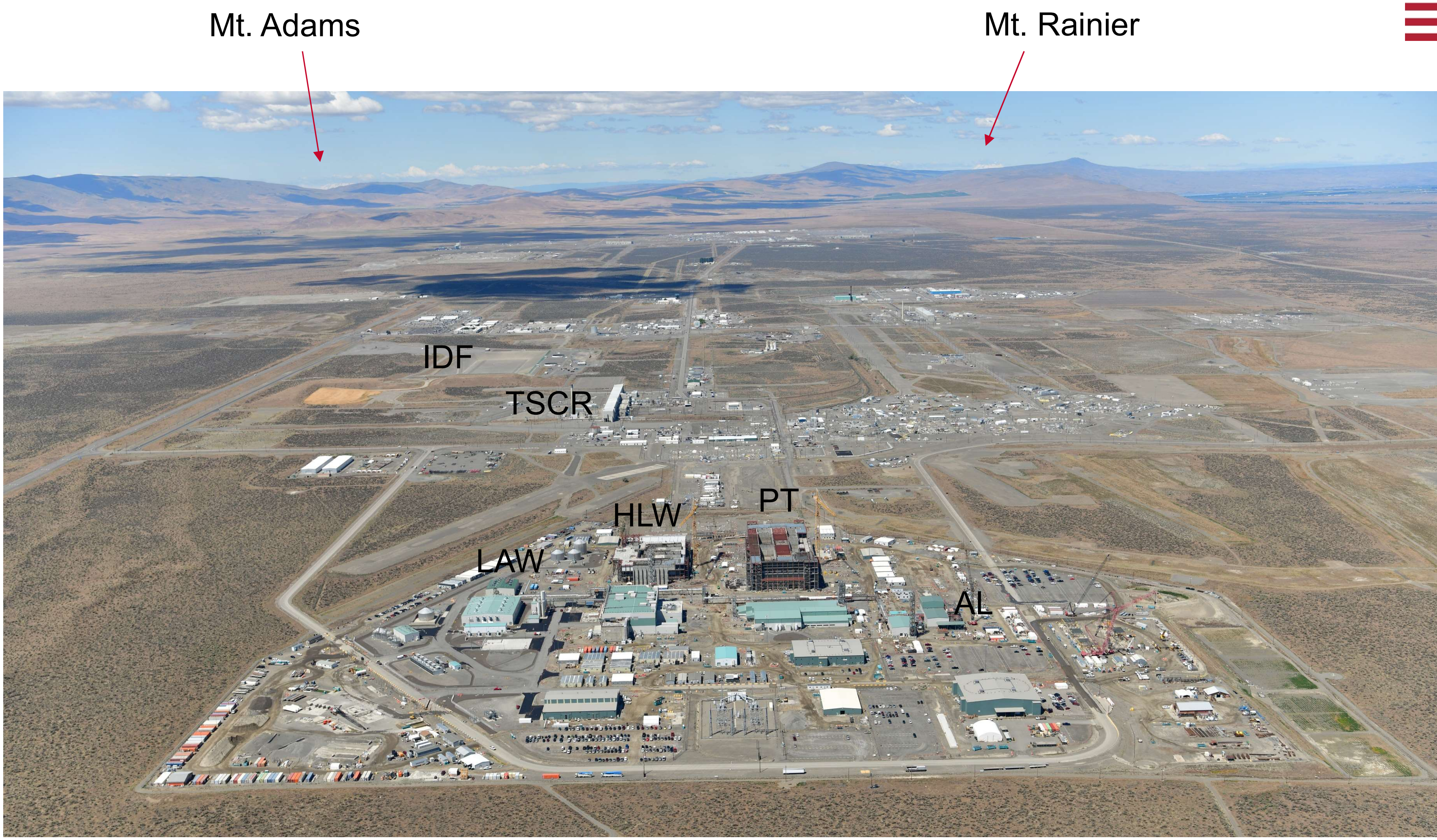


Other LLW waste forms considered:

- Grout (Portland-cement based)
- FBSR
- Bulk vitrification (~Geomelt)
- Geopolymer
- Phosphate-bonded cement

- https://www.ans.org/news/article-2521/reclassification-of-hlw-could-reduce-risks-while-saving-billions-doe-says/
- National Academies of Sciences, Engineering, and Medicine. 2020. *Final Review of the Study on Supplemental Treatment Approaches of Low-Activity Waste at the Hanford Nuclear Reservation: Review #4*. Washington, DC: The National Academies Press. https://doi.org/10.17226/25710.

Waste Treatment & Immobilization Plant (WTP)



Hanford waste

SUPERNATANT:
50-90% H_2O
Na^+, NO_3^-, NO_2^-, OH^-,
$Al(OH)_4^-$, Cs^+

SALTCAKE:
10-50% H_2O
$NaNO_3$, $NaNO_2$,
$NaAl(OH)_4$, Cs^+

SLUDGE:
50% H_2O
Oxides/hydroxides of:
Al, Fe, Bi, Mn, Zr, Si, Sr,
U, TRU

- Marcial, J., B.J. Riley, A.A. Kruger, C.E. Lonergan, and J.D. Vienna, "Hanford Low-Activity Waste Vitrification: A Review," *Journal of Hazardous Materials*, 132437 (2023).

Waste Treatment & Immobilization Plant (WTP)

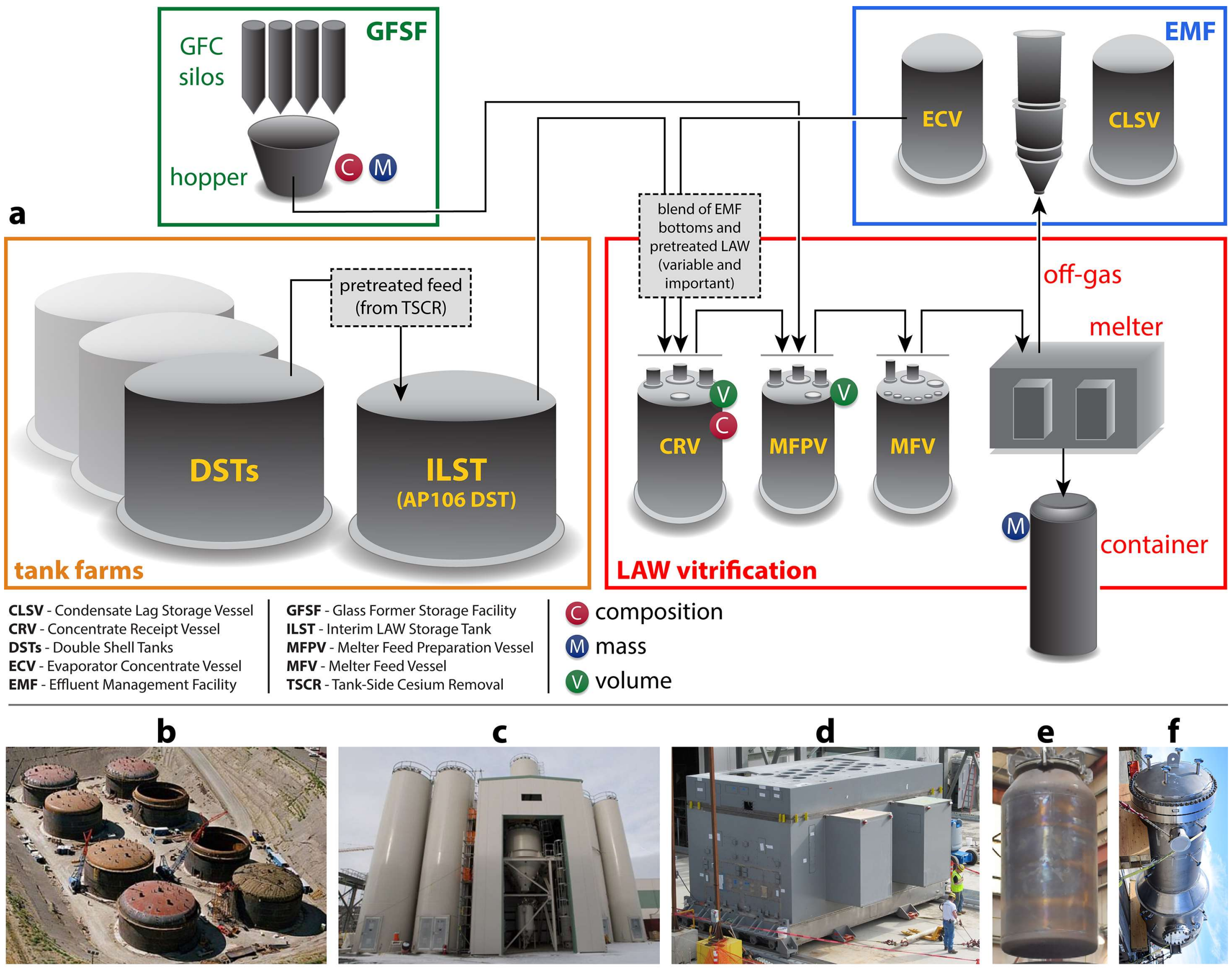


Table 2. Summary of the primary facilities existing (or planned) at the WTP.

Facility name	Abbr.	Description
Pretreatment Facility	PTF	Receives waste and separates it into LAW and HLW
Low-Activity Waste Vitrification Facility	LAW	Receives LAW, mixes with GFCs, vitrifies mixture to form immobilized low-activity waste (ILAW) glass, treats process gases
High-Level Waste Vitrification Facility	HLW	Receives HLW, mixes with GFCs, vitrifies mixture to form HLW glass, treats process gases
Analytical Laboratory	LAB	Analyzes samples from WTP operations, supplies data for safe operations, qualifies glass for disposal
Tank-Side Cesium Removal Facility (operated by Tank Farm Contractor)	TSCR	Removes radioactive Cs, Sr, and transuranics and delivers decontaminated LAW to LAW facility
Effluent Management Facility	EMF	Evaporates LAW liquid effluents into concentrated and dilute streams for recycle and treatment/disposal, respectively
Supplemental LAW Treatment (to be designed and built)	SLAW	Operation to treat LAW fractions over the treatable fraction

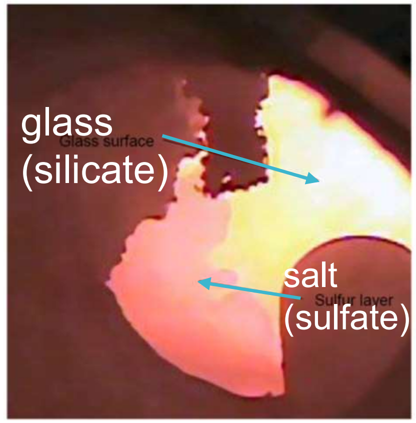
- Marcial, J., B.J. Riley, A.A. Kruger, C.E. Lonergan, and J.D. Vienna, "Hanford Low-Activity Waste Vitrification: A Review," *Journal of Hazardous Materials*, 132437 (2023).

Hanford LAW melter and container

Hanford ILAW: Composition and processing issues

Oxide (wt%)	LAW-A-44 glass[62]
Na_2O	20.00
MgO	1.99
Al_2O_3	6.20
SiO_2	44.55
P_2O_5	0.03
K_2O	0.50
CaO	1.99
TiO_2	1.99
MnO	0
Fe_2O_3	6.98
B_2O_3	8.90
Others	6.87
Total	100

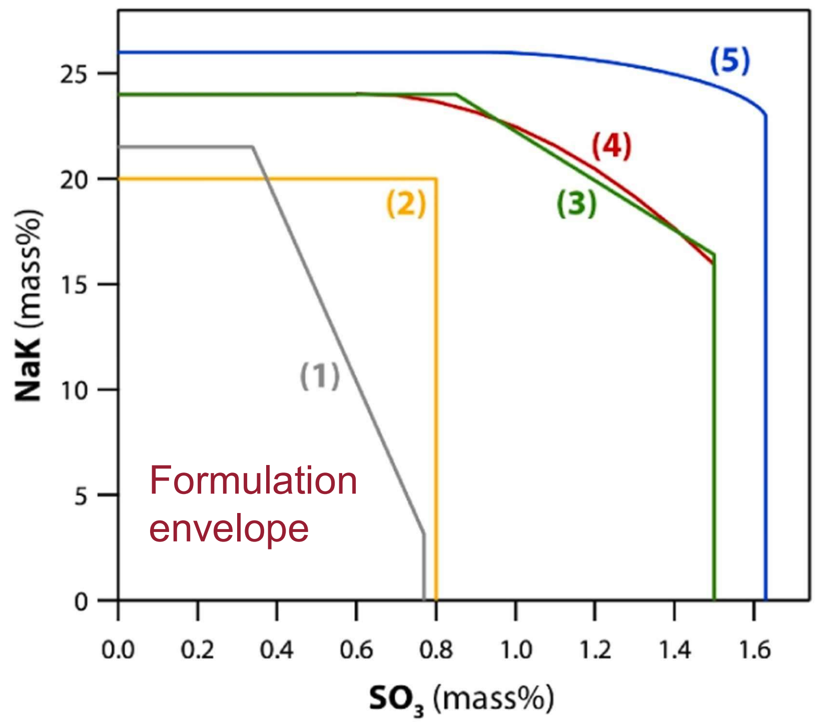
- Typical composition: high Na_2O, substantial SO_3
- **Salt phase**: sulfate, halide
- **Chemical durability**: VHT, other tests
- K-3 **refractory corrosion**



LAWA DM10 Test A1B (VSL-06R6900-1)

Ion	Mass%	Primary process contributing
Na^+	31.8	Neutralizing, corrosion control, and solvent wash
SO_4^{2-}	2.3	BPP, REDOX, PUREX, Cs/Sr recovery

NaK = Na_2O+0.66*K_2O



Effect of components on properties

Table 4. Summary of Component Concentration Effects on ILAW Glass Properties

Oxide	Al_2O_3	B_2O_3	CaO	Cr_2O_3	Fe_2O_3	K_2O	Li_2O	MgO	Na_2O	SiO_2	SnO_2	TiO_2	ZnO	ZrO_2	Other
Viscosity	↑	↓	↓	↔	↔	↓	↓	↓	↓	↑	↑	↓	↔	↑	–
EC	↔	↔	↔	↔	↔	↑	↑	↔	↑	↓	↔	↔	↔	↔	–
Crystal	↑	↓	↓	↑	↑	↓	↓	↔	↓	↓	↑	↑	↑	↑	NiO, MnO↑
PCT	↓↑	↓↑	↔	↔	↔	↑	↑	↑	↑	↓	↓	↓	↔	↓	–
VHT	↓↑	↓↔	↔	↔	↔	↑	↑	↔↑	↑	↓	↓	↓	↔	↓	–
Nepheline	↑	↓	↑	↔	↔	↑	↑	↔	↑	↓	↔	↔	↔	↔	–
Salt	↑	↓	↓	↑	↔	↓	↓	↔	↓	↑	↔	↔	↔	↔	SO_3, Cl↑, V_2O_5↓
TCLP	↓	↑	↔	↔	↔	↑	↑	↔	↑	↓	↓	↔	↑	↓	–
Corrosion	↓	↔	↔	↓	↓	↑	↑	↔	↑	↓	↓	↔	↓	↓	–

↑ = Increase property; ↓ = Decrease property; ↔ = Small effect on property. Multiple arrows are for non-linear effects; the first is for lower concentrations and the second for higher concentrations. TCLP = toxicity characteristic leaching procedure. Corrosion denotes corrosion of glass contact materials (primarily Monofrax K-3 and Inconel 690).

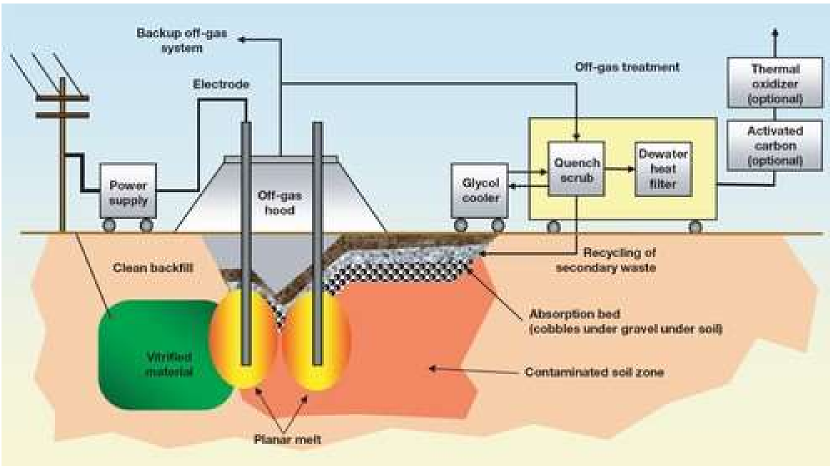
- Marcial, J., B.J. Riley, A.A. Kruger, C.E. Lonergan, and J.D. Vienna, "Hanford Low-Activity Waste Vitrification: A Review," *Journal of Hazardous Materials*, 132437 (2023).

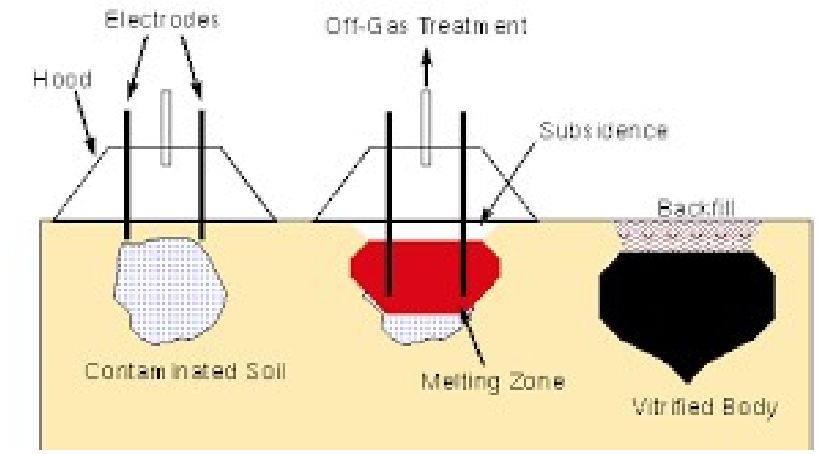
Alternative: Bulk vitrification

- Developed 1980s for SLAW: Secondary LAW (higher rate) options
  - E.g., grout, bulk vit -> No longer needed with new EWG compositions
- Bulk Vitrification by Joule-heated ceramic-lined melter (container)
  - large scale Geomelt (50 tonne boxes)
- Other US Geomelt LLW facilities:
  - Perma-Fix Solutions (Richland, WA)
  - Geomelt Andrews (Andrews, TX)

- Kim et al, PNNL-15131, Schweiger, etc
- https://www.nuclearsolutions.veolia.com/en/our-expertise/technologies/our-geomelt-vitrification-technologies-stabilize-waste

Immobilizing contaminated soil: In-situ vitrification (ISV)





- **Joule-heated**
  - Modified version of Geomelt where waste surrounded by soil inside box
  - Veolia Nuclear Solutions
  - US: PNNL, ORNL, LANL
  - Also explored in France, UK, Japan
- **Uses**
  - Radioactive contaminated soil
  - Asbestos waste
  - Generally have to add component, e.g. Na_2CO_3

Measuring the monolith created by the planar melt cold test at Los Alamos National Laboratory

- Courtesy John Vienna, PNNL
- Ojovan & Lee, *New Developments in Glassy Waste Forms* (2007), 45
- Donald, Waste Immobilization in Glass & Ceramic Based Hosts (2010), 138, 486

- Scope
- Introduction

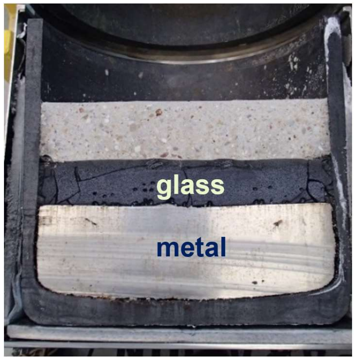
- Asia
  - Republic of Korea
  - China
  - India
  - Japan
- Europe
  - France
  - UK
- North America
  - Canada
  - US

- Comparison
- Conclusions

Considerations

Form of the waste

- Decommissioning waste
- Slurries, sludges
- Process liquids
- Ion exchange media/ sorbents
- Contaminated material
- Materials types (solids)
  - Plastic (PVC, etc.)
  - Metal
  - Masonry
  - Mixed



Cross section of a PIVIC can (Perret et al., 2016)

Technological components for LILW immobilization

- Calcination/ Incineration/ Plasma melting
  - Liquid->solid
  - Volume reduction
  - Destruction of hydrocarbons, nitrates, etc.
- Off-gas treatment

	External resist.	HWIM	CCIM	JHCM
External Container			HLW: France LLW: Korea, Japan,	Hanford LAW
"In-canister"	DEM& Melt	PIVIC		Geomelt
None				(In-situ Vit)

Glass formulation issues and strategies

- **What is in the waste:**
  - Sorbents: e.g., silicotitanate, zeolite = Si, Al, Ti, etc.; sim to 'ash'
  - Certain components: e.g., sulfate
  - Masonry, construction debris: high Ca
  - Metals, plastics, mixed
  - Radionuclides (which ones)
- **What melting temperature can be tolerated:**
  - Cs and volatility
  - Amounts of refractory components (Al, Fe)
  - Capping layers to adjust volatility
- **Waste pre-processing needed:**
  - Incineration, plasma -> reduce volume
  - Changes composition
- **How much waste (volume, batch size):**
  - Small amount, special waste -> in-can
  - Larger amount -> CCIM or JHCM

And of course…

$ € ₩

¥ £ ₹

LILW waste form choice always requires engineering trade study

- Still must meet all **requirements**:
- Regulatory (disposal, durability, radiation stability)
- Processing envelope (viscosity, volatility, etc.)

Thank you
Merci
ありがとうございました
감사합니다
धन्यवाद

Talks before mine at Sumglass

	Oral J1				
3509	French HLW Vitrification History and Major Achievements	gop	OJ1-1	Didierlaurent	Régis
2930	Waste Vitrification Technologies and Details of the Office of River Protection's Enhanced Waste Glass Program	gop	OJ1-2	Kruger	Albert
3556	Geomelt In Container Vitrification Technology : Latest Developments and Overview of Operational Installations	gop	OJ1-3	VERONNEAU	Cyrille
2932	Thermal Plasma Treatment of Dry Waste from Nuclear Power Plants	gop	OJ1-4	Xu	Kai
3125	Advancement in Waste Glass Formulation Methodology	gop	OJ1-5	Vienna	John
3732	Vitrification of high-level nuclear waste worldwide: Historical perspective, current status and future challenges	gop	OJ1-6	Goel	Ashutosh
3213	International Perspectives on Glass Waste Form Development for Low and Intermediate Level Radioactive Waste	gop	OJ1-7	McCloy	John
2573	Engineering of inorganic waste mixtures for new usable glasses: from glass-ceramics to alkali-activated materials	gop	OJ1-8	Bernardo	Enrico
3384	Glass recycling and decarbonization of glass industry – Exemple of French glass industry roadmap	gop	OJ1-9	Capilla	Xavier

Dose rates, classification

Area	Dose rate limit (μSv/h) Average	Maximum	Remarks
Non designated	≤ 0.15	≤ 0.5	• No film badge required • Public exposure < 1mSv/year
Supervised	≤ 2.5	≤ 7.5	• No film badge required • Employees exposure < 1 mSv/year
Simple controlled	≤ 25	≤ 100	• Film badge required • Employees exposure cannot exceed 15mSv/year
Limited stay	≤ 2 mSv/h		• Film badge and personal dosimeter required • Work needs authorization of RP or RSO
High radiation	> 2 mSv/h but ≤ 100 mSv/h		• Film badge and personal dosimeter required • Strict access control enforced • Access needs authorization of RP or RSO
Prohibited	≥ 100 mSv/h		• Access protected by machine interlocks • Access needs authorization of division leader, medical service and RP group • Access monitored by RP group

https://www.slideserve.com/abrial/radiation-safety-issues-in-the-sps-experimental-areas

A. CLASSIFICATION & CHARACTERISTICS OF RADIOACTIVE WASTE

CLASS	DEFINITION	CHARACTERISTICS
High Level Waste (HLW)	fission and activation products resulting from reprocessing of spent fuel	high heat, high γ activity, fairly short t_H
SPENT FUEL (SF)	non-reprocessed spent fuel	high heat, high γ activity, α emitters; fairly short t_H for γ, long t_H for α
Transuranic (TRU)	$Z > 92$ $t_H > 20$ yr Act. > 100 nCi/g	low heat, α emitters, long t_H
Mill tailings	residue of U mills	natural radioactivity, Ra & Rn, α emitters
Low Level Waste (LLW)	all else - none of the above	low heat, moderate γ activity, short t_H

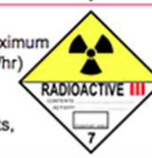
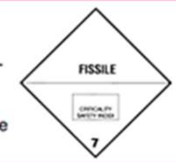
Defense vs. Commercial waste - depends on the origin of the waste and the nature of the activity that created the waste

https://www.slideshare.net/erletshaqe1/lecture-9-30005231

DOT classifications

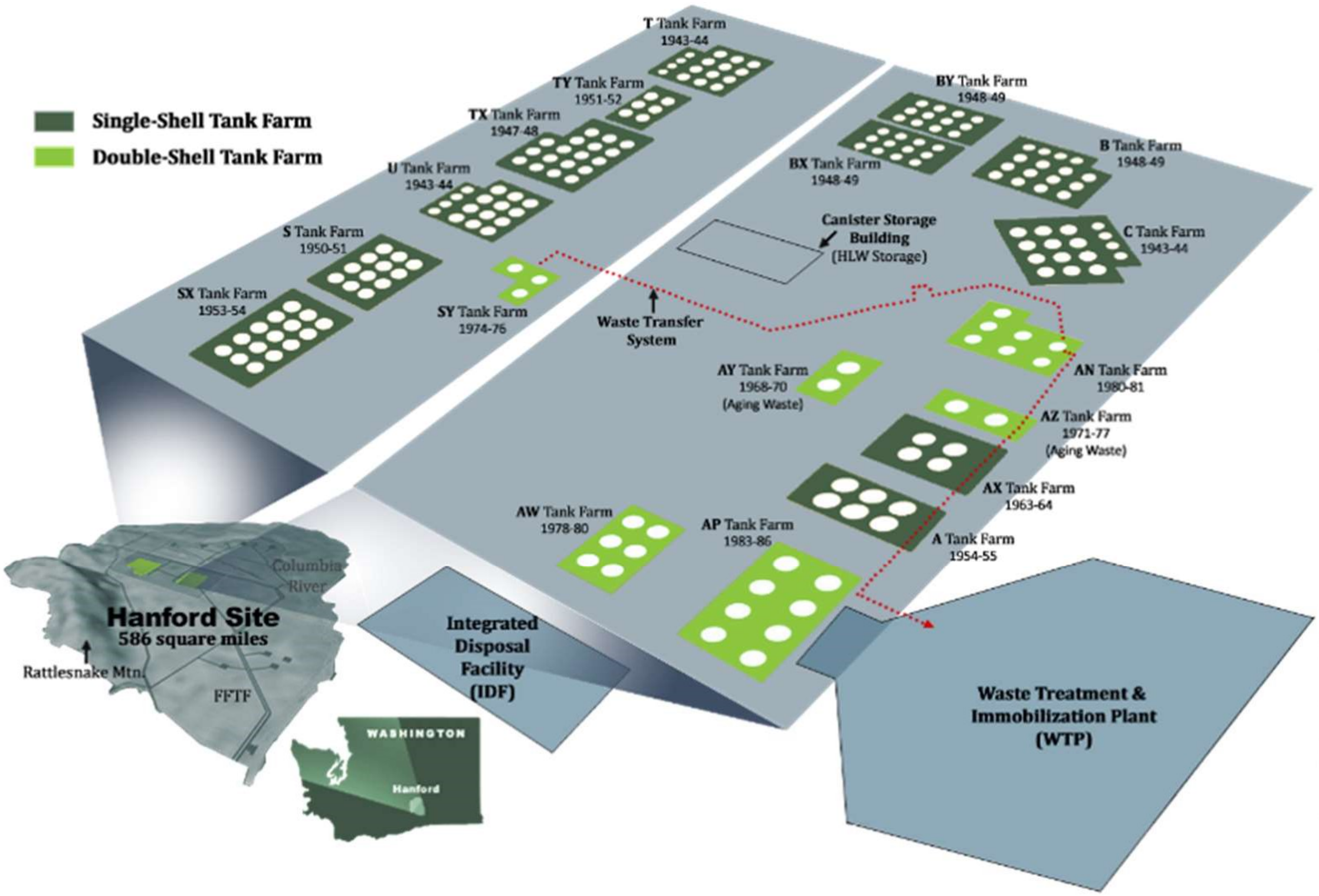
Labels Used on Radioactive Materials Packages

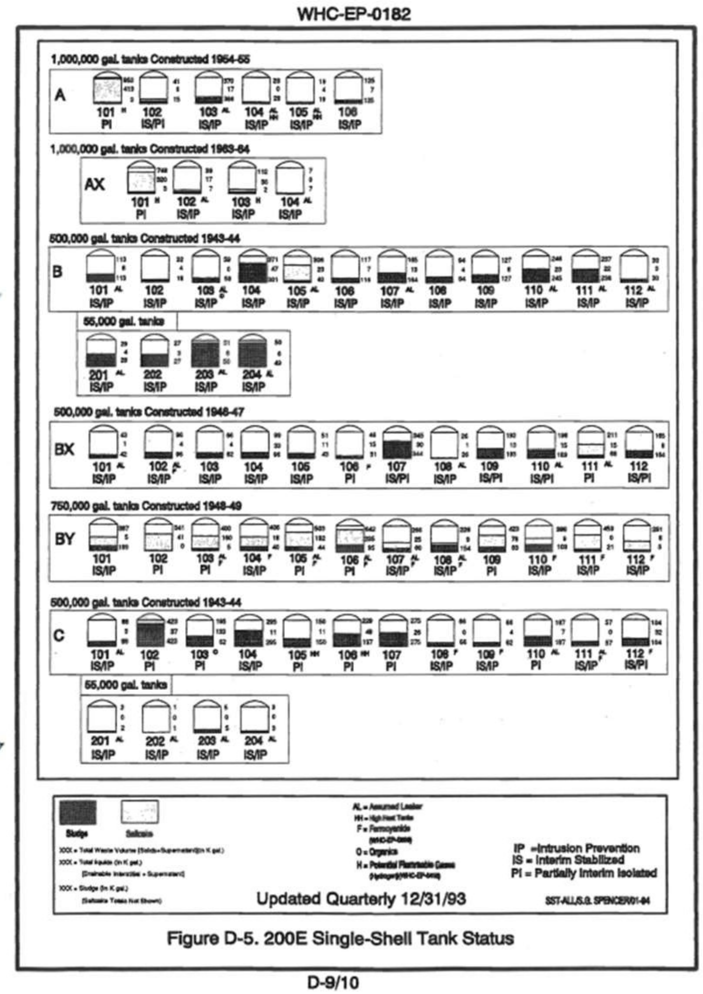
Standard size is approximately 4 inches x 4 inches.

Label	Label Information	Example
Radioactive White-I	Extremely low radiation levels 0.5 mrem/hr (0.005 mSv/hr) maximum on surface	
Radioactive Yellow-II	Low radiation levels >0.5 - 50 mrem/hr (0.5 mSv/hr) maximum on surface; 1.0 mrem/hr (0.01 mSv/hr) maximum at 1 meter	
Radioactive Yellow-III	Higher radiation levels >50 - 200 mrem/hr (2 mSv/hr) maximum on surface; 10 mrem/hr (0.1 mSv/hr) maximum at 1 meter Also required for *HRCQ* shipments, regardless of radiation level	
Fissle	Applied to packages that contain *fissile materials*. The Criticality Safety Index (CSI) for each package will be noted on the label. When used, the fissile label will appear adjacent to the radioactive material label.	
Empty	Applied to packages that have been emptied of their contents as far as practical but may still contain regulated amounts of internal contamination and minimal radiation levels detectable outside the package (<0.5 mrem/hr).	EMPTY

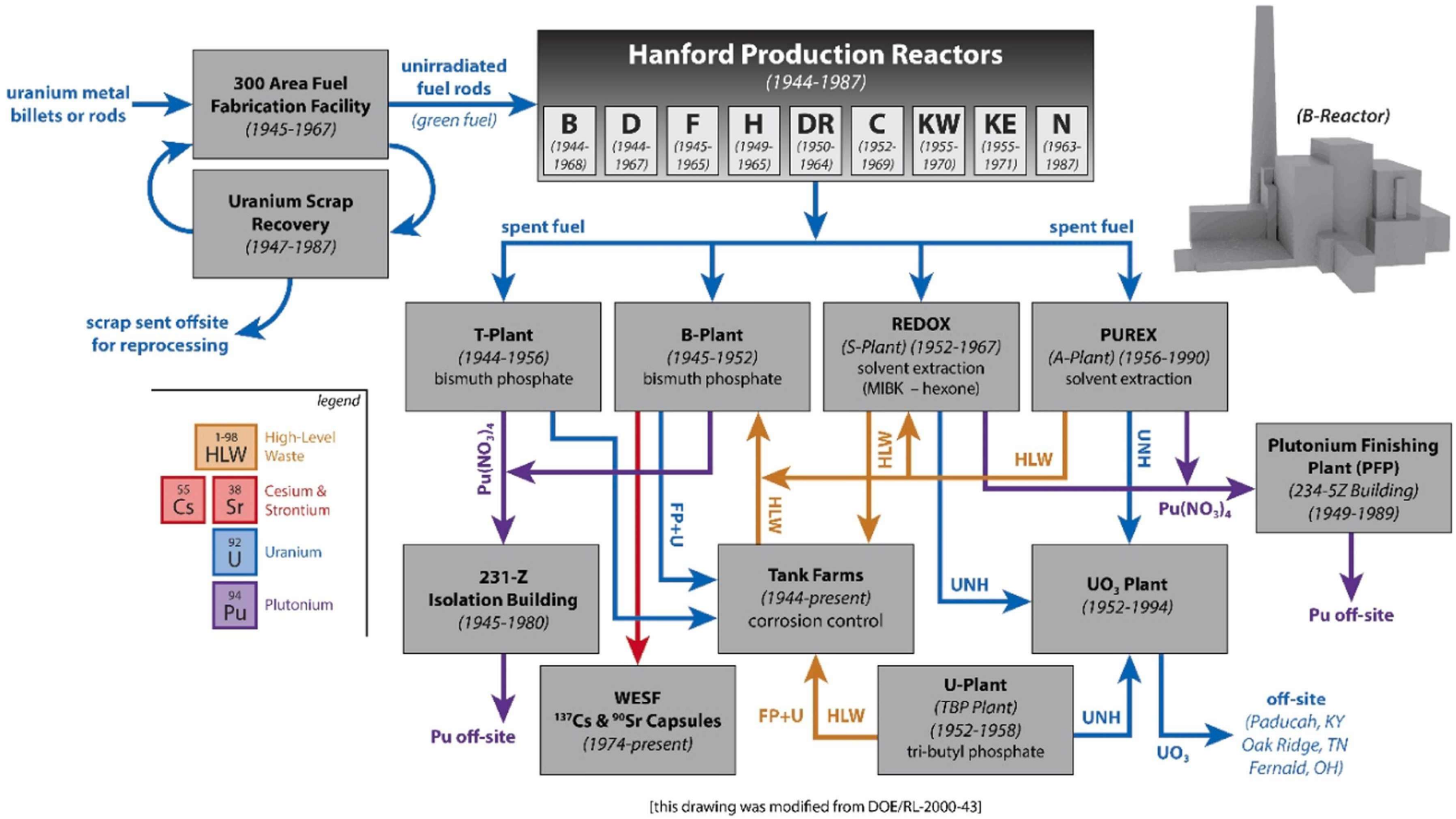
https://www.quora.com/How-can-the-dot-class-for-radioactive-materials-be-described

Tank Farms


Single-Shell Tank Farm
Double-Shell Tank Farm
T Tank Farm 1943-44
TY Tank Farm 1951-52
TX Tank Farm 1947-48
U Tank Farm 1943-44
S Tank Farm 1950-51
SX Tank Farm 1953-54
SY Tank Farm 1974-76
BY Tank Farm 1948-49
BX Tank Farm 1948-49
B Tank Farm 1948-49
C Tank Farm 1943-44
Canister Storage Building (HLW Storage)
Waste Transfer System
AY Tank Farm 1968-70 (Aging Waste)
AN Tank Farm 1980-81
AZ Tank Farm 1971-77 (Aging Waste)
AX Tank Farm 1963-64
A Tank Farm 1954-55
AW Tank Farm 1978-80
AP Tank Farm 1983-86
Integrated Disposal Facility (IDF)
Waste Treatment & Immobilization Plant (WTP)
Columbia River
Hanford Site
586 square miles
Rattlesnake Mtn.
FFTF
WASHINGTON
Hanford


WHC-EP-0182
1,000,000 gal. tanks Constructed 1954-55
A
1,000,000 gal. tanks Constructed 1963-64
AX
500,000 gal. tanks Constructed 1943-44
B
55,000 gal. tanks
500,000 gal. tanks Constructed 1946-47
BX
750,000 gal. tanks Constructed 1948-49
BY
500,000 gal. tanks Constructed 1943-44
C
55,000 gal. tanks
IP = Intrusion Prevention
IS = Interim Stabilized
PI = Partially Interim Isolated
Updated Quarterly 12/31/93
Figure D-5. 200E Single-Shell Tank Status
D-9/10

Hanford waste – generation history



Marcial, J., B.J. Riley, A.A. Kruger, C.E. Lonergan, and J.D. Vienna, "Hanford Low-Activity Waste Vitrification: A Review," *Journal of Hazardous Materials*, 132437 (2023).

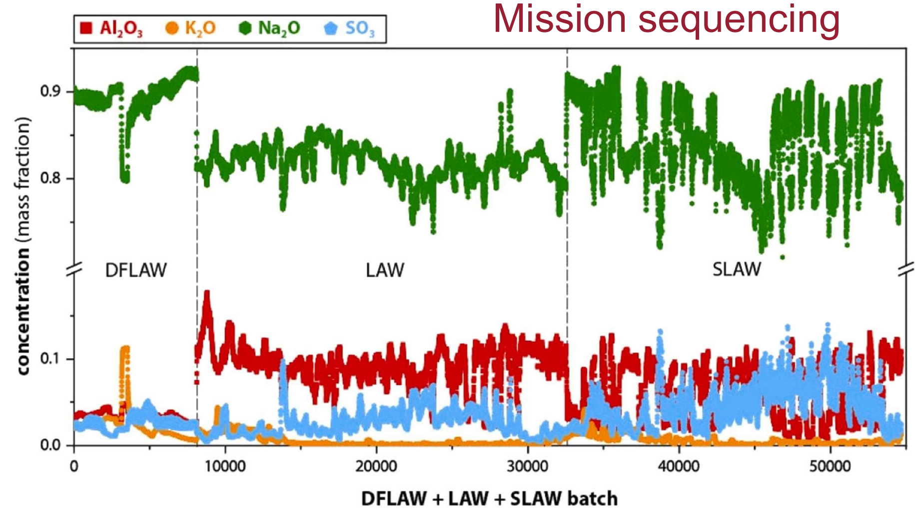
Hanford waste

Source of waste components

Table 1. Tank waste chemical constituents from Best Basis Inventory [29] (excluding water and hydroxide). TOC denotes total organic carbon.

Ion	Mass%	Primary process contributing
NO_3^-	35.2	Nitric acid additions from fuel dissolution, BPP, REDOX, and PUREX
Na^+	31.8	Neutralizing, corrosion control, and solvent wash
NO_2^-	8.2	Corrosion control
CO_3^{2-}	6.7	Atmospheric absorption and solvent wash
Al^{3+}	5.6	Cladding removal and REDOX
PO_4^{3-}	3.2	BPP, THOREX, Cs/Sr recovery
SO_4^{2-}	2.3	BPP, REDOX, PUREX, Cs/Sr recovery
$C_2O_4^{2-}$	1.0	Oxalate precipitation
TOC	0.8	Several
F^-	0.8	Cladding removal, BPP, REDOX
Fe^{3+}	0.8	PUREX, BPP, REDOX, corrosion product
K^+	0.7	U recovery, solvent wash, neutralization, corrosion control
Cl^-	0.6	Chemical impurity, U recovery
Si^{4+}	0.5	Diatomaceous earth, PUREX, REDOX
U^{4+}, U^{6+}	0.4	BPP
Cr^{3+}, Cr^{6+}	0.4	BPP, corrosion control, corrosion products
Bi^{3+}	0.4	BPP
Zr^{4+}	0.3	Cladding removal
Ca^{2+}	0.2	Several
Other	0.1	Includes nearly the entire periodic table

Mission sequencing



Effect of components on properties

Table 4. Summary of Component Concentration Effects on ILAW Glass Properties

Oxide	Al_2O_3	B_2O_3	CaO	Cr_2O_3	Fe_2O_3	K_2O	Li_2O	MgO	Na_2O	SiO_2	SnO_2	TiO_2	ZnO	ZrO_2	Other
Viscosity	↑	↓	↓	↔	↔	↓	↓	↓	↓	↑	↑	↓	↔	↑	–
EC	↔	↔	↔	↔	↔	↑	↑	↔	↑	↓	↔	↔	↔	↔	–
Crystal	↑	↓	↓	↑	↑	↓	↓	↔	↓	↓	↑	↑	↑	↑	NiO, MnO↑
PCT	↓↑	↓↑	↔	↔	↔	↑	↑	↑	↑	↓	↓	↓	↔	↓	–
VHT	↓↑	↓↔	↔	↔	↔	↑	↑	↔↑	↑	↓	↓	↓	↔	↓	–
Nepheline	↑	↓	↑	↔	↔	↑	↑	↔	↑	↓	↔	↔	↔	↔	–
Salt	↑	↓	↓	↑	↔	↓	↓	↔	↓	↑	↔	↔	↔	↔	SO_3, Cl↑, V_2O_5↓
TCLP	↓	↑	↔	↔	↔	↑	↑	↔	↑	↓	↓	↔	↑	↓	–
Corrosion	↓	↔	↔	↓	↓	↑	↑	↔	↑	↓	↓	↔	↓	↓	–

↑ = Increase property; ↓ = Decrease property; ↔ = Small effect on property. Multiple arrows are for non-linear effects; the first is for lower concentrations and the second for higher concentrations. TCLP = toxicity characteristic leaching procedure. Corrosion denotes corrosion of glass contact materials (primarily Monofrax K-3 and Inconel 690).

Marcial, J., B.J. Riley, A.A. Kruger, C.E. Lonergan, and J.D. Vienna, "Hanford Low-Activity Waste Vitrification: A Review," *Journal of Hazardous Materials*, 132437 (2023).

WTP Constraints

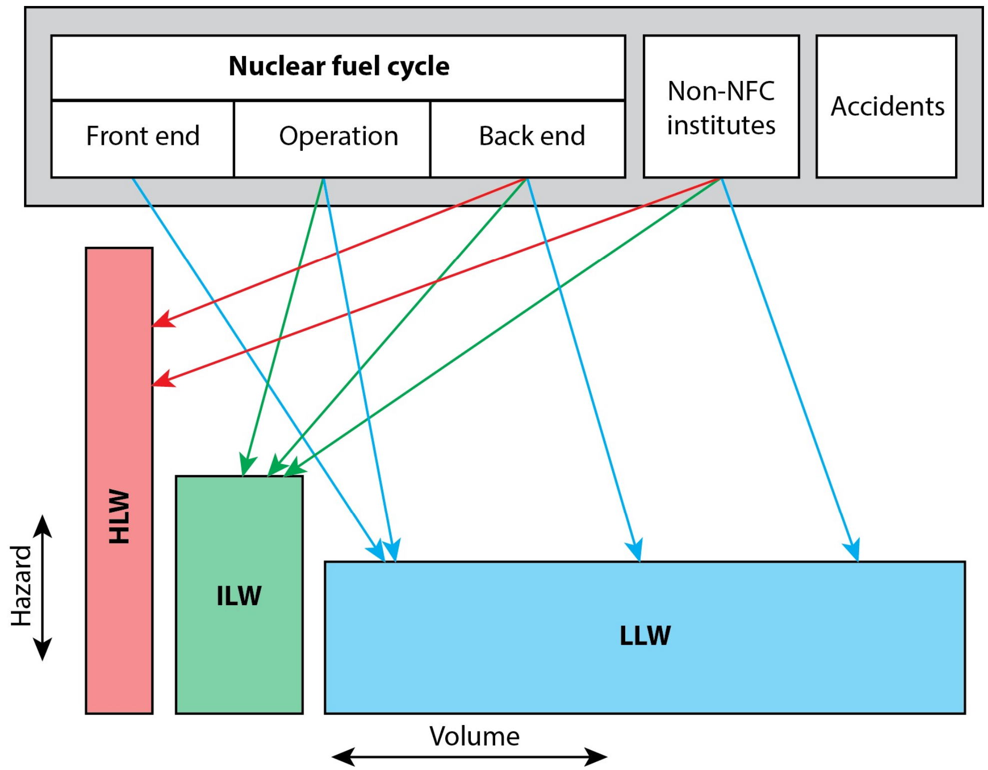
Table 3. Summary of glass property constraints, the associated limits, and the driver for why the limit exists.

Property	Limit	Driver	Ref.
Melt viscosity at 1150°C (η_{1150})	$2 \le \eta_{1150} \le 8$ Pa·s	Process efficiency, mixing, and corrosion	[57]
Melt viscosity at 1100°C (η_{1100})	$\eta_{1100} \le 15$ Pa·s	Pouring and idle process efficiency	[58]
Melt electrical conductivity at 1100°C (ε_{1100})	$\varepsilon_{1100} \ge 10$ S·m^{-1}	Power delivery to the melt	[58]
Melt electrical conductivity at 1200°C (ε_{1200})	$\varepsilon_{1200} \le 70$ S·m^{-1}	Current density on electrodes	[58]
Melt crystal content at 950°C (C_{950})	$C_{950} \le 1$ vol%	Melter pour spout pluggage	[58]
6-d Monofrax K3 refractory corrosion (k_{1208})	$k_{1208} \le 0.00102$ m	Melter lifetime	[59]
Sulfur solubility/sulfur concentration (S/C)	S/C ≥ 1	Excessive corrosion of melter components	[60]
Product consistency test (PCT) response normalized Na, B, and Si losses ($NL_{[Na,B,Si]}$)	$NL_{[Na,B,Si]} \le 2$ g·m^{-2}	Reduce risk of excessive corrosion rate in the Integrated Disposal Facility (IDF), Specification 2.2.2.17	[30]
Vapor hydration test (VHT) alteration rate (r_a)	$r_a \le 50$ g·m^{-2}·d^{-1}	Reduce risk of accelerated corrosion in the IDF, Specification 2.2.2.17	[30]
Phase changes during slow cooling in the container	No significant impact to performance	Ability to satisfy disposal criteria	[61]
Waste classification (W_C)	W_C ≤ class C	Demonstrate waste is incidental to reprocessing, Specification 2.2.2.8	[61]
^{90}Sr activity	^{90}Sr ≤ 20 Ci·m^{-3}	Demonstrate waste incidental to reprocessing (WIR), Specification 2.2.2.8	[61]
^{137}Cs activity[(a)]	^{137}Cs ≤ 3 Ci·m^{-3}	Demonstrate WIR, Specification 2.2.2.8	[61]
^{137}Cs activity[(a)]	^{137}Cs ≤ 0.3 Ci·m^{-3}	Contact maintenance dose, Section C.7	[61]
Container surface dose rate (D_S)	$D_S \le 500$ mrem·h^{-1}	Container handling, Specification 2.2.2.9	[61]
Land disposal restrictions (LDR)	Satisfy petition	IDF acceptance criteria, Specification 2.2.2.20	[61]

(a) There are two ^{137}Cs constraints in the contract. One is required for waste disposal while the other for contact maintenance. The higher limit determines the maximum that can be put in glass while the lower can potentially be exceeded on a case-by-case basis if process safety can otherwise be assured.

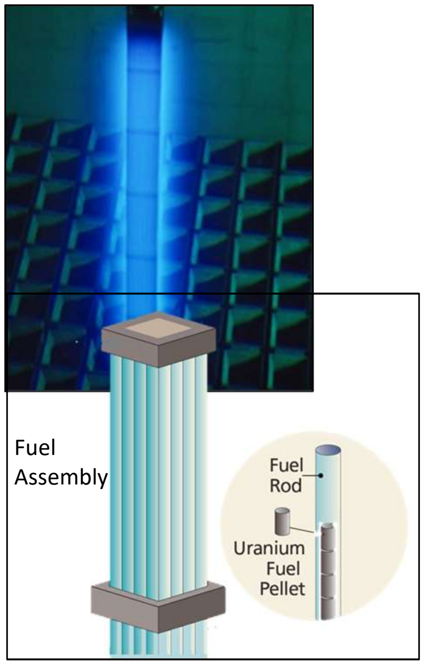
Marcial, J., B.J. Riley, A.A. Kruger, C.E. Lonergan, and J.D. Vienna, "Hanford Low-Activity Waste Vitrification: A Review," *Journal of Hazardous Materials*, 132437 (2023).

What is Nuclear Waste?



- **Commercial fuel**
- **Legacy weapons production**
- **Non-Nuclear Fuel Cycle**
  - Medical
    - Isotope production
  - Industrial
    - Well logging
  - Research
    - Academic reactors

What waste? (international categories)



SNF

Spent Nuclear Fuel

In US, this is HLW
but legally different

HLW

High Level Waste

ILW

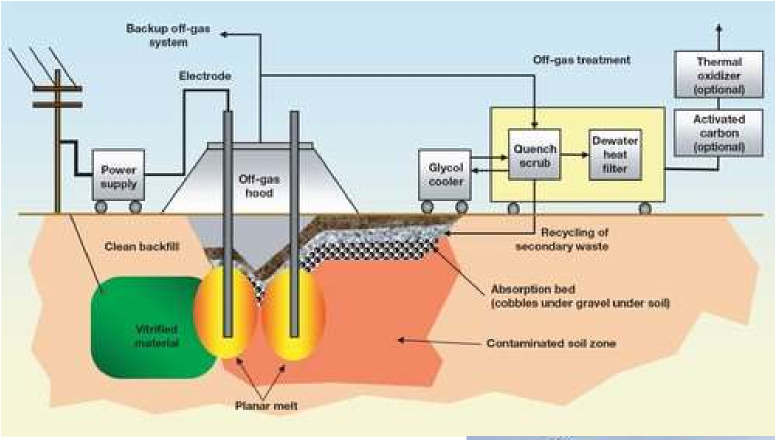
Intermediate Level Waste

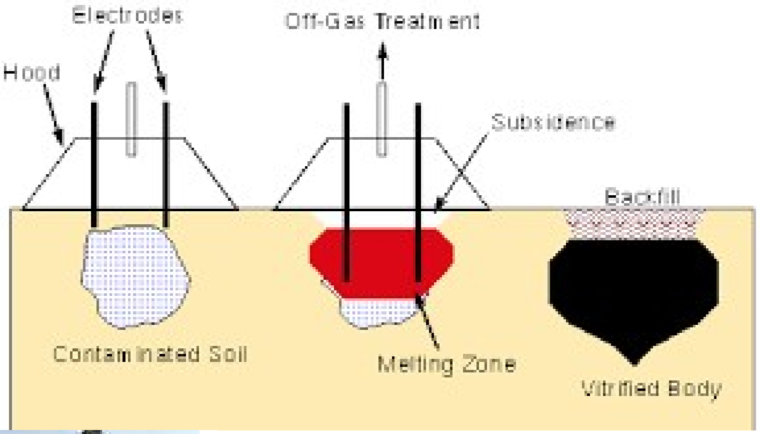
In US, we do not
have this category

LLW

Low Level Waste

Immobilizing contaminated soil: In-situ vitrification (ISV)

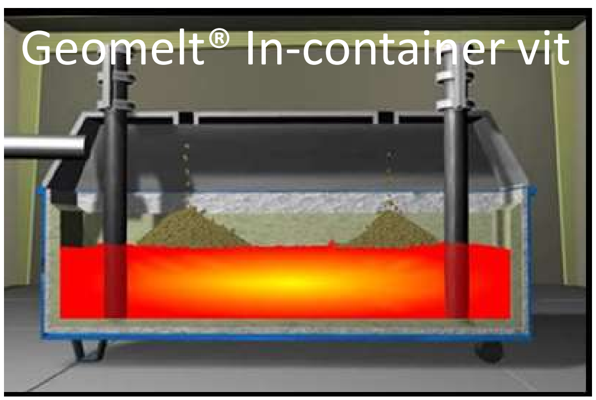


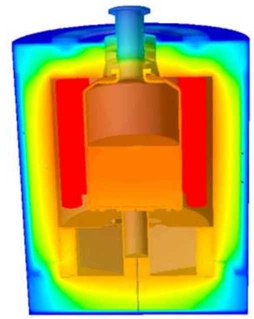


Measuring the monolith created by the planar melt cold test at Los Alamos National Laboratory.

- Courtesy John Vienna, PNNL

In-(can, container) vitrification





CEA in-can liquid waste immobilization

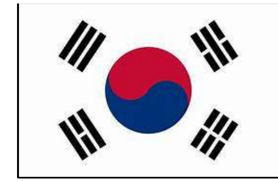
WHEN HETEROGENEOUS IS OKAY

- https://www.nuclearsolutions.veolia.com/en/our-expertise/technologies/our-geomelt-vitrification-technologies-stabilize-waste
- Courtesy S. Schuller, CEA
- Kim et al, PNNL-15131, etc

Immobilizing contaminated soil: In-situ vitrification

MULTIPHASE MATERIAL IS OK!

Case study: South Korea



- ion-exchange resins
- zeolites and other inorganic filters
- dry active waste (which includes contaminated packaging, clothing, and paper products)
- other minor waste streams from the nuclear energy industry

- Sodium aluminoborosilicate glasses (specifically, the SG and DG-2 compositions) were selected
- CCIM process
- Wolsong Low- and Intermediate-Level Radioactive Waste Disposal Facility
- Lead-Boron Polyethylene (classified as LLW) radiation shielding material into a lead borate glass-based form

Case study: Korea

- Nuclear Environment Technology Institute (NETEC), a division of Korea Hydro & Nuclear Power (KHNP) Co.
- Cold crucible induction melter
- Study of electrical and viscosity

Table 1. Constraint of Several Properties of Melts for CCM Process

Glass property	Constraint
Processing temperature	1423 K
Electrical conductivity	0.1~1.0 S/cm
Viscosity	10~100 dPa·s

Table 2. Candidate Glass Compositions for Vitrification of LILW

	AG8W1	AG8W2	IG1W2	DG-2
SiO_2	43.14	41.14	41.12	41.25
Al_2O_3	12.30	12.76	12.52	7.07
Alkali oxides	20.44	24.56	23.19	19.78
Alkaline earth oxides	6.94	2.33	5.66	14.4
Transition metal oxides	6.81	8.37	7.69	4.86
B_2O_3	9.97	10.71	7.46	11.29
Others	0.40	0.13	2.36	1.35

[1]

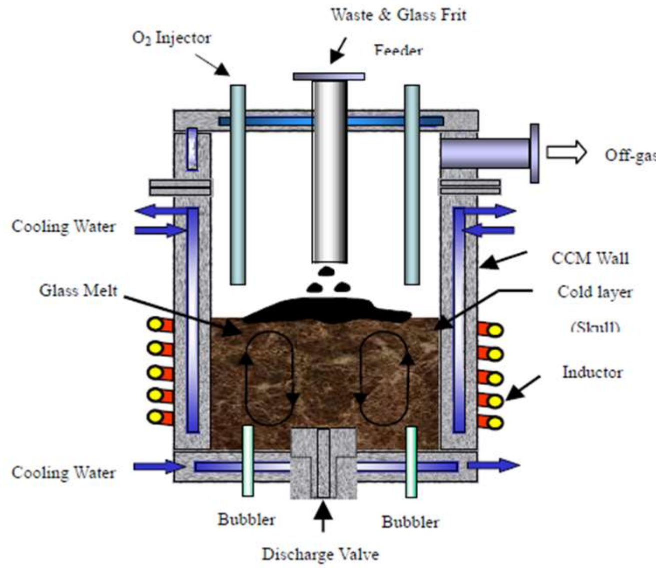


Fig. 2. Cross sectional view of the CCM developed by NETEC.

100-200 kW, 250-270 kHz
20 kg/h

[2]

Table 1 Composition of glass samples (wt%)

Oxide	DG2B	DG2	AG8	AG8W1
Li_2O	6.45	5.55	2.58	1.33
Na_2O	8.83	7.95	23.60	16.50
K_2O	2.20	4.43		1.88
MgO	0.46	1.90		0.64
CaO		10.54		5.25
SrO		0.16		
BaO		0.06		
B_2O_3	15.85	12.54	8.70	10.60
Al_2O_3	9.66	7.26	14.20	10.70
SiO_2	52.96	41.53	44.40	44.10
As_2O_5			1.19	0.72
CoO	1.07	1.04	0.99	1.07
Cs_2O	1.11	0.82	0.95	0.78
CeO_2			0.08	0.18
CuO		0.02		
Fe_2O_3		0.42		1.76
MnO_2		0.18		0.05
NiO		0.12		
P_2O_5		0.79		0.29
PbO		0.04		
TiO_2		3.25		1.26
VO_2		0.11	2.09	1.26
ZnO		0.24		
ZrO_2	1.36	1.04	1.52	0.86
SUM	100	100	100	100

[3]

1. Jung, H.-S., K.-D. Kim, S.-H. Lee, S.-K. Kwon, C.-W. Kim, J.-K. Park, T.-W. Hwang, and Z.-S. Ahn, "Characterization of Glass Melts Containing Simulated Low and Intermediate Level Radioactive Waste," *J. Korean Ceram. Soc*, 43(3), 148-0 (2006).
2. Kim, C.W., J.K. Park, S.W. Shin, T.W. Hwang, J.H. Ha, and M.J. Song, "Vitrification of Simulated LILW Using Induction Cold Crucible Melter Technology," Waste Management 2006 Symposium - WM'06, United States (2006).
3. Kim, C.-W., J.-K. Park, and T.-W. Hwang, "Analysis of Leaching Behavior of Simulated LILW Glasses by Using the MCC-1 Test Method," Journal of Nuclear Science and Technology, 48(7), 1108-1114 (2011).

Case study: Korea

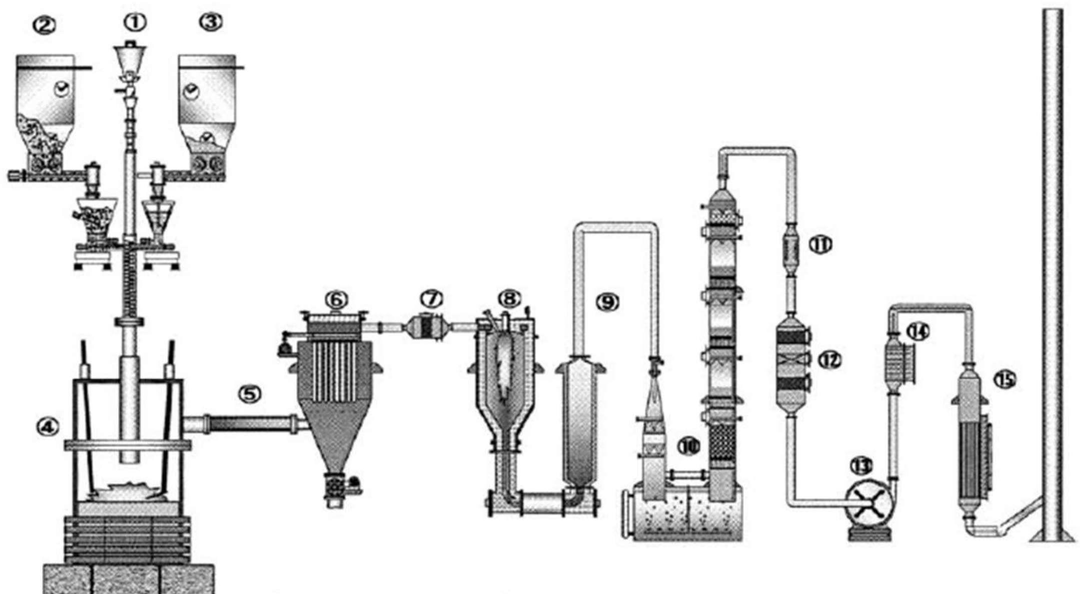


Fig. 1 Schematic diagram of pilot scale vitrification plant composed of CCM and OGTS.

Table 1 The chemical composition of the blended DAW.

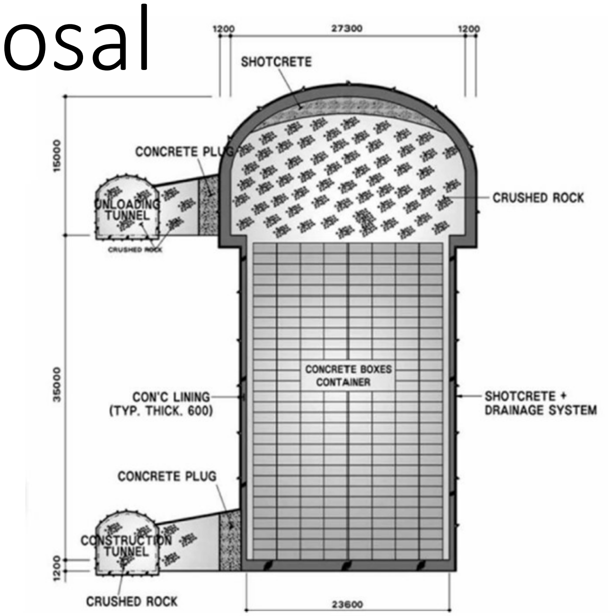
Component	DAW mineral wt%
SiO_2	0.01
B_2O_3	0.18
Na_2O	7.24
CaO	39.09
MgO	17.03
Fe_2O_3	1.39
Al_2O_3	4.27
TiO_2	12.36
K_2O	11.89
MnO_2	0.67
P_2O_5	3.29
ZrO_2	0.03
Others	2.55

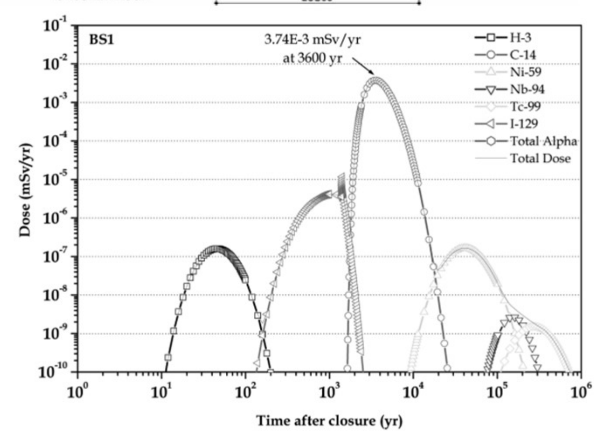
Cold crucible melter (CCM) and off-gas treatment system (OGTS)

Song, M.-J. and C.-W. Kim, "Vitrification of Combustible Dry Active Waste Generated from Korean Nuclear Power Plants," *Japanese Journal of Health Physics*, 39(3), 250-256 (2004).

Backup – Republic of Korea: Disposal

- Wolsong Low- and Intermediate-Level Radioactive Waste Disposal Facility
  - Shallow (~100m) geologic disposal silo-based site with engineered barrier
  - 100,000 “barrel” capacity, up to 800,000 with further construction
  - Fuel arrived 2010, initial construction completed 2015
  - Consent based siting approach (after numerous previous failures)
  - Spurred by constriction of storage space at nuclear plants
- Spent fuel and other high level waste currently stored at reactor sites
  - Interim facility then deep geologic repository planned, siting not complete
  - Variety of waste steams - direct canister storage, borosilicate, and iron phosphate glasses investigated for immobilization





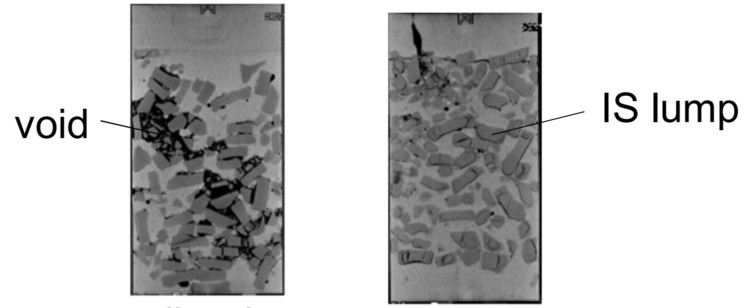
Park, Jin-Beak, et al. “Wolsong Low- and Intermediate-Level Radioactive Waste Disposal Center: Progress and Challenges.” *Nuclear Engineering and Technology*, vol. 41, no. 4, May 2009, pp. 477–92.
Lee, Cheong Won, et al. “Local Atomic Structure of Uranium Ions and Dissolution Behavior of Iron Phosphate Glass Hosts to Immobilize Spent Nuclear Fuel.” *Journal of Radioanalytical and Nuclear Chemistry*, vol. 328, no. 2, May 2021, pp. 701–06.
Hwang, Yongsoo, and Ian Miller. “Integrated Model of Korean Spent Fuel and High Level Waste Disposal Options.” *ASME 2009 12th International Conference on Environmental Remediation and Radioactive Waste Management, Volume 1*, ASMEDC, 2009, pp. 733–40.

Cement form

Homogeneous waste form and Filled waste form were developed using ordinary Portland cement (OPC).

- ✓ Homogeneous waste form is a mixture of OPC, wastes (slurries) and water. Suitable mixing ratio of each component was examined. 20L-scale waste form was successfully demonstrated for carbonate slurry (CS) and iron co-precipitation slurries (IS). In 200L-scale test, fast solidification phenomenon was observed. The reason will be determined in 2023-2024.
- ✓ Filled waste form : squeezed and dewatered slurry lump was put in a container, and OPC was poured with vibration to fill the interspaces.

20L-scale homogeneous waste form



0.2L-scale filled waste form for IS

Ref: HP of Management Office for the Project of Decommissioning, Contaminated Water and Treated Water Management; https://en.dccc-program.jp/4810

AAM

Waste form using AAM (Alkali activated Material) was produced by condensation polymerization of alkali silicate solution (liquid glass) with metakaolin, slug (BFS) and slurry wastes.

- ✓ Homogeneous waste form : 20L and 200L-scale waste forms were successfully produced.
- ✓ Filled waste form : Due to higher fluidity of AAM than OPC, 20L-scale dense waste form could produce without vibration.

Ref: HP of Management Office for the Project of Decommissioning, Contaminated Water and Treated Water Management; https://en.dccc-program.jp/4810

Pipes for core sampling

200L-scale homogeneous waste form (CS: 30wt%)

20L-scale filled waste form (IS lump: 37wt%)

Thermal Decomposition

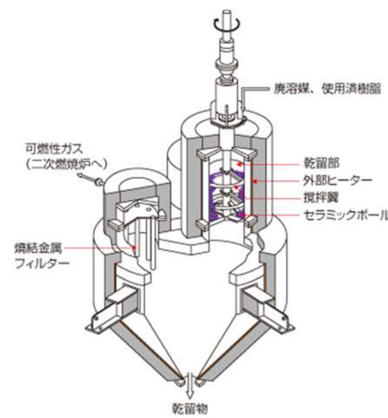
To reduce the waste volume and risk of solution leakage during storing, thermal decomposition of the wastes was investigated. Further treatment of the sintered waste will be required to make a monolithic waste form.

- ✓ Decomposition behavior under several atmosphere (inert, water vapor, etc.) is determined by TG/DTA.
- ✓ Engineering scale thermal decomposition device (1dry-kg/h) was developed, and its performance was tested.

Ref: HP of TEPCO:
https://www.tepco.co.jp/decommission/information/committee/roadmap_progress/2023-j.html

Initial resin　　After sintered

Thermal decomposition of simulated spent resin

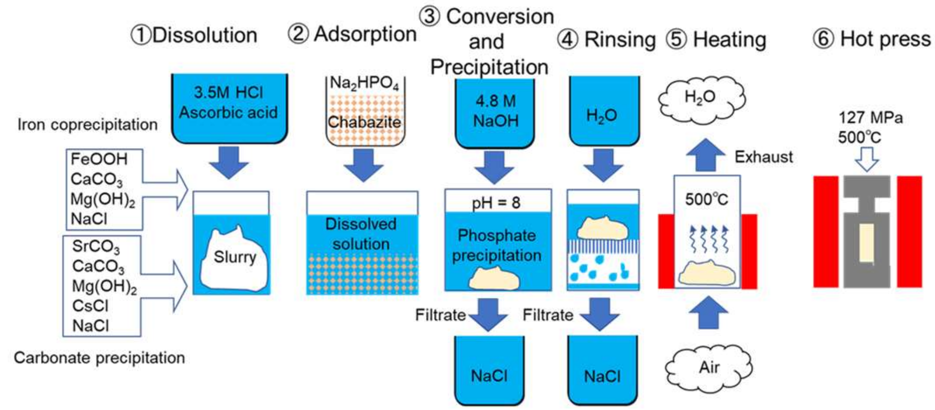


Ball-type thermal decomposer
(source: HP of NGK)

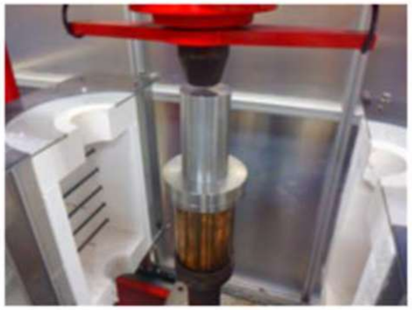
Apatite form

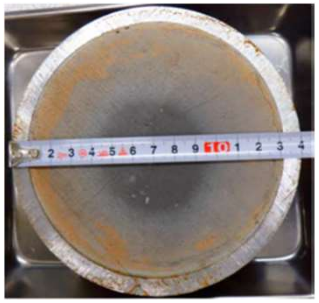
Apatite waste form containing CS and IS was developed. Apatite has high chemical durability and is synthesized around 500˚C

- ✓ Suitable formulation and synthesis procedure to form homogeneous apatite was surveyed.
- ✓ Up to 1kg-scale monolithic form was produced by press heating. Waste loading of CS was 48mol% which was nearly twice as much as that of the glass waste.



Synthesis procedure of apatite waste form

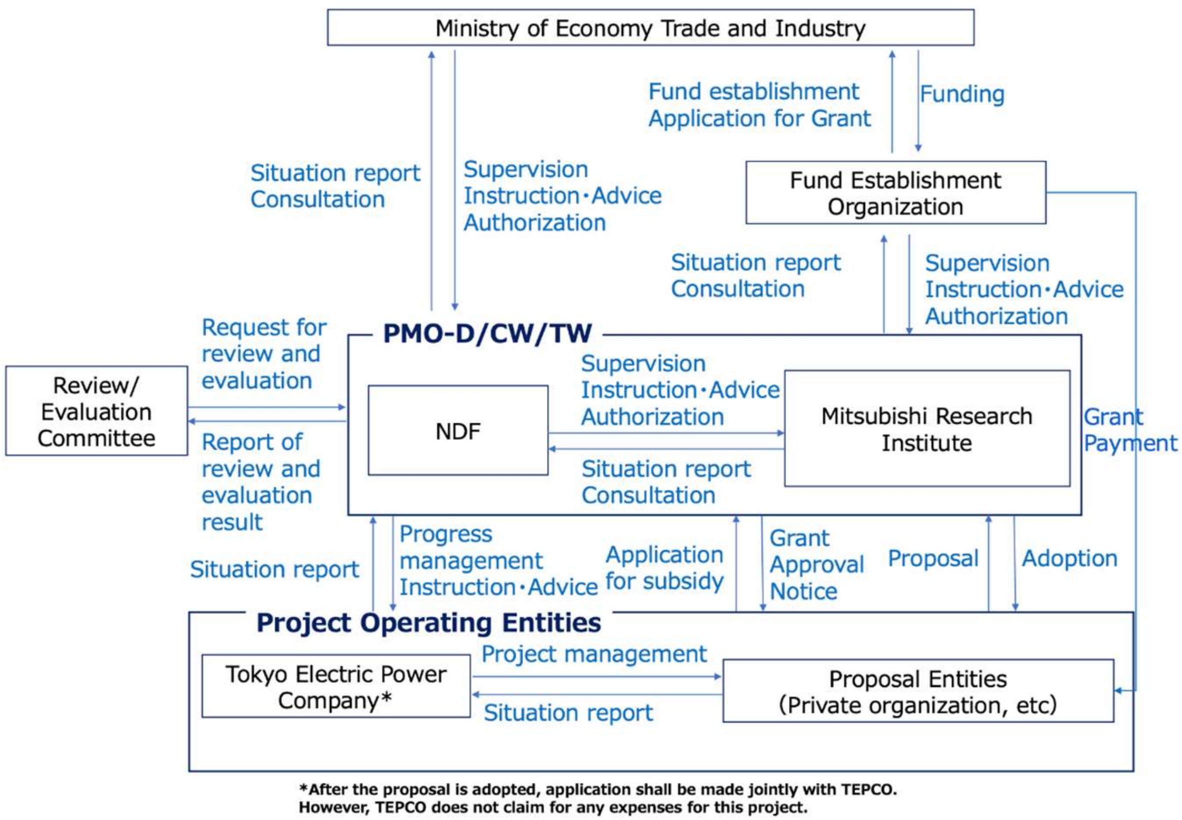




Hot press equipment and produced waste

Ref: JAEA-Review 2022-076 (2020).
Kanagawa et al., Proc. FDR2022-1002, Fukushima, Japan (2022).

R&D Relation Map



Case study: Japan

- Fused Glass Technology
  - In development at IHI
  - Uses silica within waste to reduce glass additives
  - Cold Crucible Induction Technology
  - Designed to dispose of unique waste streams from Fukushima
    - Rubble, trees
    - Effluent from secondary wastes
  - Waste loading, 20 - 65 wt%
- In-Can Vitrification Technology
  - Technologies in development: GeoMelt®; DEM&MELT®

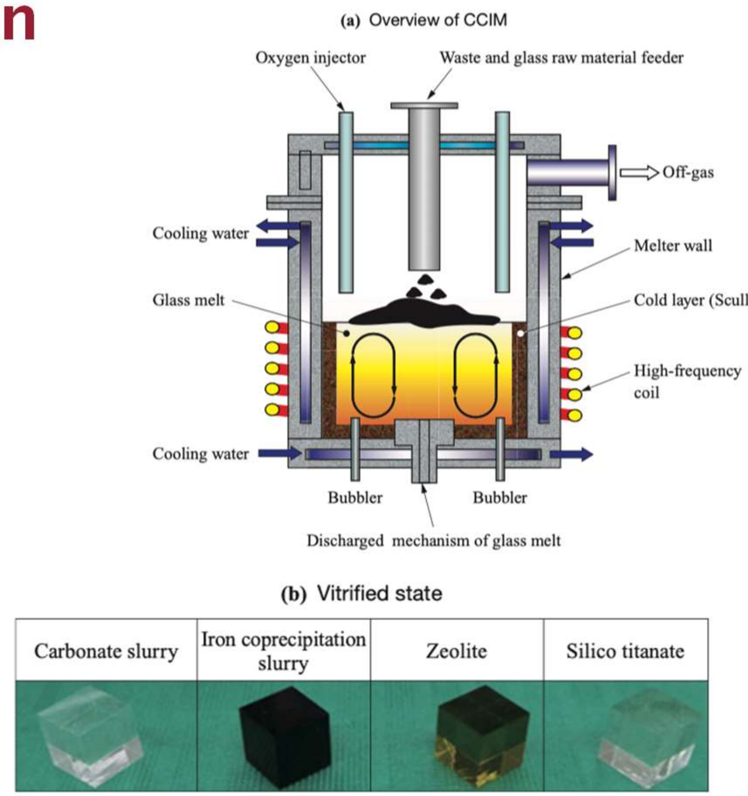


Fig. 3 Examples from the results of the review of glass compositions

IHI Review Vol. 53 No. 1 2020

Case study: Japan

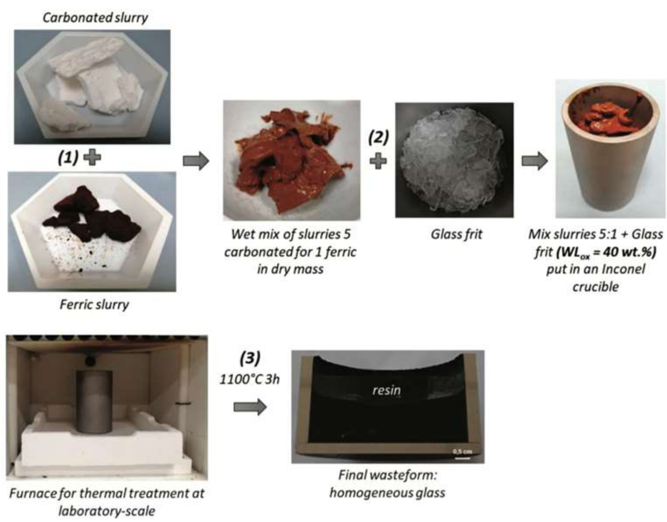
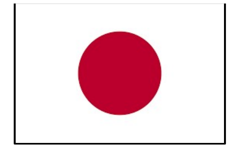


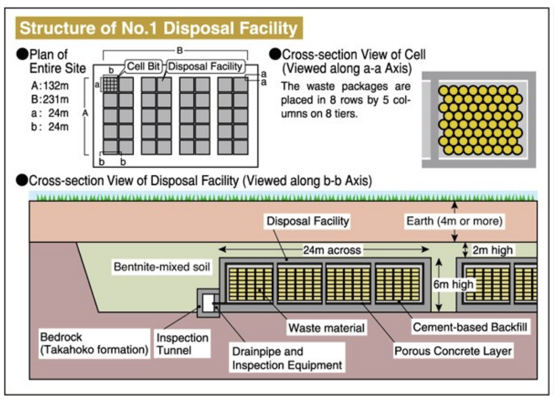
Fig. 2. (1) Mixture of the two slurries, (2) mixture of mixed slurries with the glass frit placed in a crucible (3) thermal treatment in a muffle furnace and crucible cut in the height direction to see the material. An epoxy resin is poured after the thermal treatment to maintain the material during cutting.

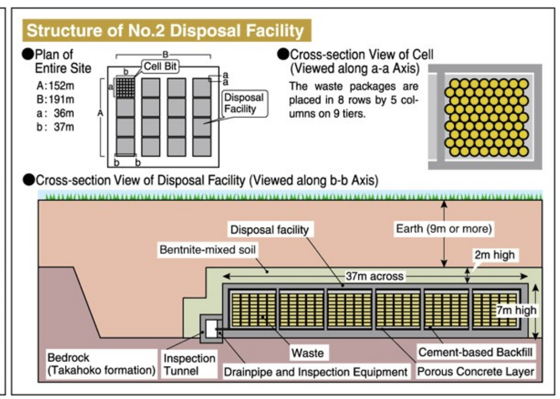
Table 1. Composition in wt.% of mixed ALPS slurries surrogates.

Dry composition (wt.%)	Surrogate ALPS slurry mix (5:1)
$CaCO_3$	47.30
$Mg(OH)_2$	29.47
Na_2CO_3	3.52
SiO_2	2.98
$SrCO_3$	1.90
$FeO(OH)\cdot H_2O$	11.97
Al_2O_3	0.94
$Co(OH)_2$	0.50
$Ti(OH)_2$	0.45
$Zn(OH)_2$	0.38
$Ca(OH)_2$	0.32
Cl	0.26



Low-level Waste Disposal





JNFL has been approved the operation of the disposal facilities with a total capacity of 80,000 m³ (400,000 of 200-liter waste drums)

https://www.jnfl.co.jp/en/business/llw/

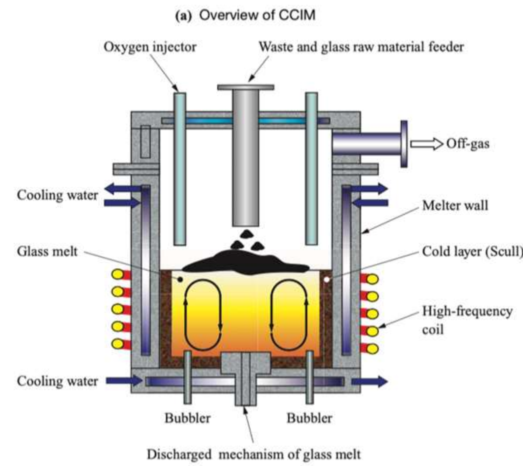
Japan

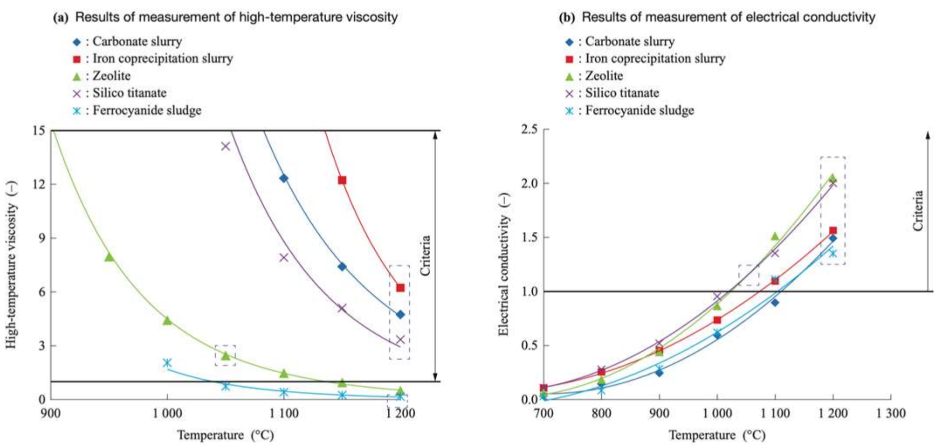
Radioactive Waste Disposition

Jonathan Evarts

Fused Glass Technology

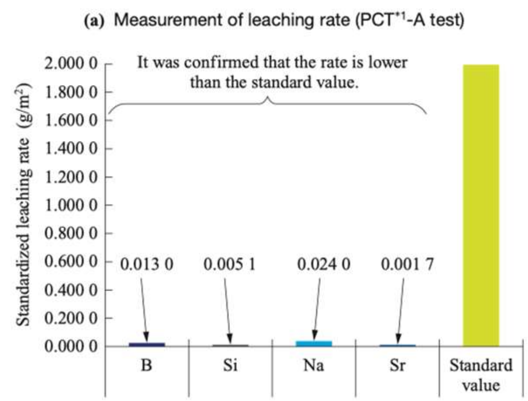
- In development at IHI
- Uses silica within waste to reduce glass additives
- Cold Crucible Induction Technology
- Designed to dispose of unique waste streams from Fukushima
    - Rubble, trees
    - Effluent from secondary wastes
- Waste loading, 20 - 65 wt%





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

Fig. 4 Result of evaluation of glass properties



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

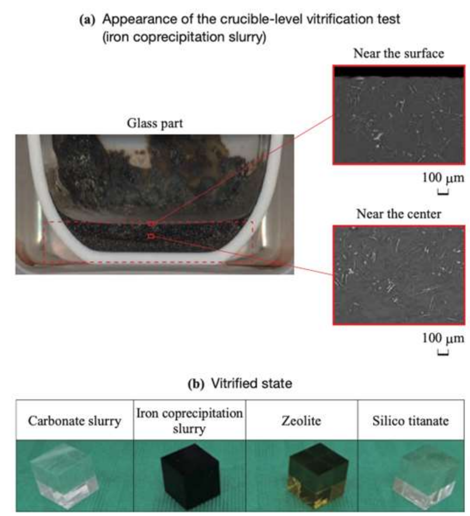


Fig. 3 Examples from the results of the review of glass compositions

IHI Review Vol. 53 No. 1 2020

In-Can Vitrification Technology

Technologies in development

- GeoMelt®
- DEM&MELT®

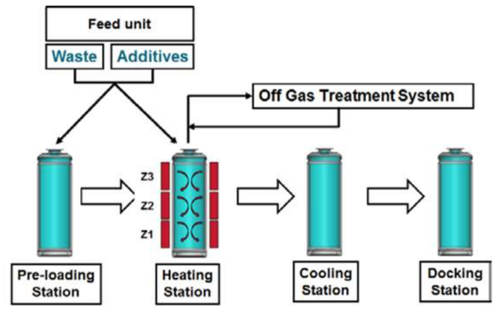


Fig. 5. Melt 2 Glass Cross-Section

2020 Finucane, GeoMelt

Fig. 10. Melt 2 Bulk Glass

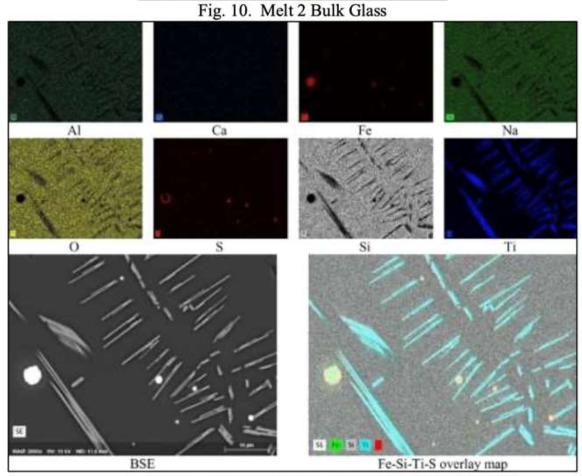


Fig. 11. SEM-EDS Maps of Melt 2 Glass

2020 Finucane, GeoMelt

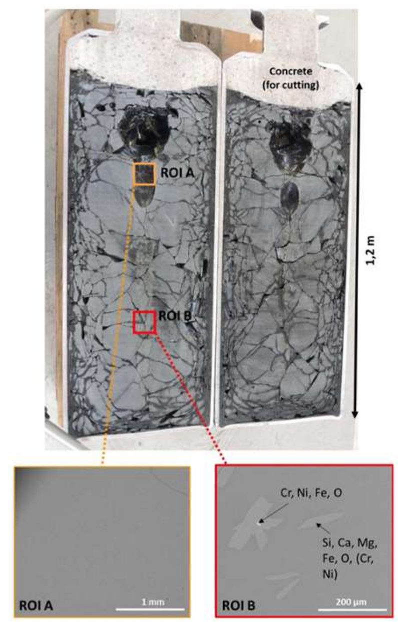


Fig. 8. Half-cut container obtained after vitrification of ALPS

2022 Vernay, DEM&MELT

Cementation and Geopolymer

Timeline of Radioactive Waste Disposition Regulations

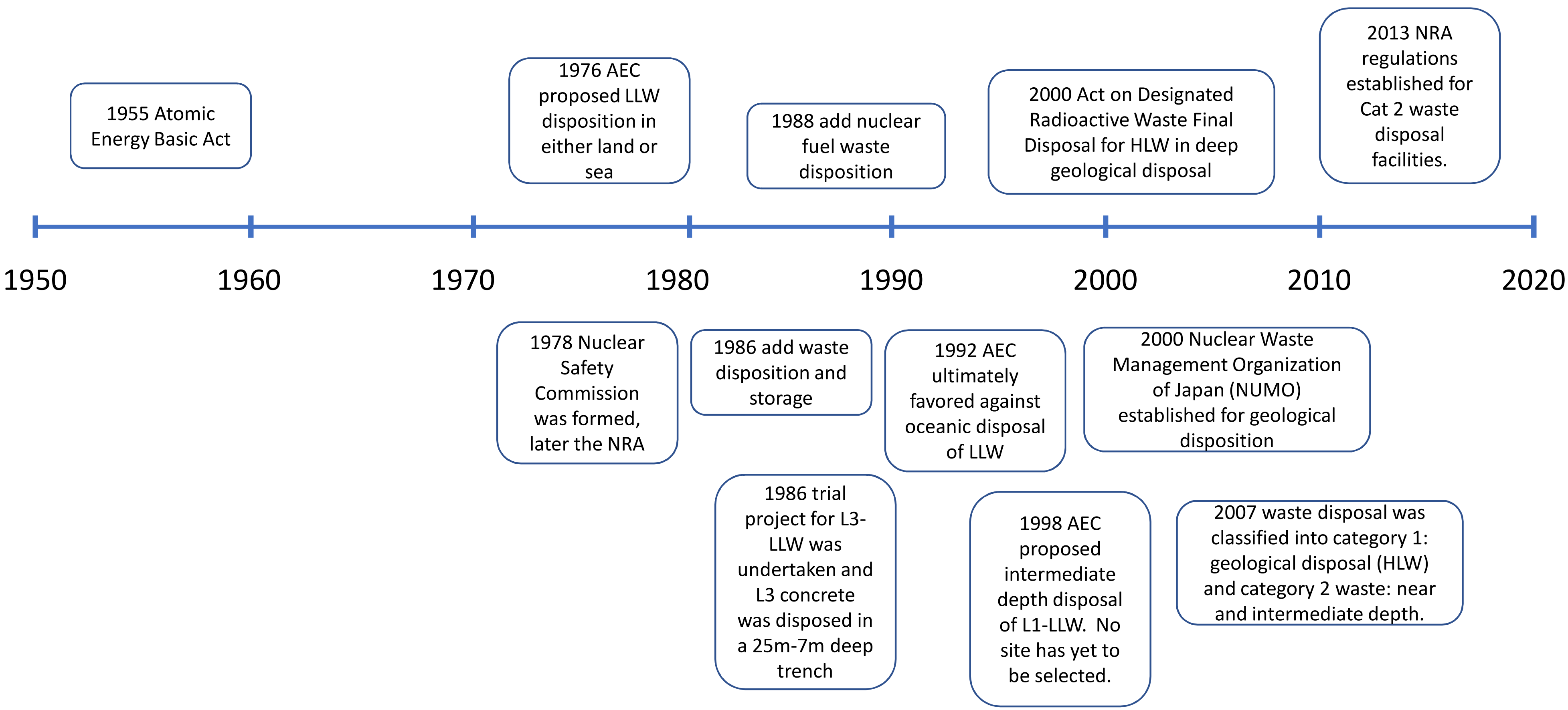
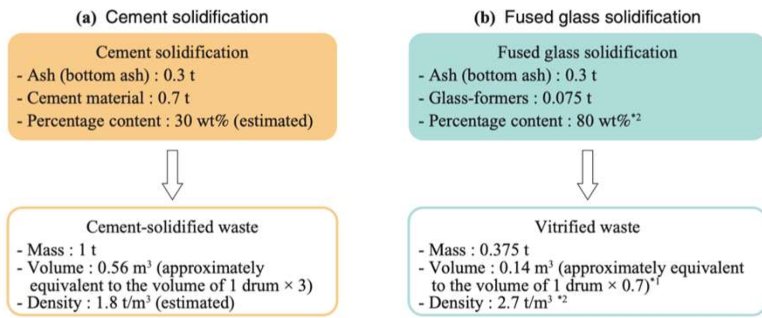


Table 1 Comparison of vitrification processes

Item	Vitrification technology		Melt solidification technology
	Vitrification (conventional)	Fused glass solidification	
Brief description	Method in which vitrification is performed by adding a predetermined glass raw material (e.g., borosilicate glass) to waste	Method in which vitrification is performed by using an component of the waste (e.g., SiO_2) or the like as a glass-formers, thereby minimizing the amount of additive	Method in which waste is melted and solidified as slag
	Waste + Glass raw material → Melting → Vitrified waste	Waste + Additive → Melting → Vitrified waste	Waste → Melting → Melt solidification
Volume reduction	△	○	◎
	Volume reduction is low because a constant waste loading factor is maintained by adding a glass raw material.	Volume reduction is relatively high because the amount of additive is minimized to the extent that stability can still be maintained. However, volume reduction varies depending on the waste composition.	Volume reduction is high because no additive is used.
Operability	◎	○	△
	Heating and pouring conditions are fixed (do not vary among melting operations) because the properties of fused glass at high temperature can be controlled to within a fixed range. In cases of vitrification for high-level liquid waste, however, operation is affected by the control of noble metals.	Operation without substantial fluctuations in heating and pouring conditions is ensured because the properties of fused glass at high temperature can be controlled to within a predetermined range.	Heating and pouring conditions must be specified per melting operation because the properties at high temperature vary depending on the waste composition.
Stability of solidified waste	◎	○	△
	Excellent stability is exhibited because the post-vitrification composition is constantly controlled to within a fixed range.	Relatively high stability is exhibited because the amount of additive is minimized to the extent that stability can still be maintained. However, stability varies depending on the waste composition.	Stability is variable because the slag composition depends on the waste composition.

(Notes) 1. Characteristic of low-level wastes
Many low-level wastes contain a glass-formers such as SiO_2 or Al_2O_2.
2. Technology evaluation results
◎ : Excellent, ○ : Good, △ : Acceptable



(Notes) *1 : A shift from cement solidification to fused glass solidification resulted in the volume being reduced to 1/4.
*2 : This value was set based on the results for FY2015.

Fig. 3 Comparison between vitrification and cement solidification

Table 2 Features of waste from nuclear facilities

Target waste	Purpose I	Purpose II	Characteristics	Solves problem: Glass composition development	Solves problem: Operation control development
Ion exchange resin	○		- High dose - Contains moisture and organic matter.	◎	◎
Low-level radioactive concentrate liquid waste, radioactive liquid waste from decontamination (Liquid waste with a high sodium nitrate concentration)	○	○	- High sodium nitrate concentration	◎	◎
Low-level radioactive concentrate liquid waste (Phosphate liquid waste)		○	- Contains phosphate ions and a small amount of nitric acid.	◎	◎
Boric acid liquid waste		○	- Contains B, Na, and moisture.	◎	—
Ion exchange resin eluent		○	- High dose - High S concentration	◎	◎
Ash (including fly ash)		○	- High dose - Substantial composition variation	◎	—
HEPA filter, Metal (Al) plate, etc.	○		- Contains metal (Al).	—	◎
Sludge, etc.		○	- High Fe concentration	◎	—
Asbestos	○		- Chemically stable. Hazardous form.	—	◎
Toxic metal waste	○		- Contains heavy metals, such as lead and mercury.	◎	◎
Abrasive paper		○	- Made of polypropylene.	—	◎
Liquid filter	○		- Contains organic matter.	—	◎
Abrasive for blasting		○	- Al_2O_3 (main component), Si, Fe, etc.	◎	—
Activated coal		○	- Main component: C	—	◎

(Notes) Objective I : To stabilize waste that is difficult to treat using the currently considered treatment technology
Objective II: To outperform the currently considered treatment technology in terms of reducing the volume of waste
(shaded box) : Waste to be tested in the basic research programs
○ : Target waste suited to the objective
◎ : Technology development is required to solve problems.

Table 3 Evaluation of the applicability of vitrification technology in treating low-level waste

Low-level wastes: Name	Low-level wastes: Main component	Reagent added	Vitrification: Waste loading factor (wt%)	Vitrification: Melting temperature (°C)	High temperature viscosity	Leaching rate*1
Ion exchange resin	Fe	$SiO_2 - Na_2O$	40→35	1 100	○	△
		P_2O_5	40	1 100	—	○
Ash (Bottom ash)	Si/Ca/Al	$B_2O_3 - Li_2O$	75 or more	1 100	○	○
Low-level radioactive concentrate liquid waste (Sodium nitrate liquid waste)	Na	SiO_2	40	1 100	—	—
		$SiO_2 - B_2O_3$	40	1 100	×	×
		$SiO_2 - B_2O_3 - Al_2O_3 - CaO$	30	1 100	○	△

(Notes) *1 : PCT (Product Consistency Test) results
○ : No problem, △ : Slight deviation from the standard value,
× : Considerable deviation from the standard value, — : No data (Untested)

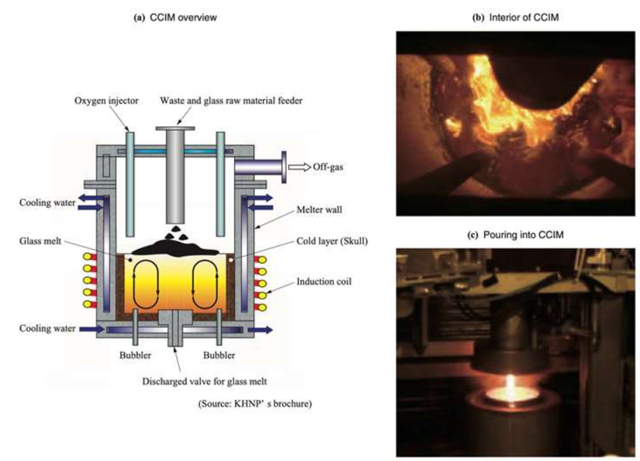
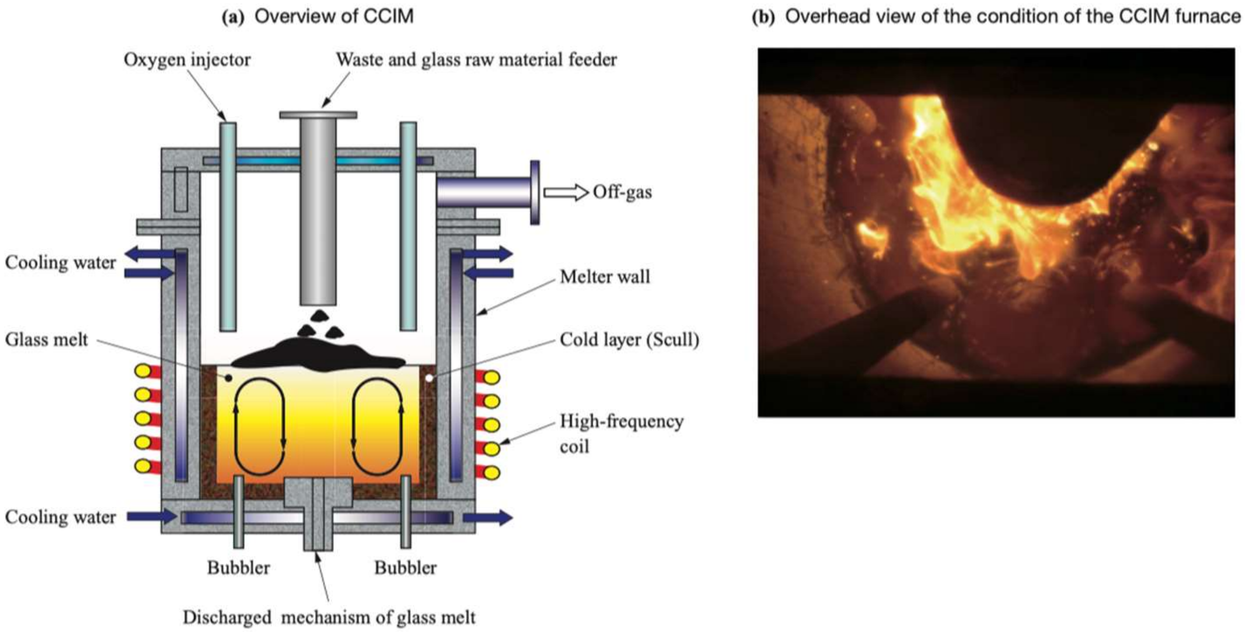
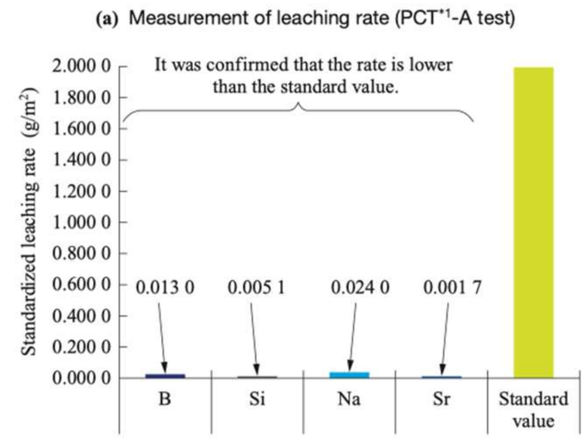


Fig. 4 Appearance of a cold crucible induction melter (CCIM)



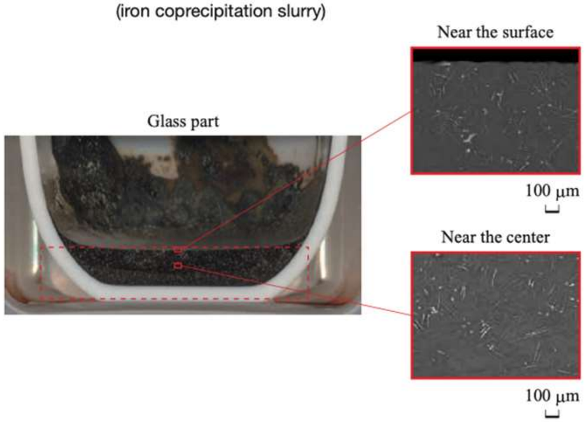
(Source : KHNP's brochure)

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



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

(a) Appearance of the crucible-level vitrification test (iron coprecipitation slurry)



(b) Vitrified state

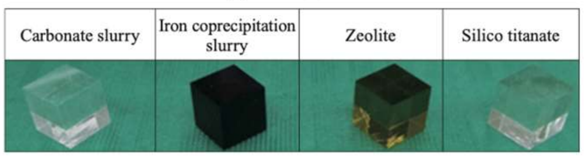
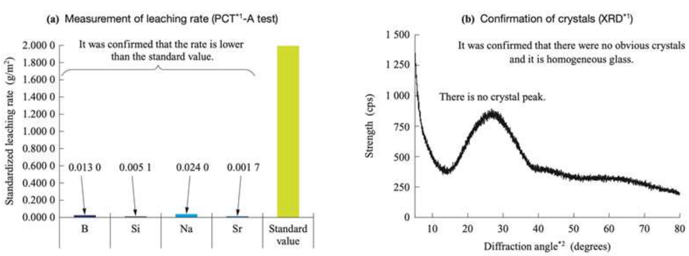


Table 3 Results of this review of glass compositions

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

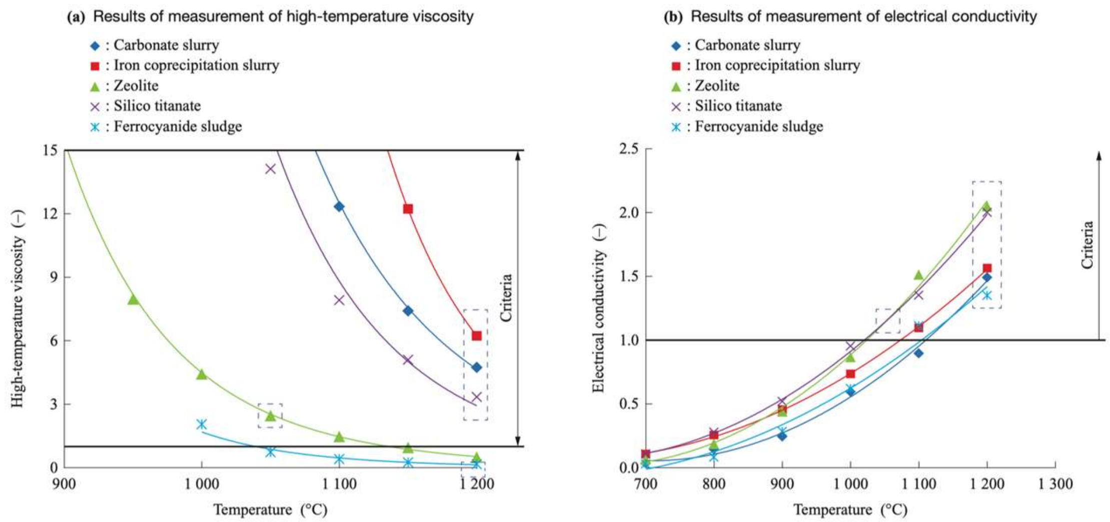
(Notes) *1 : In the case of 50 wt% water content.
*2 : The waste loading rates are the values obtained in this development.
*3 : Weight reduction rate = Weight of vitrified waste / Weight of waste. For this calculation, the density of the vitrified waste is the value obtained in this development. Bulk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



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

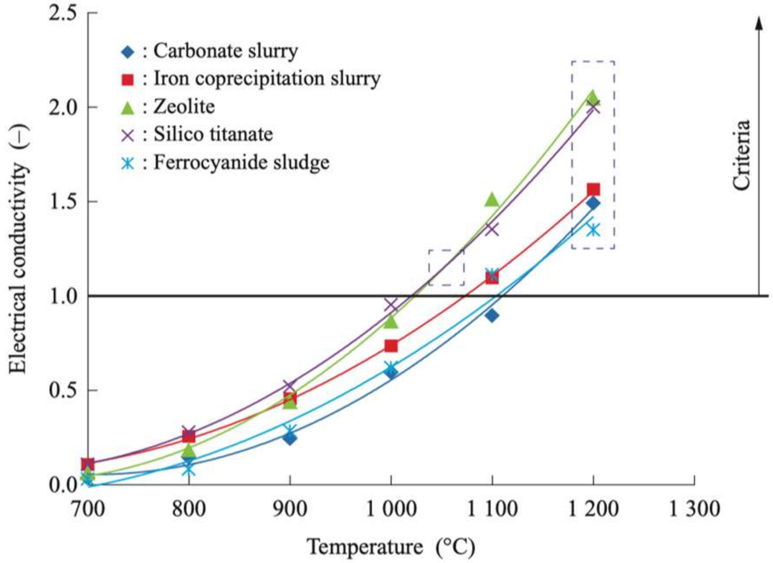
(Notes) *1 : X-Ray Diffraction
*2 : 2θ, angle between the incident beam and diffraction beam

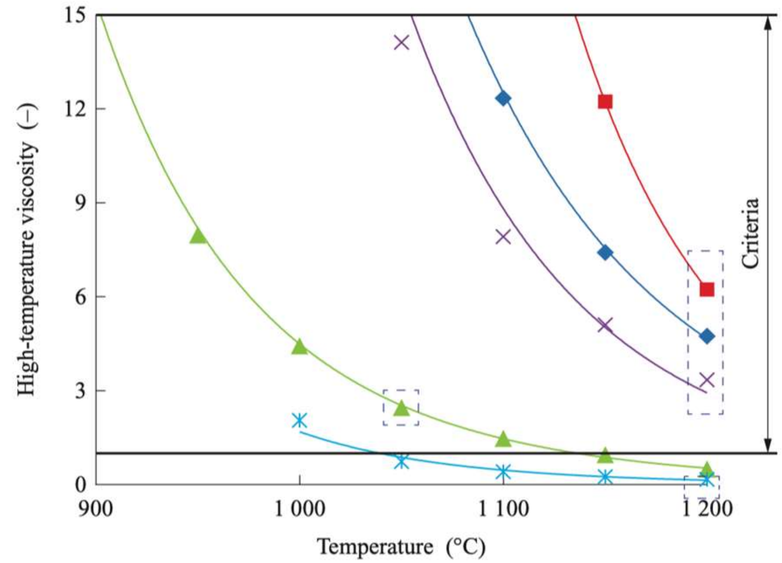
Fig. 5 Result example of demonstration test

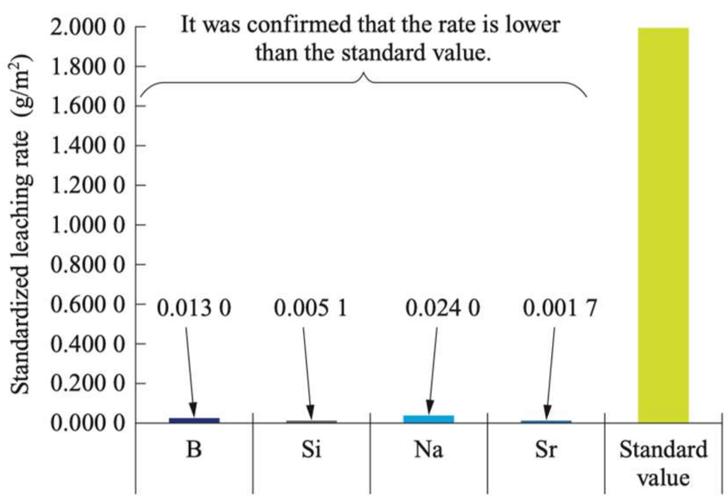


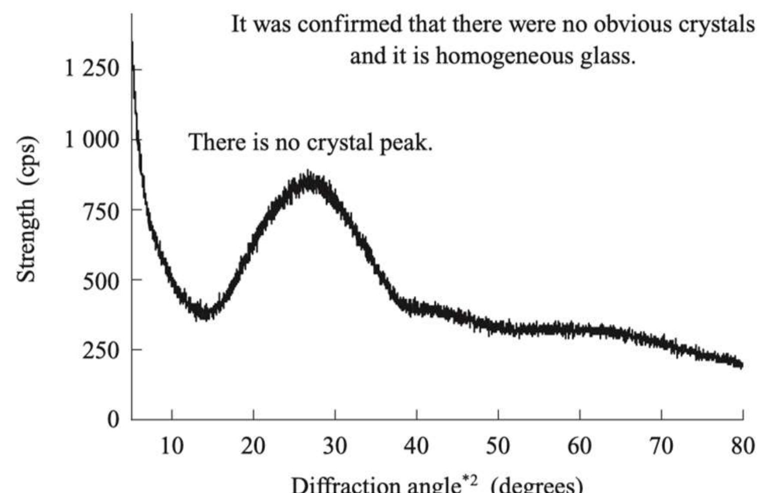
(Note) The blue-dashed portions of the figure indicate the temperatures (melting temperatures) of evaluated high-temperature physical properties.

Fig. 4 Result of evaluation of glass properties









Applicability of Vitrification Technology for Secondary Waste Generated from Contaminated Water Treatment Systems at Fukushima Daiichi Nuclear Power Station, IHI Review Vol. 53 No. 1 2020

Table 2 Features of waste from nuclear facilities

No.	Target waste	Purpose		Characteristics	Solves problem	
		I	II		Glass composition development	Operation control development
1	Ion exchange resin	○		- High dose - Contains moisture and organic matter.	◎	◎
2	Low-level radioactive concentrate liquid waste, radioactive liquid waste from decontamination (Liquid waste with a high sodium nitrate concentration)	○	○	- High sodium nitrate concentration	◎	◎
3	Low-level radioactive concentrate liquid waste (Phosphate liquid waste)		○	- Contains phosphate ions and a small amount of nitric acid.	◎	◎
4	Boric acid liquid waste		○	- Contains B, Na, and moisture.	◎	—
5	Ion exchange resin eluent		○	- High dose - High S concentration	◎	◎
6	Ash (including fly ash)		○	- High dose - Substantial composition variation	◎	—
7	HEPA filter, Metal (Al) plate, etc.	○		- Contains metal (Al).	—	◎
8	Sludge, etc.		○	- High Fe concentration	◎	—
9	Asbestos	○		- Chemically stable. Hazardous form.	—	◎
10	Toxic metal waste	○		- Contains heavy metals, such as lead and mercury.	◎	◎
11	Abrasive paper		○	- Made of polypropylene.	—	◎
12	Liquid filter	○		- Contains organic matter.	—	◎
13	Abrasive for blasting		○	- Al_2O_3 (main component), Si, Fe, etc.	◎	—
14	Activated coal		○	- Main component: C	—	◎

(Notes) Objective I : To stabilize waste that is difficult to treat using the currently considered treatment technology
Objective II: To outperform the currently considered treatment technology in terms of reducing the volume of waste
▭ : Waste to be tested in the basic research programs
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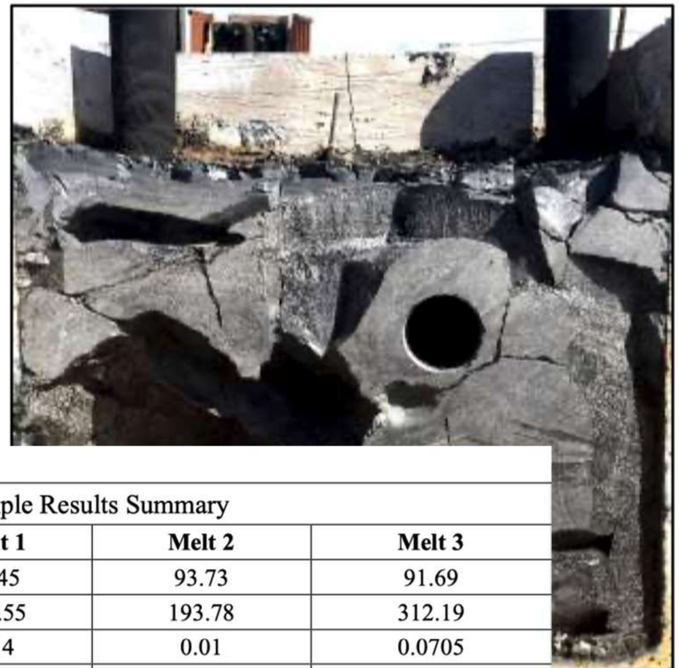

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Fig. 7. Melt 3 Glass Cross-Section

TABLE I. Process Sample Results Summary				
Basis	**Mass (g)**	**Melt 1**	**Melt 2**	**Melt 3**
Feed Samples	Cs in Feed	86.45	93.73	91.69
	Sr in Feed	166.55	193.78	312.19
Wipe Samples	Cs on Hood	0.14	0.01	0.0705
	Sr on Hood	0.004	0.0003	0.0001
Refractory Samples	Cs in Cast Refractory	0.005	0.001	0.00
	Sr in Cast Refractory	0.00	0.00	0.00
Wipe Samples	Cs in Piping	0.002	0.022	0.051
	Sr in Piping	0.03	0.012	0.003
Particulate Samples	Cs in Baghouse	1.84	0.01	0.0082
	Sr in Baghouse	0.06	0.0006	0.032
Filter Paper Samples	Cs in HEPA	0.01	0.20	0.04
	Sr in HEPA	0.007	0.02	0.06

2020 Finucane, GeoMelt

Fig. 10. Melt 2 Bulk Glass

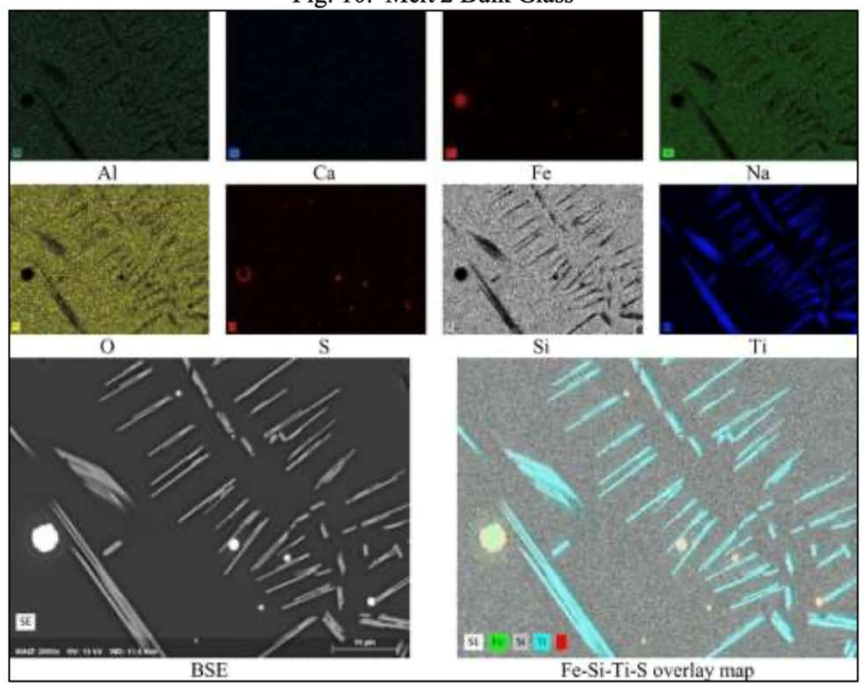

Fig. 11. SEM-EDS Maps of Melt 2 Glass

TABLE III. Post-Melt Cesium Distribution (wt%)			
Location	**Melt 1**	**Melt 2**	**Melt 3**
Glass	91.46	99.30	93.76
Hood and Refractory	0.62	0.03	2.59
Off-Gas Pipe	0.01		
Baghouse	7.87		
HEPA	0.04		

TABLE VII. Engineering-Scale Melt Test Metrics			
Metric	**Melt 1**	**Melt 2**	**Melt 3**
Total Material Processed	221.00 kg	212.00 kg	240.00 kg
Energy	219.82 kWh	232.67 kWh	336.06 kWh
Melt Duration	13.58 hours	16.75 hours	15.00 hours
Processing Rate	16.29 kg/hour	12.66 kg/hour	16.00 kg/hr
Processing Efficiency	0.99 kWh/kg	1.10 kWh/kg	1.40 kWh/kg
Mass Loss	20%	27%	29%
Volume Reduction	74%	77%	79%

TABLE V. MCC-1 Alteration Rates of Engin		
Experiment	**NL_{Na} at 28 days (g/m^2)**	
ES-1	6.85	
ES-2	6.20	1.4×10^{-1}
ES-3	4.96	3.7×10^{-2}
Reference Glasses		
	NL_{Na} at 28 days (g/m^2)	**r_{Na} ($g/m^2/d$) (14 to 28 days)**
EA Glass	34.97	1.4
P0797	11.46	1.3×10^{-1}
P0798	9.59	1.4×10^{-1}

2020 Finucane, GeoMelt

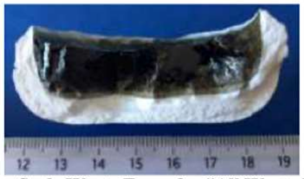

Fig. 3 Laboratory Scale Waste Form for "All Waste Mixing" Assembly

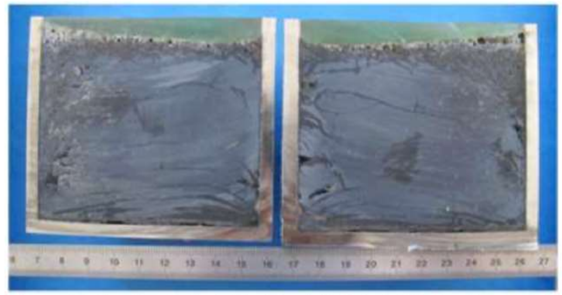

Fig. 6 Visual Aspect of the Bench Scale Test for "All Waste Mixing Assembly" after Half Cut

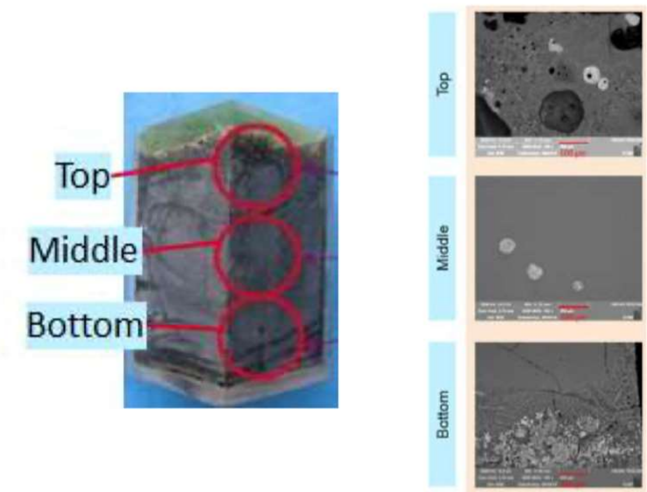

Fig. 7 SEM Exam of the Bench Scale Test for "All Waste Mixing Assembly"

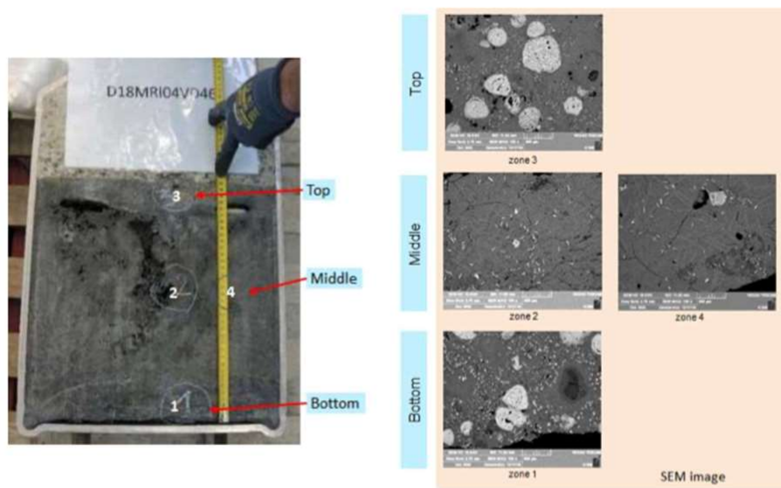

Fig. 9 Can after Cut and SEM Exams

2020 Didierlaurent, DEM&MELT

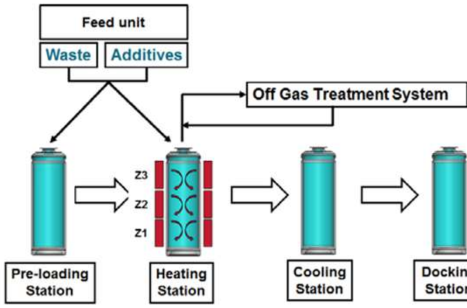

Fig. 1 Dem&Melt In-Can Vitrification Process functions diagram

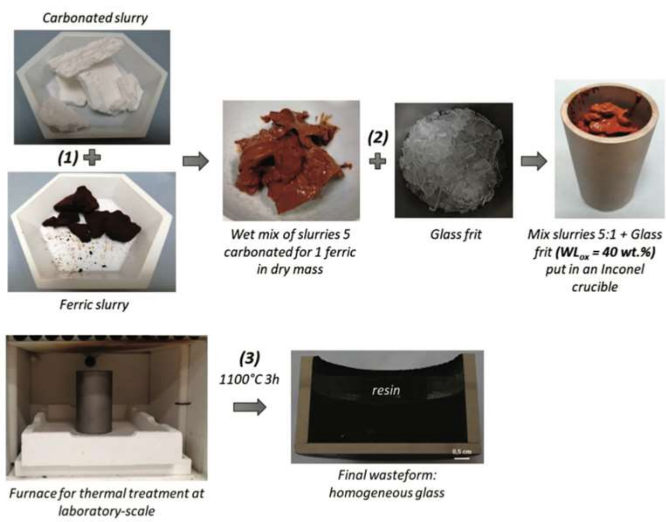

Fig. 2. (1) Mixture of the two slurries, (2) mixture of mixed slurries with the glass frit placed in a crucible (3) thermal treatment in a muffle furnace and crucible cut in the height direction to see the material. An epoxy resin is poured after the thermal treatment to maintain the material during cutting.

Table 1. Composition in wt.% of mixed ALPS slurries surrogates.

Dry composition (wt.%)	Surrogate ALPS slurry mix (5:1)
$CaCO_3$	47.30
$Mg(OH)_2$	29.47
Na_2CO_3	3.52
SiO_2	2.98
$SrCO_3$	1.90
$FeO(OH){\cdot}H_2O$	11.97
Al_2O_3	0.94
$Co(OH)_2$	0.50
$Ti(OH)_2$	0.45
$Zn(OH)_2$	0.38
$Ca(OH)_2$	0.32
Cl	0.26

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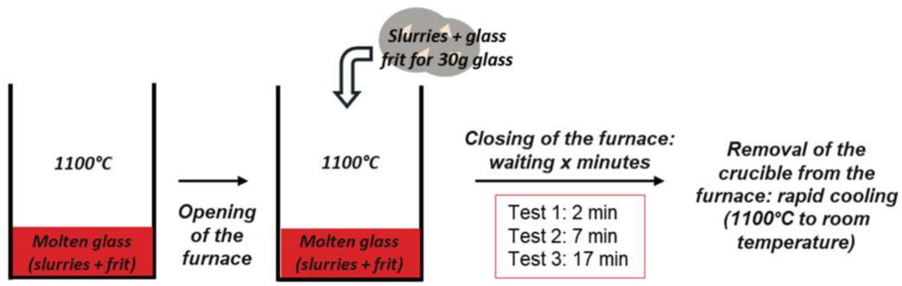

Fig. 5. Principle of the reactivity tests at high temperature.

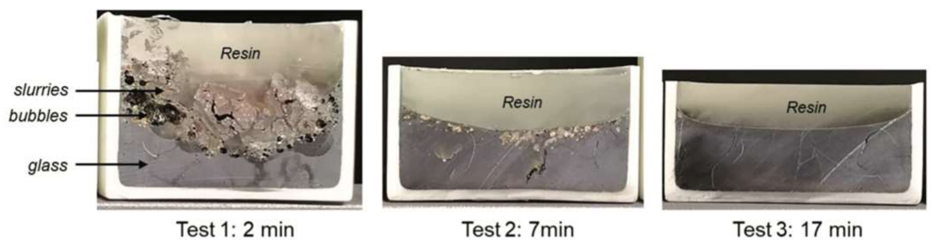

Fig. 6. Half-cut crucibles after the tests to see the evolution of the material with the time of digestion.

Fig. 8. Half-cut container obtained after vitrification of ALPS

2022 Vernay, DEM&MELT

(a)

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$Ti(OH)_2$	0.45
$Zn(OH)_2$	0.38
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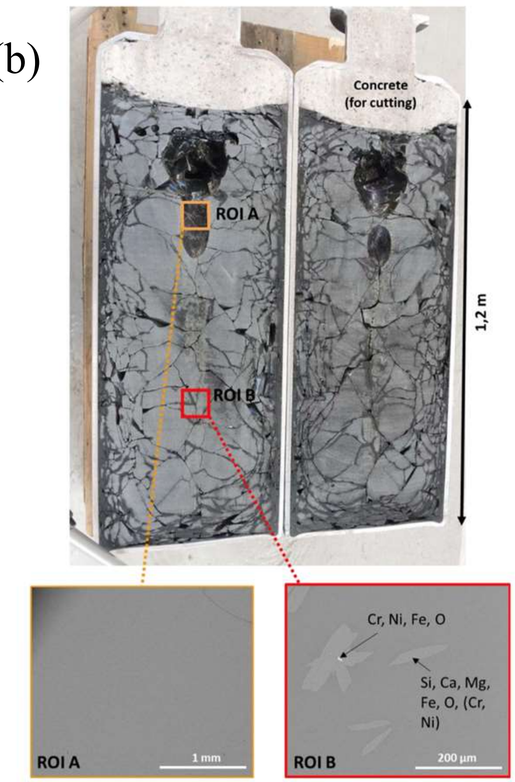
Cl	0.26

(b)



2022 Vernay, DEM&MELT

Other French Case Studies

orano

ECM

Molten glass coating for ashes conditioning

H2020 PREDIS Pre-disposal management of radioactive waste Project

European Union's Horizon 2020 research and innovation programme under grant agreement No 945098 (2020-2024)

Partners: 27 European partners

Objective : WP6 is dedicated to the development/conditioning of organic solid waste

Case study: **Ashes**

Challenge: Cf poster Hélène

See Hélène Nonnet posters on Monday

Vitrification of waste arising from dismantling operations using DEM&MELT technology

PROVIDENCE project (BPI France relance 2030)

Partners: Orano, CEA and ECMT

Objective: Optimize the DEM&MELT process to demonstrate its ability to treat and condition a large inventory of radioactive wastes

Case study: **Sulfated STE2** (Effluent Treatment Plant) co-precipitation sludge

Challenge: Formulate a low-temperature coating matrix to limit volatilization of certain elements (Cs, S)

See Aliénor Vernay posters on Monday

In-Can vitrification of spent mineral sorbents using DEM&MELT technology

See Caroline Michel posters on Monday

Molten glass coating for ashes conditioning

See Hélène Nonnet poster's on Monday

H2020 PREDIS Pre-disposal management of radioactive waste Project

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Case study: **Ashes**

Challenge: Cf poster Hélène

The utilisation of molten glass coating for the safe, efficient densification of loose simulant radioactive ashes has been investigated. As part of the h2020 PREDIS project, our work focused on the pre-disposal thermal treatment of organic material, we have investigated several glass formulations to maximize the waste load incorporation inside the glassy matrix. Short term lixiviation tests have been performed to assess the performances of such matrices. The ashes arise from processing organic materials surrogates (simulating materials contaminated by α-emitting actinides) within the IRIS process (Installation for Research on Incineration of Solids) in CEA Marcoule France. It is a multi-step process able to treat high chloride containing wastes via a combined pyrolysis and calcination process. Simulant inactive ashes arising from the IRIS process are comprised of a calcium-zinc aluminosilicate rich material, with a very low level of residual carbon – making these ashes ideal candidates for HIP (Hot Isostatic Pressing) processing. Molten glass coating trials were undertaken by mixing IRIS ashes into glass powder at low melting temperatures, resulting in a 30 to 40 % waste loading. Post-processing characterisation revealed the formation of a polycrystalline material. These trials have demonstrated the suitability of molten glass process towards the processing of such ash materials, resulting in a solidified product. Though forming a solid product, substantial porosity remains within the final product, creating potential for wasteform improvements. Further wasteform optimisation is ongoing to investigate the impact of the glass composition, along with studies into the long-term aqueous durability of these materials.

orano

In-Can vitrification of spent mineral sorbents using DEM&MELT technology

See Caroline Michel poster's on Monday

Another example if you want ?

The numerous constraints associated with the management of highly active nuclear waste lead to the consideration of thermal treatment solutions given that these offer multiple advantages. Thermal treatments such as vitrification processes enable significant volume reduction, chemical waste stabilization and efficient radioelements containment in a glassy or glass-ceramic matrix. Moreover, vitrification processes have proven their adaptability to intermediate and high-level waste and can be flexible enough to accommodate a varied waste stream composition. In this context, Orano, CEA and ECM Technology, with the support of Andra through the French governmental program “Programme d’Investissement d’Avenir” have developed a new full scale In-Can vitrification tool, called DEM&MELT. The DEM&MELT process is an innovative and compact process that can be deployed in the existing premises or nearby. This process benefits from wide experience, coming from more than 40 years of operation at Marcoule first and then at La Hague plant with 6 high level waste vitrification lines currently operating. It has been designed to match the requirements and constraints of waste streams arising from remediation or decommissioning and dismantling operations; it is an easy-to-run process, equipped with a multiple resistive zone furnace and an off gas system designed to obtain high decontamination factors, which is crucial when it comes to the last step of a plant life. It benefits from a modular design, adaptable to nuclear operator needs and its operation takes into account the compositional uncertainties linked to such types of waste. The process allows a significant volume reduction in addition to safe radionuclide containment with moderate investment and operating costs. It can deal with a wide range of nuclear waste, ranging from intermediate to high-level waste, with different compositions and forms such as sludge, liquid or solid, including for the latter, one of the most common dismantling wastes: mineral sorbents, used for the radiological decontamination of effluents, such as zeolites or silicotitanates. This waste must be conditioned in a safe and durable manner and its powdery nature eliminated. This paper presents, through an up-scaling methodology, going from laboratory-scale tests up to full-scale pilot tests, the most significant results obtained, performed for mineral sorbent conditioning. The results are presented, with an emphasis on the process parameters such as temperature, waste loading and glass throughput. A first viscosity domain in which the DEM&MELT process can be applied, is approached. The wasteform properties and the radionuclide volatility are also presented. Perspectives on the evolution of the prototype are discussed.