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High Level Waste Vitrification Worldwide – Past, Present and Future

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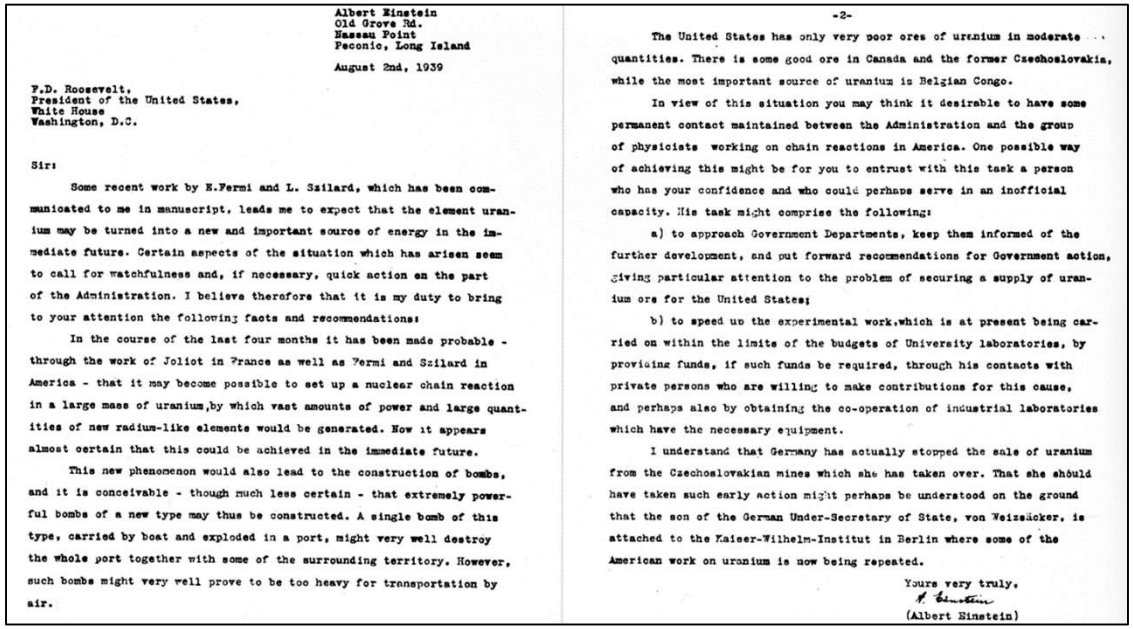
DEPARTMENT OF ENERGY · UNITED STATES OF AMERICA

EPSRC
Engineering and Physical Sciences Research Council

Radioactive Waste – A Historical Perspective

Radioactive waste – A historical perspective

- **1930s:** The first radioactive waste is reported to be produced in Canada and France during the mining of uranium and radium, and use of radium for medical purposes, respectively. Later, uranium was destined for nuclear fuel and military applications. *[nuclearsafety.gc.ca; international.andra.fr]*
- **1933:** Leo Szilard conceived the idea of nuclear chain reaction.
- **1934:** Leo Szilard and Enrico Fermi patent the idea of a nuclear reactor.
- **1939:** Leo Szilard wrote a letter for Albert Einstein's signature. This letter was addressed to the US president, Franklin D. Roosevelt bringing to his notice the possibility of creating a bomb from uranium, and that Germany has already started working on replicating the US research on uranium with intentions of making a bomb.



Albert Einstein
Old Grove Rd.
Nassau Point
Peconic, Long Island

August 2nd, 1939

F.D. Roosevelt,
President of the United States,
White House
Washington, D.C.

Sir:

Some recent work by E.Fermi and L. Szilard, which has been communicated to me in manuscript, leads me to expect that the element uranium may be turned into a new and important source of energy in the immediate future. Certain aspects of the situation which has arisen seem to call for watchfulness and, if necessary, quick action on the part of the Administration. I believe therefore that it is my duty to bring to your attention the following facts and recommendations:

In the course of the last four months it has been made probable - through the work of Joliot in France as well as Fermi and Szilard in America - that it may become possible to set up a nuclear chain reaction in a large mass of uranium,by which vast amounts of power and large quantities of new radium-like elements would be generated. Now it appears almost certain that this could be achieved in the immediate future.

This new phenomenon would also lead to the construction of bombs, and it is conceivable - though much less certain - that extremely powerful bombs of a new type may thus be constructed. A single bomb of this type, carried by boat and exploded in a port, might very well destroy the whole port together with some of the surrounding territory. However, such bombs might very well prove to be too heavy for transportation by air.

-2-

The United States has only very poor ores of uranium in moderate quantities. There is some good ore in Canada and the former Czechoslovakia, while the most important source of uranium is Belgian Congo.

In view of this situation you may think it desirable to have some permanent contact maintained between the Administration and the group of physicists working on chain reactions in America. One possible way of achieving this might be for you to entrust with this task a person who has your confidence and who could perhaps serve in an inofficial capacity. His task might comprise the following:

a) to approach Government Departments, keep them informed of the further development, and put forward recommendations for Government action, giving particular attention to the problem of securing a supply of uranium ore for the United States;

b) to speed up the experimental work,which is at present being carried on within the limits of the budgets of University laboratories, by providing funds, if such funds be required, through his contacts with private persons who are willing to make contributions for this cause, and perhaps also by obtaining the co-operation of industrial laboratories which have the necessary equipment.

I understand that Germany has actually stopped the sale of uranium from the Czechoslovakian mines which she has taken over. That she should have taken such early action might perhaps be understood on the ground that the son of the German Under-Secretary of State, von Weizsäcker, is attached to the Kaiser-Wilhelm-Institut in Berlin where some of the American work on uranium is now being repeated.

Yours very truly,

A. Einstein

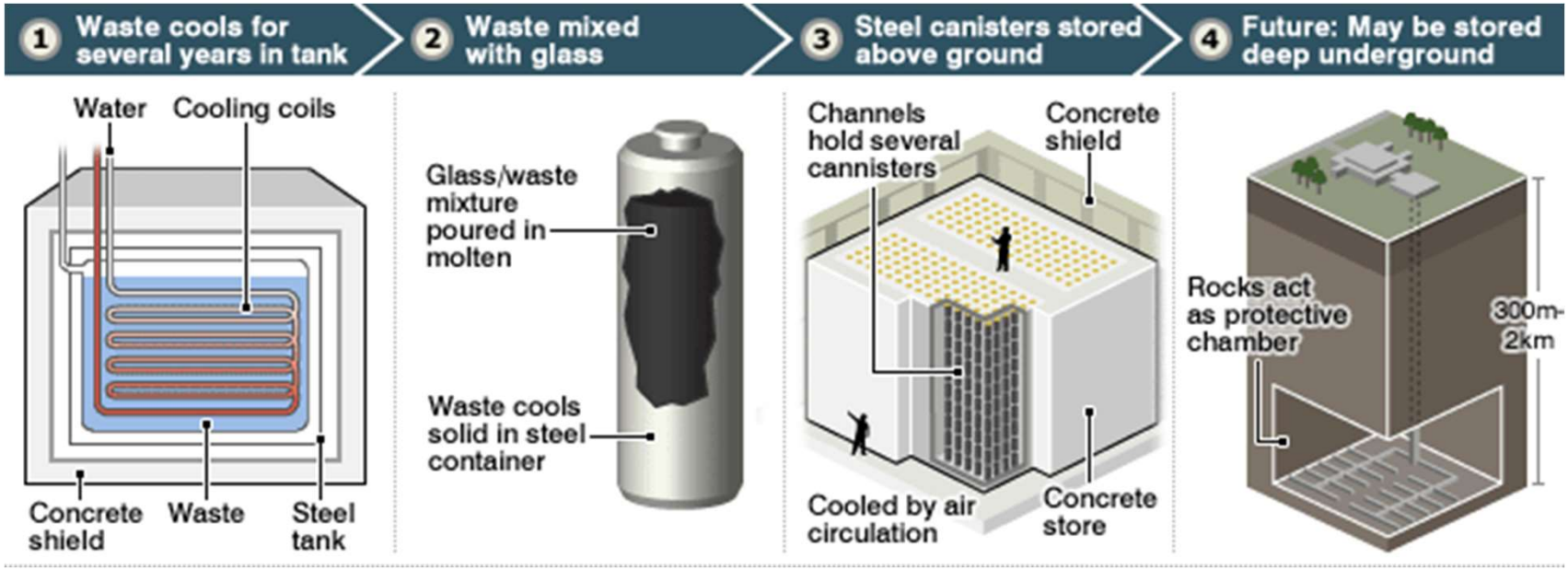
(Albert Einstein)

This letter led to the start of the famous "Manhattan Project" and building up nuclear reactors at Hanford site in Washington State leading to the generation of ~56 million gallons radioactive waste stored in steel tanks.

What is High Level Waste?

What is high-level waste?

According to *International Atomic Energy Agency (IAEA)*, the HLW is waste with large concentration of long-lived radionuclides. Disposal in deep, stable geological repositories usually several hundred meters or more below the surface is the generally recognized option for disposal of HLW.



A schematic of HLW immobilization in glass followed by its disposal in a geological repository.

[Guide to UK nuclear power, news.bbc.co.uk]

Although the HLW accounts for only 10 vol.% of the 56 million gallons of Hanford tank waste or 0.3 vol.% of the nuclear waste in the UK, it accounts for more than half the total radioactivity.

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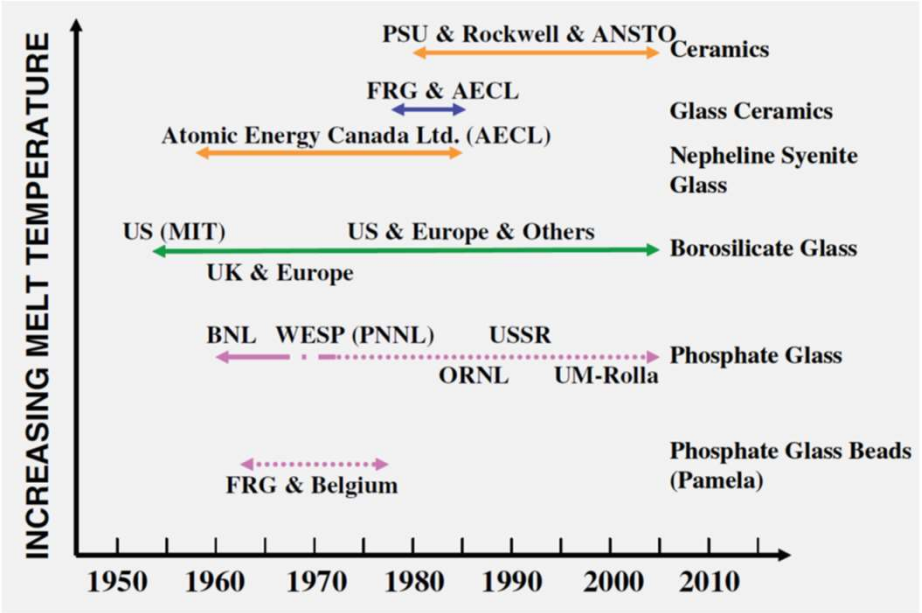
Glass as a Matrix for the HLW Immobilization – A Historical Perspective

Timeline for selecting glassy matrix for HLW immobilization

The concept of immobilizing radioactive waste in either vitreous or crystalline materials is more than 50 years old.

- The first research on solidification of fission product solutions began in 1950s in the USA, France, UK and Canada. The only requirement for a waste form was that it be a stable solid.
- Early efforts in the UK were focused on using natural soils as the base material for glass formulation. However, the process required high temperatures (~1500 ˚C) for the production of homogeneous glass.
- The aluminosilicate (nepheline syenite) glass formulations were being developed in Canada in 1957 – 1958.
- The first borosilicate glass formulation was developed between 1956 and 1957 by Goldman et al. at MIT. The researchers examined calcium aluminosilicate porcelain glazes into which they had added B_2O_3 to reduce viscosity and minimize volatilization of radionuclides.

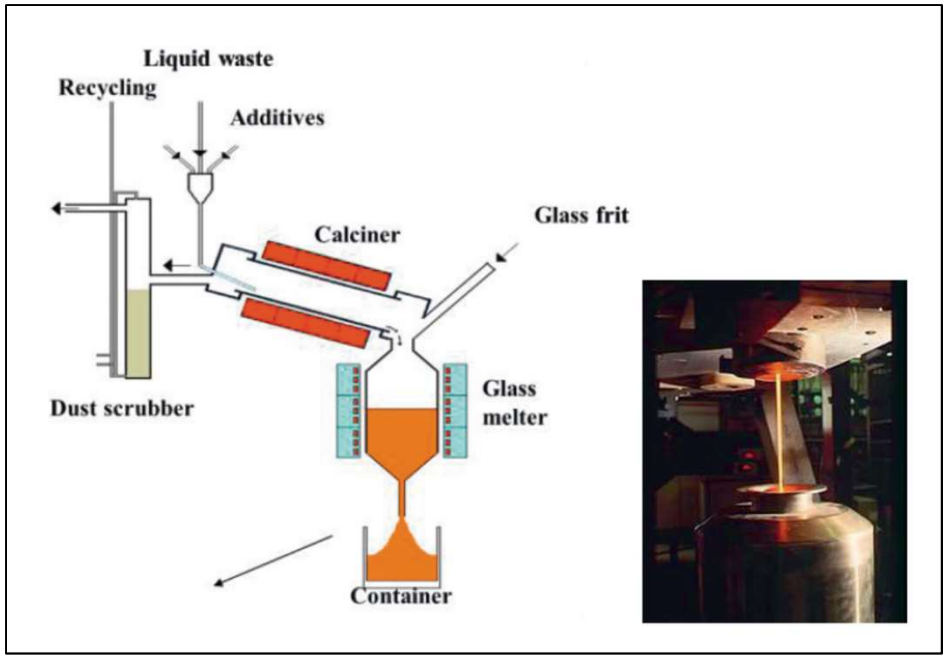


Historical development of the use of glass to solidify nuclear waste. *[Bao et al., J. Am. Ceram. Soc. 88 (2005) 3287]*

- M.I. Goldman et al. *Retention of Fission Products in Ceramic-Glaze-Type Fusions*. in *2nd UN Int. Conf. on Peaceful Uses of Atomic Energy*. 1958. Geneva: United Nations, New York.
- W. Lutze, R.C. Ewing, *Radioactive waste forms for the future.* 1988.
- M.T. Harrison, Proc. Mater. Sci. 7 (2014) 10.

Timeline for selecting glassy matrix for HLW immobilization

- **1957:** The first radioactive glass was synthesized at laboratory scale at Saclay (France).
- **By 1968,** the PIVER facility in the Marcoule Pilot Plant was capable of vitrifying up to 200 kg high-activity solutions.
- **1960s:** The UK selects borosilicate glass and focuses on the development of a single-stage 'in-can' batch process based on induction heating, i.e., FINGAL (Fixation in Glass of Active Liquors).
- **1960s:** In parallel, the French were developing a two-stage continuous vitrification process known as AVM (Atelier de Vitrification Marcoule), where calcination and melting stages were carried out separately. This two-step process was later sold to the UK (BNFL) resulting in the start-up of Sellafield vitrification plant in 1990.
- **1969-1971:** USSR decides to create laboratory facilities for the solidification of HLLW into an aluminophosphate glass using direct electrical heating.



Two step calciner/hot crucible French vitrification process. FP solution is continuously introduced in a calciner, and the glass is melted in a metallic furnace by induction.

- Vernaz and Brueziere, Proc. Mater. Sci. 7 (2014) 3
- W. Lutze, R.C. Ewing, *Radioactive waste forms for the future.* 1988.
- M.T. Harrison, Proc. Mater. Sci. 7 (2014) 10.
- *Yu. V. Glagolenko, Management of High-Level Radioactive Wastes from the Mayak Production Association and Plans for the Creation of an Underground Laboratory, 2005. https://doi.org/10.17226/11320.*

Timeline for selecting glassy matrix for HLW immobilization

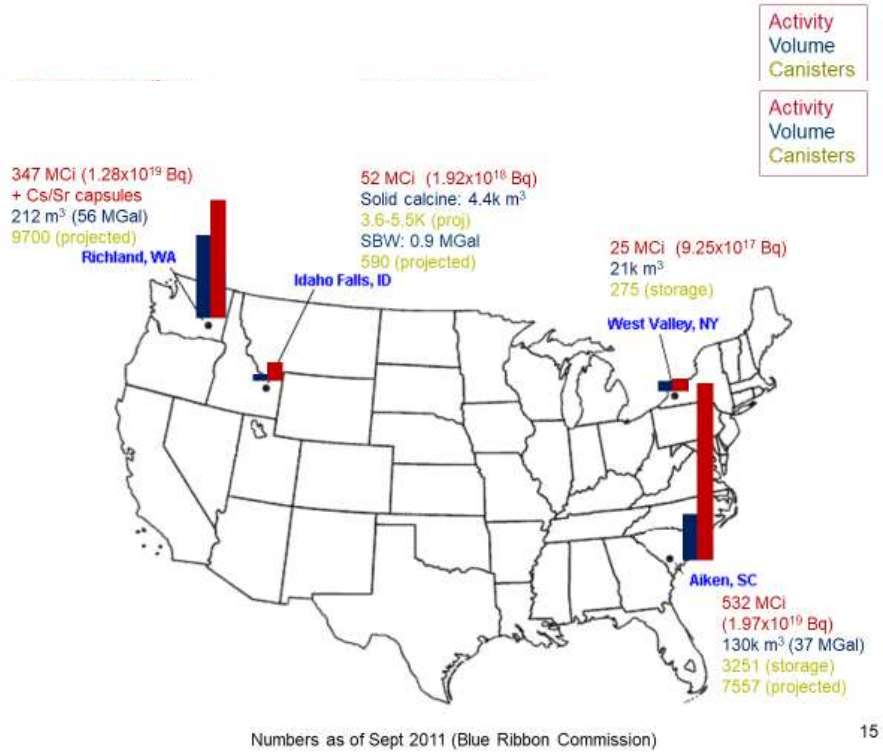
- **1970s:** In the US, "low leachability" or high chemical durability had become the main criterion for waste form selection.

- There were discussions about comparison of "low leachability" between glass and ceramic waste forms.

- **1979-1981:** Between 1979 – 1981, the US DOE conducted its National High-Level Waste Technology Program to develop and evaluate candidate waste forms for immobilization of HLW at DOE defense sites. A total of 17 waste forms were initially considered for development and evaluation.

- **1981:** Based on waste form evaluations conducted at the DOE national laboratories, independent laboratories, peer review assessments, product performance evaluations, and a processability assessment, two waste forms were chosen:

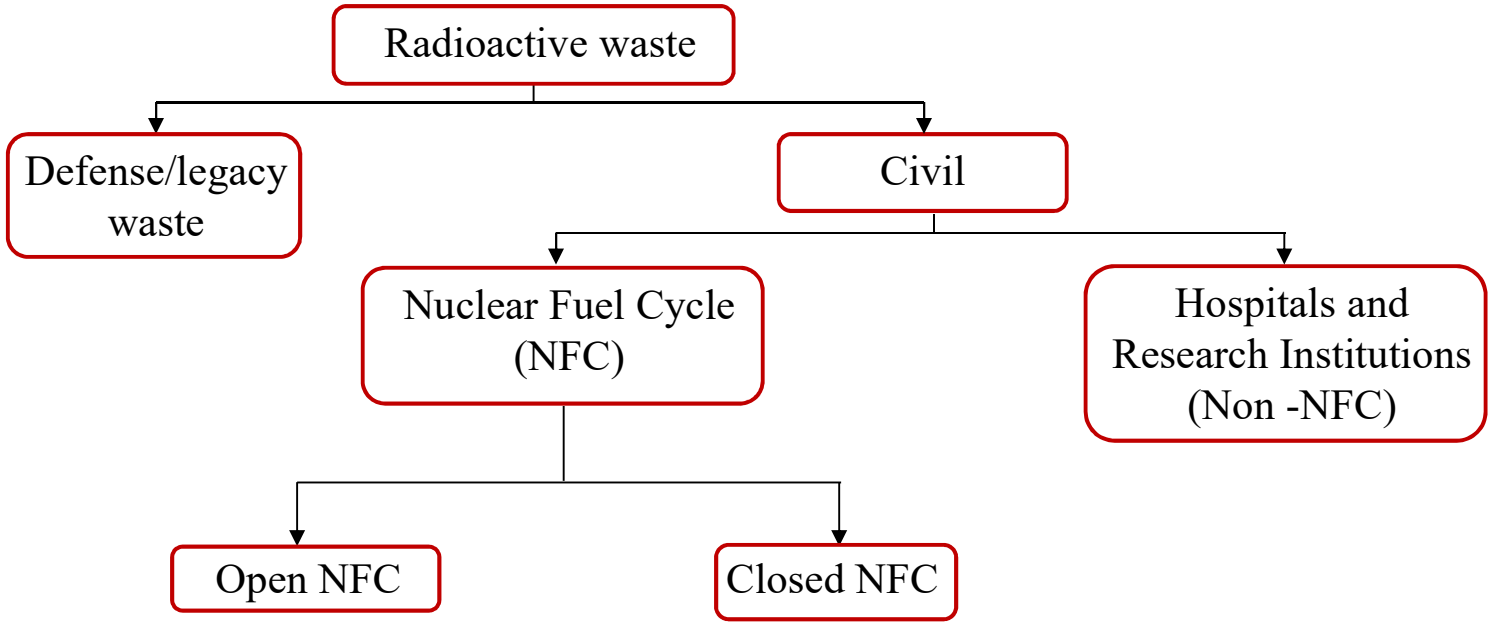
1. Borosilicate glass – as the reference waste form
2. Synroc – as an alternative waste form.



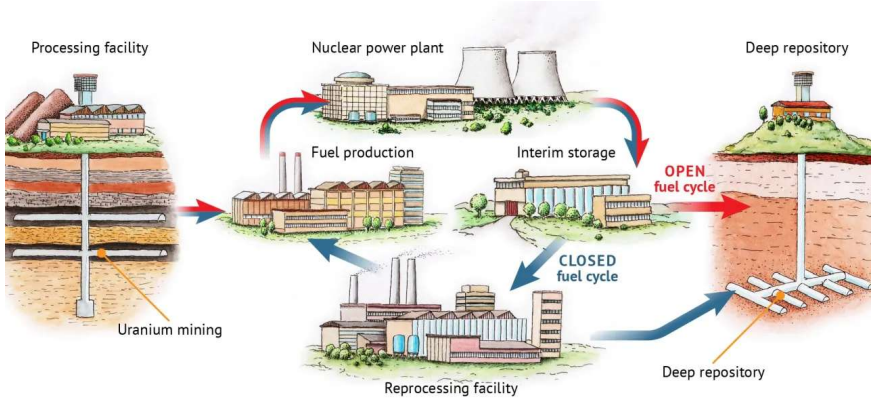
Legacy HLW in the United States

- J. Vienna, Closed fuel cycle treatment strategy, 2015, PNNL 24114.

Source and complexity of radioactive waste



- In an open NFC, the spent fuel is disposed of without reprocessing (as HLW). US, Canada, Sweden, and many more countries have adopted open NFC.
- In the closed NFC, spent fuel is reprocessed to extract fissile U and Pu and only the remaining HLW is disposed.
- Worldwide, there are only five commercial reprocessing plants operable: namely in France, UK, Japan, Russia, India.



A schematic representation of open and closed NFCs
Reference: energyencycopedia.com

Chemical complexity of Hanford legacy tank waste

Spent fuel

Three chemical processes were used to separate plutonium (and uranium) from the spent nuclear fuel.

- $BiPO_4$ Process
- Reduction – Oxidation (Redox) Process
- Plutonium Uranium Extraction Process (PUREX)

Total Radioactivity in the waste

Tank solids: ~128 million Curie

Tank liquids: ~70 million Curie

177 TOTAL TANKS

149 SINGLE-SHELL TANKS Constructed 1943-1964

28 DOUBLE-SHELL TANKS Constructed 1968-1986

- Each of the three processes began with dissolution of the aluminum or zirconium cladding material in boiling solutions of $NaNO_3$ and NaOH (for aluminum) or NH_4OH, NH_4NO_3 and NH_4F (for zirconium).
- The declad fuel slugs were dissolved in nitric acid (HNO_3) solutions.
- Plutonium was extracted as plutonium nitrate using the above-mentioned three processes.
- This resulted in large quantities of HNO_3-based liquid waste, which was neutralized with NaOH.
- A total of ~56 million gallons of waste is stored in 177 underground steel tanks. The wastes are rich in sodium, aluminum, phosphorus, sulfur and iron, chromium, etc. ~6.15×10^5 kg uranium is also present in the Hanford tanks in the form of sodium urinates and uranium iron oxide complexes.

Chemical complexity of Hanford tank waste

Plan is to separate this tank waste into two different waste streams

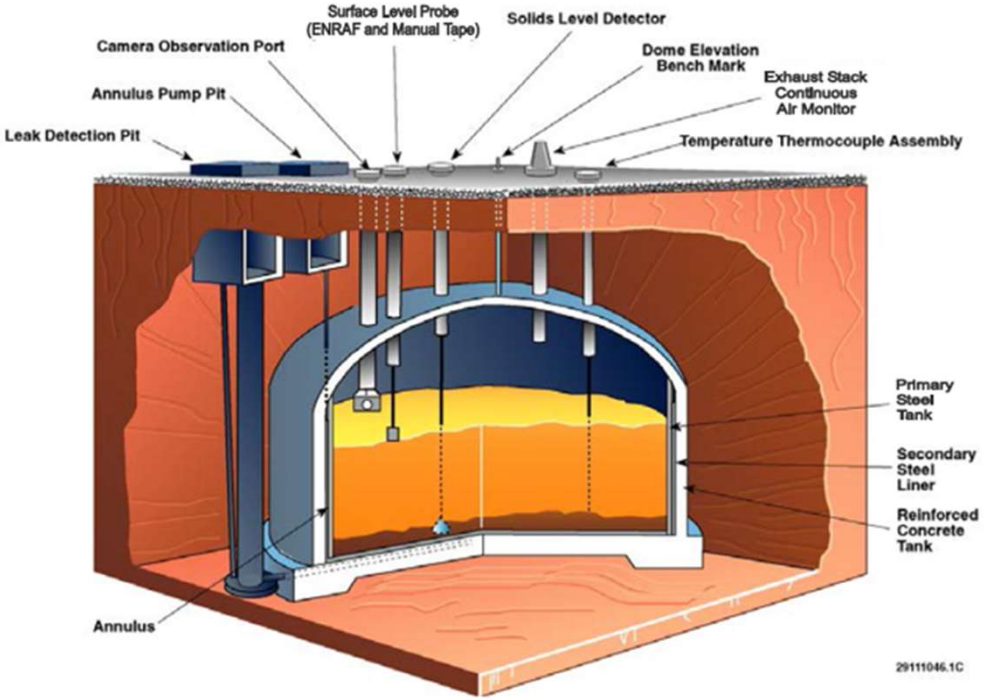
Low Activity Waste (LAW)

- High volume (~90 vol.%)
- Supernatant liquid
- Comprising aqueous solutions of Na^+, K^+, $Al(OH)_4^-$, Cl^-, F^-, NO_2^-, NO_3^-, SO_4^{2-}, ^{99}Tc and ^{129}I.

High Level Waste (HLW)

- Low volume (~10 vol.%)
- Mostly in the form of sludge and salt cake
- Rich in sodium, and aluminum oxides, hydroxides and nitrates, along with significant portion of spinel forming oxides, such as Fe_2O_3, NiO, Cr_2O_3 and MnO.

Most of the radioactivity in the tank waste comes from ^{137}Cs and ^{90}Sr. The ^{137}Cs is soluble in supernate, and ^{90}Sr is largely contained in the sludge.

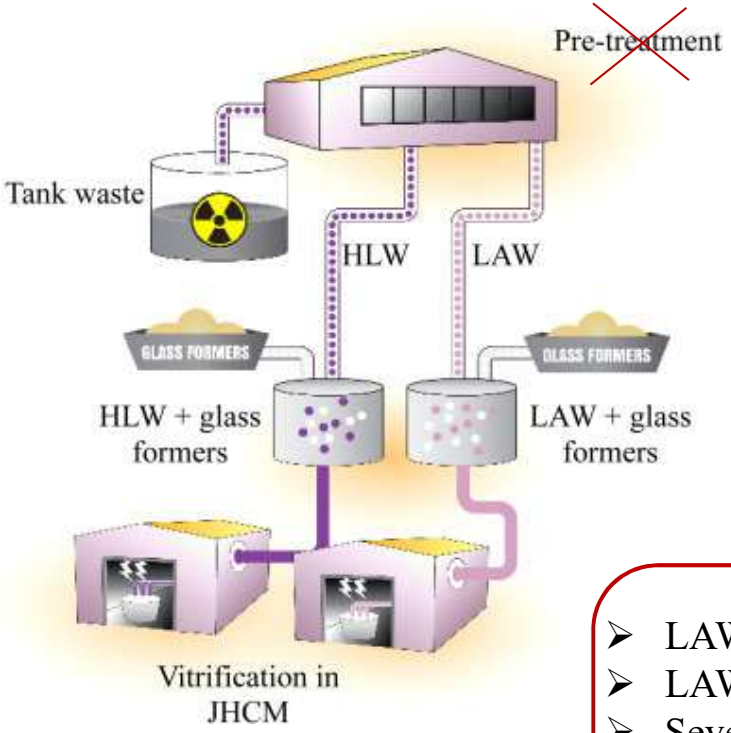


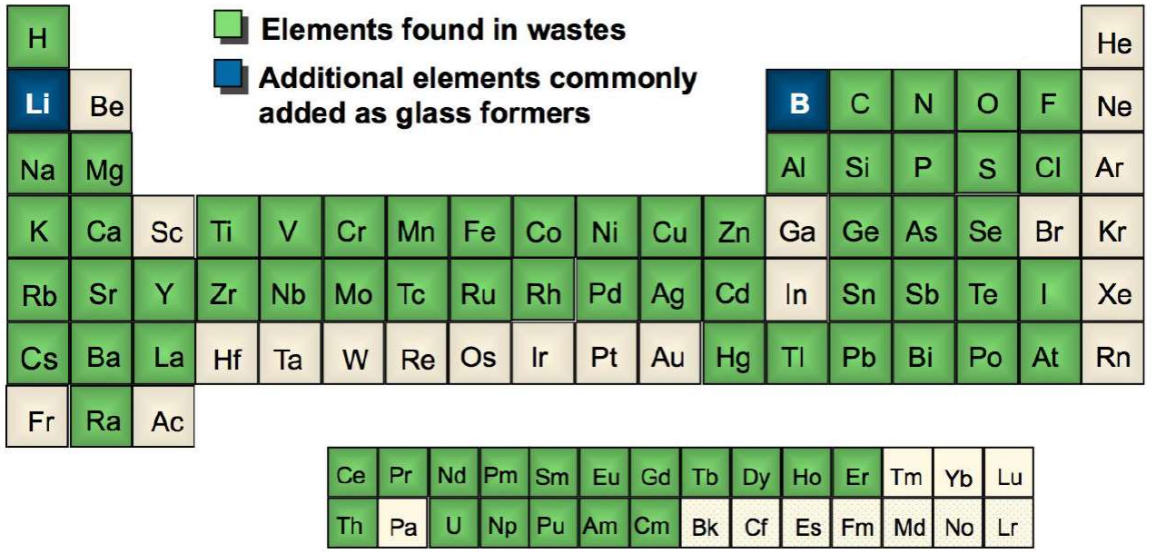
Representative image of a single shell tank at Hanford site depicting layer-by-layer arrangement of radioactive and chemical waste.

Courtesy: John Vienna

HLW Vitrification at Hanford

Direct Feed HLW

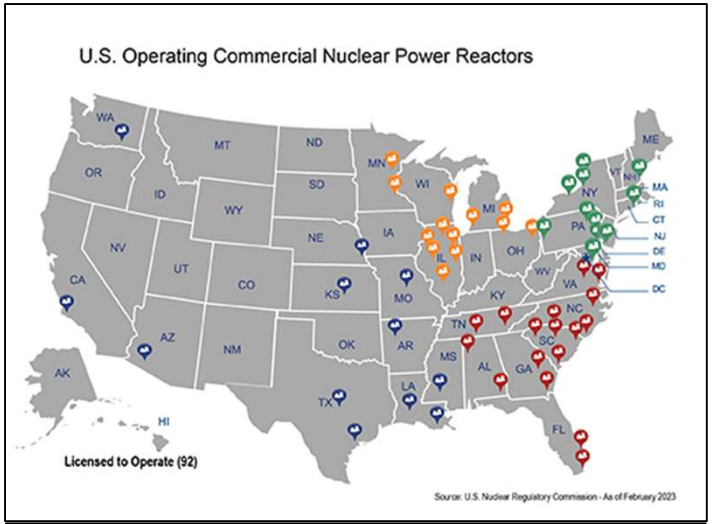




Current Status

- LAW vitrification will start before HLW vitrification.
- LAW melters are in testing and demonstration phase.
- Several options (including DF-HLW) are being considered for the vitrification of HLW.
- Research is focused on expanding the compositional domains and develop composition – structure – property models with respect to DF-HLW glasses.

Civil HLW in the US



Nuclear reactors within the United States as of Feb 2023; marker colors indicate respective administrative Regions of the Nuclear Regulatory Commission. ***Ref:*** *nrc.gov*

Current fleet: Light Water Reactors (LWR) comprising Pressurized Water Reactors (PWR) and Boiling Water Reactors (BWR)
Licensed to operate: 92
Nuclear fuel cycle: Open
Spent fuel generated annually: ~2,000 MT
Spent fuel generated since 1950s: >90,000 MT
Ref: *nrc.gov; energy.gov*

Current Status

The U.S. Department of Energy is now exploring the possibility of consolidating this spent nuclear fuel at one or more federal interim storage facilities using a **consent-based siting process**.

Ref: *energy.gov*

Advanced Reactors

Several Gen IV reactor designs are under consideration. Nothing has been deployed yet.

Reactor Type	NFC	HLW	Expected WF
TRISO	Open	Graphite, fuel kernels	Undecided
MSR	Closed	Fluoride or chloride-based salts	Several options are being considered – glass, ceramic, cermets
Na-metal cooled	Closed	Chloride-based salts	

French legacy HLW (UMo) vitrification

- UMo waste solutions are fission products from the reprocessing of U-Mo-Sn-Al spent nuclear fuel used in Gas Cooled Reactors (GCRs).
- The UMo waste is rich in molybdenum (from spent fuel) and phosphorus (additive for reprocessing).
- An aluminoborosilicate glass, which phase separates and crystalizes upon slow cooling resulting in powellite ($CaMoO_4$) as the crystalline phase dispersed in the glassy matrix has been designed as the waste form.
- The UMo glass-ceramic has 4× higher waste loading than a borosilicate glass.
- UMo solutions vitrification in the La Hague CCIM started in 2013 and was completed in 2017.

HLW

Legacy
UMO and MoSnAl waste

Civil
UOx and MOx spent fuel from PWRs

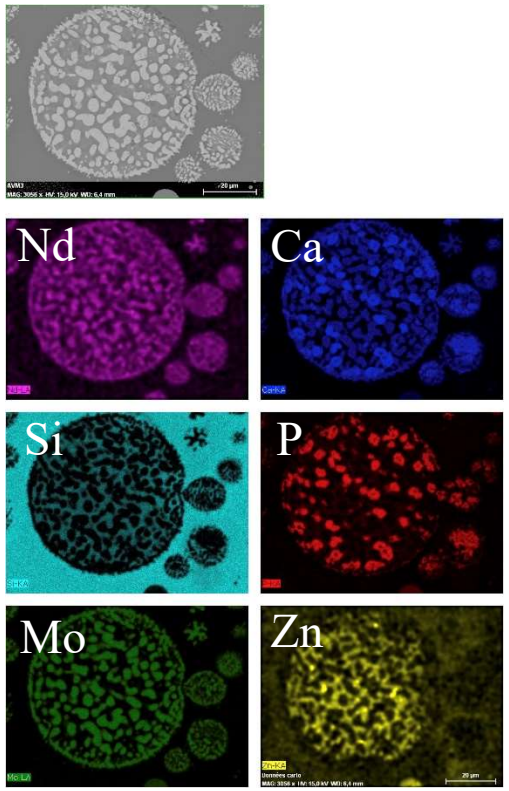
Table I. UMo solution main characteristics

Composition (g/L)	MoO_3	137
	P_2O_5	42
	Na_2O	11
	Other	15
Volume	~66,000 US gallons	250 m^3
Activity		< 222 10^{10} Bq/L

Pinet et al., WM2011

Oxides	wt.%	Oxides	wt.%
SiO_2	38.7	MoO_3	10.0
Na_2O	9.4	ZnO	6.0
B_2O_3	13.9	ZrO_2	3.3
Al_2O_3	7.1	CaO	6.1
P_2O_5	3.1	Nd_2O_3	0.52
Others	1.9		

Pinet et al., JNM 2019



Phase separation and crystallization in UMo glass melt during slow cooling.

French civil HLW vitrification

Nuclear reactors in France. The numbers indicate how many nuclear reactors are found at a particular plant site. *Ref: iaea.org*

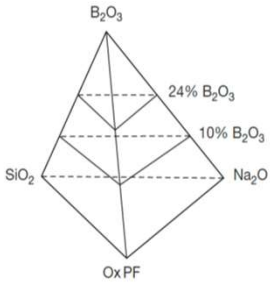
Current fleet: Pressurized Water Reactors (PWR)
Reactors in operation: 56
Nuclear fuel cycle: Closed
Spent fuel (UOx and MOx) generated annually: ~1,150 tonnes
Ref: *iaea.org*

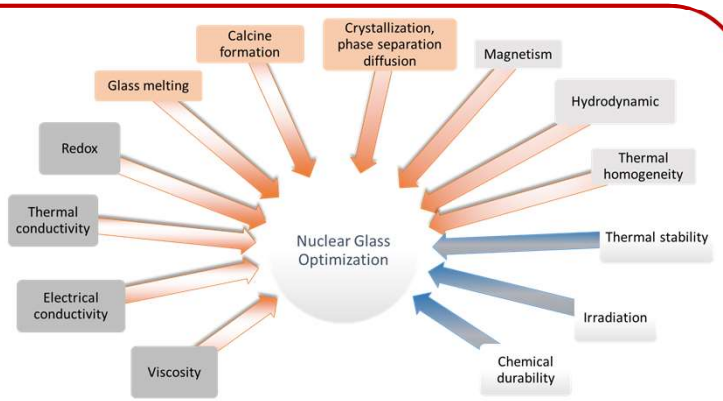
Closed NFC

- UOx fuel is reprocessed via PUREX process.
- **Waste chemistry from recycling of UOx SNF:** Nitrates, alkali (Na^{+}, Cs^{+}, Rb^{+}), alkaline-earths (Sr^{2+}, Ba^{2+}), chalcogenides (Se^{4+}, Te^{4+}), transition metals ($Fe^{2+,\,3+}$, Cr^{3+}, Zr^{4+}, Mo^{6+}), P^{5+}, Al^{3+}, noble metals, lanthanides, and actinides.
- A campaign to recycle MOx spent fuel has been initiated.
- The HLW from MOx SNF is expected to contain higher concentration of actinides compared to the UOx waste. Therefore, an optimization of glass formulation is required to immobilize this waste.

Design of glass formulations

- The glass forming domain is determined by establishing quaternary phase diagrams with the expected four major components of glass to identify the glass-forming regions.
- The glass formulations need to be designed and optimized to meet/satisfy criteria related to processing and performance.





French civil HLW vitrification

1978 Start-up of AVM

2000
Development of CCIM Technology

2010
CCIM starts to operate at La Hague plant (replaces an IHMM)

2020 - present

1 CCIM and 5 IHMM in operation at La Hague plant for the vitrification of HLW (UO_X spent fuel)

Glass type: R7T7

Present R&D effort:
Vitrification of UO_x spent fuel – Higher waste loading

Future outlook

- Plan to build at least six new European Pressurized reactors (advanced version of PWRs) by 2050. Therefore, higher volume of HLW is expected in future.
- Glass formulations with higher waste loadings for HLW from UOx and MOx SNFs are needed.
- Better understanding of the thermo-chemical properties, e.g., phase separation and crystallization, in HLW glasses.

Courtesy: S. Schuller; Ref: Focus: France seeks strategy as nuclear waste site risks saturation point, reuters.com; Vernaz and Brueziere, Proc. Mater. Sci. 7 (2014) 3

Chemical composition range of R7T7 glasses produced in the AREVA – La Hague plant workshops

Oxides	Specified interval for the industry (wt%)		Average composition of industrial glasses (wt%)
	Min	Max	
SiO_2	42.4	51.7	45.6
B_2O_3	12.4	16.5	14.1
Al_2O_3	3.6	6.6	4.7
Na_2O	8.1	11.0	9.9
CaO	3.5	4.8	4.0
Fe_2O_3		<4.5	1.1
NiO		<0.5	0.1
Cr_2O_3		<0.6	0.1
P_2O_5		<1.0	0.2
Li_2O	1.6	2.4	2.0
ZnO	2.2	2.8	2.5
Oxides (FP + Zr + actinides) fines suspension	7.5	18.5	17.0
Actinide oxides			0.6
$SiO_2 + B_2O_3 + Al_2O_3$	>60		64.4

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UK HLW Thermal Treatment / Vitrification

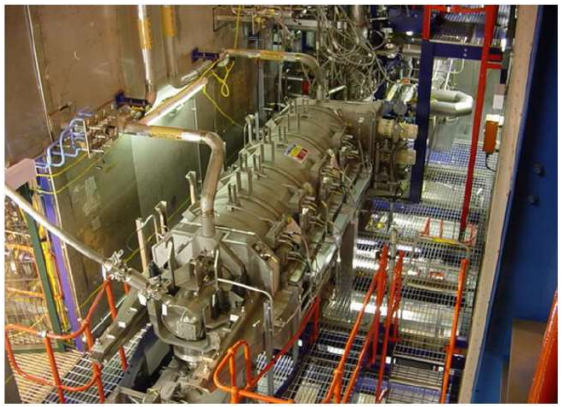
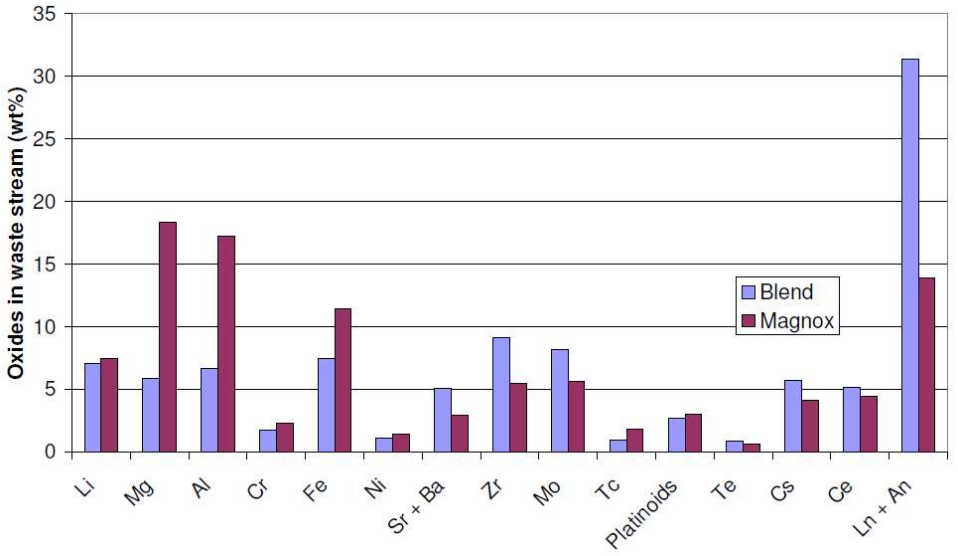


Table 1. Key stages in the development of HLW vitrification in the UK

Research into vitrification of radioactive waste started	1950s
FINGAL developed at the UK Atomic Energy Authority (AEA) laboratories, Harwell	1960 - 1962
FINGAL operations (72 glass-making runs)	1962 - 1966
Development suspended	1966 -1972
Review decision to continue vitrification development for HARVEST process	1972
Detailed comparison of HARVEST and French AVM process	1979 - 1980
Decision to implement the AVM process for HLW vitrification in the UK	1980
Full scale inactive facility (FSIF) replica of AVM process built	1981 - 1983
Decision that WVP should use the AVH process	1982
FSIF operational	1983 - 1991 (completion of trials in 1989)
Commissioning of WVP Lines 1 and 2	1989 - 1990
WVP Lines 1 and 2 operational	1990 – date
Commissioning of WVP Line 3	1998 - 2002
WVP Line 3 operational	2002 - date
Vitrification Test Rig (VTR) constructed	2002 - 2004
VTR operational	2004 - date

- Two reprocessing facilities operated at Sellafield:
- Magnox plant for reprocessing natural U based fuel from 1st generation Magnox reactors (1964 - 2022)
- THORP (Thermal Oxide Reprocessing Plant) for enriched UOx fuels from AGRs / LWRs (1994 - 2018)



M. T. Harrison, Proc. Mater. Sci. 7 (2014) 10-15; R. Short, Proc. Mater. Science 7 (2014) 93-100.

UK HLW Thermal Treatment / Vitrification

- MW Glass 1990 onwards:
- Pure Magnox Waste
- Blend 75/25, 50/50 Thorp/Magnox
- Waste loading 25 wt% increased towards 35 wt% over time
- CaZn Glass from ~2018 onwards
- Tanks contain large quantities of settled solids accumulated over many decades of operation:
  - Caesium phosphomolybdate, $Cs_3PMo_{12}O_{40}.14H_2O$
  - Zirconium molybdate, $ZrMo_2O_7(OH)_{22}H_2O$

Oxide	Wt% of oxide in MW base glass	Wt% of oxide in Ca/Zn base glass
SiO_2	61.2 ± 1.0	47.6 ± 1.0
B_2O_3	22.4 ± 0.8	23.4 ± 0.8
Li_2O	5.4 ± 0.4	4.2 ± 0.4
Na_2O	11.0 ± 0.5	8.6 ± 0.4
Al_2O_3	-	4.2 ± 0.4
CaO	-	6.0 ± 0.4
ZnO	-	6.0 ± 0.4
Others	≤2300 ppm	<2000 ppm

- MW glass still in use but being phased out
- CaZn Glass being phased in since 2018

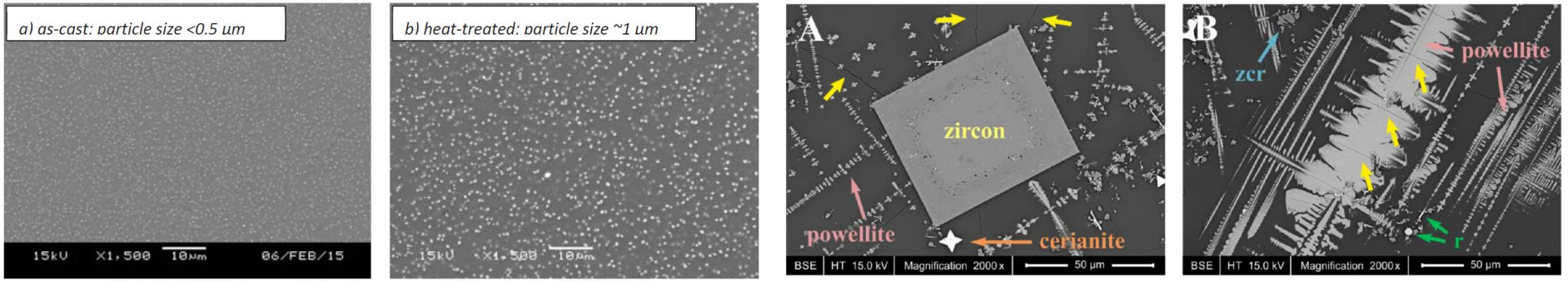


Figure 1. SEM images of the a) as-cast and b) heat treated *ZM10_Li0*

T. Zagyva *et al*., Microstructure and radiation tolerance of molybdenum-rich glass composite nuclear waste forms, *J. Nuclear Materials* 585 (2023) 154635.

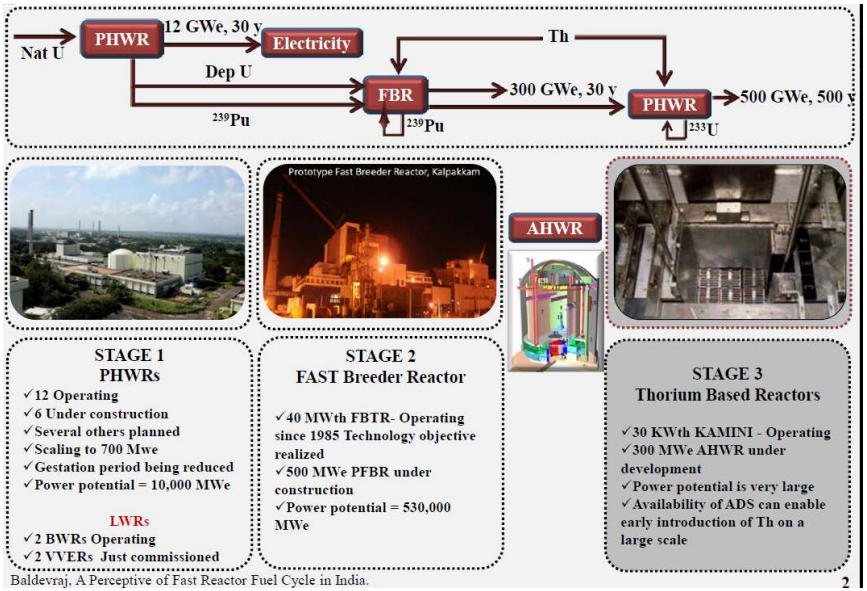
M. T. Harrison & G. C. Brown, Chemical durability of UK vitrified high level waste in Si-saturated solutions, *Materials Letters* 221 (2018) 154-156.

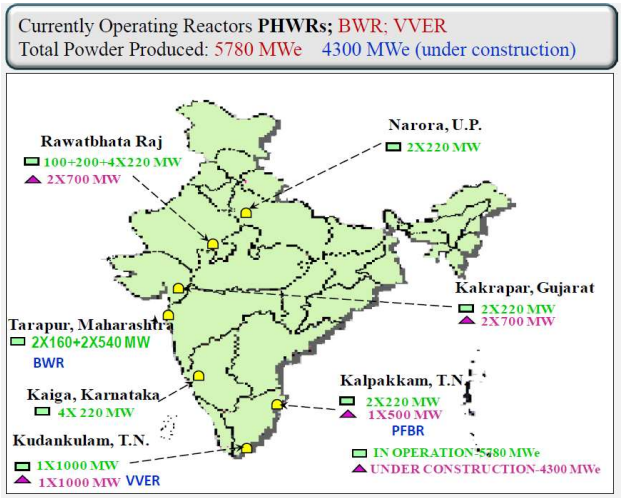
M. T. Harrison & C. J. Steele, Vitrification of simulated highly active calcines containing high concentrations of sodium & molybdenum, MRS Adv. 214 (2017) 4233-4238.

M. T. Harrison, Vitrification of high level waste in the UK, *Procedia Materials Science* 7 (2014) 10-15.

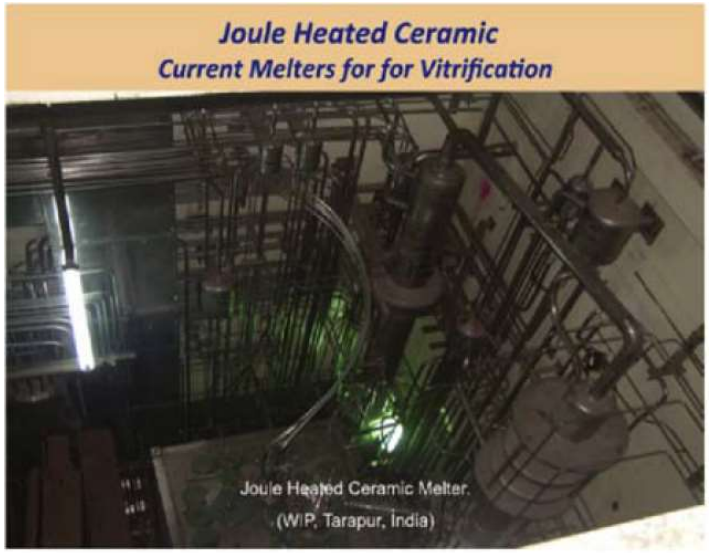
R. Short, Phase separation and crystallisation in UK HLW vitrified products, *Procedia Materials Science* 7 (2014) 93-100.

India HLW Thermal Treatment / Vitrification





K. Ananthasivan, Reducing radioactive wastes an Indian perspective, Int. Symp. Present Status and Future Perspectives for Reducing Radioactive Wastes, Challenge for the Relief in Next Generation, Japan AEA, 2016.



In cell view of joule heated ceramic melter (JHCM) at WIP Tarapur.

Interim storage facility for radioactive vitrified waste products at Tarapur.

P. K. Wattal, Back end of Indian nuclear fuel cycle – a road to sustainability, *Progr. Nucl. Energy* 101 (2017) 133-145.

India HLW Thermal Treatment / Vitrification

- HLW vitrification has been using induction heated metallic melters but JHCMs are currently the mainstay.
- CCIM has also been developed and an engineering-scale facility is in operation at BARC, Trombay
- Sodium borosilicate glasses required ~950 °C for plant operation - too high to avoid volatilisation of Cs and Ru.
- Ti^{4+} added to suppress Cs volatilisation by forming Cs-titanates. Reduced Cs volatilisation but greater crystallisation / immiscibility during melting.
- Not suitable for high sulphate content legacy HLW due to phase separation.
- The SiO_2-B_2O_3-PbO glass system (WTR-62) was also not suitable.
- Led to development of alkaline earth borosilicate glasses (SB-44) inspired by barite ($BaSO_4$), abundant sulphate mineral which exists over geological time scales.

Table 2.5 Waste glass compositions preently being produced in India (Source : Raj et al. 2006; Raj and Kaushik 2009; Yeotikar et al. 2011)

Composition (Oxide mol %)	Tarapur IR111	Trombay WTR 62	Trombay SB 44	Tarapur AVS
SiO_2	43.50	30	38.8	42.68
B_2O_3	7.0	20	21.96	20.13
Na_2O	17.5	20	11.71	10.06
BaO	–	–	9.47	–
TiO_2	6.0	5.0	–	6.35
MnO	10.0	–	–	–
Fe_2O_3	–	–	–	1.57
PbO	–	25	–	–
Waste oxide	16.0	20	18.06	19.21
Properties				
Fusion temp. (°C)	850		850	875
Softening temp. (°C)	540	490	536	
Pouring temp. (°C)	1,000	950	925	950
Thermochemical conductivity at 100 °C (W/m/°K)	1.0	1.15	0.92	0.925
Co-efficient of thermal expansion ($°C^{-1}$)	102×10^{-7}	83×10^{-7}	–	103×10^{-7}
Glass transition temp (T_g,°C)	560		496	540
Viscosity (Poise at 900 °C)	40	135	70	
Impact strength (RIAJ)	1.09	1.12	0.85	–
Average leach rate at 100 °C (g/cm^2.day)	$\sim 10^{-6}$	$\sim 10^{-5}$	$\sim 10^{-6}$	$\sim 10^{-6}$
Density (g/cm^3)	2.992	3.500	3.200	2.850

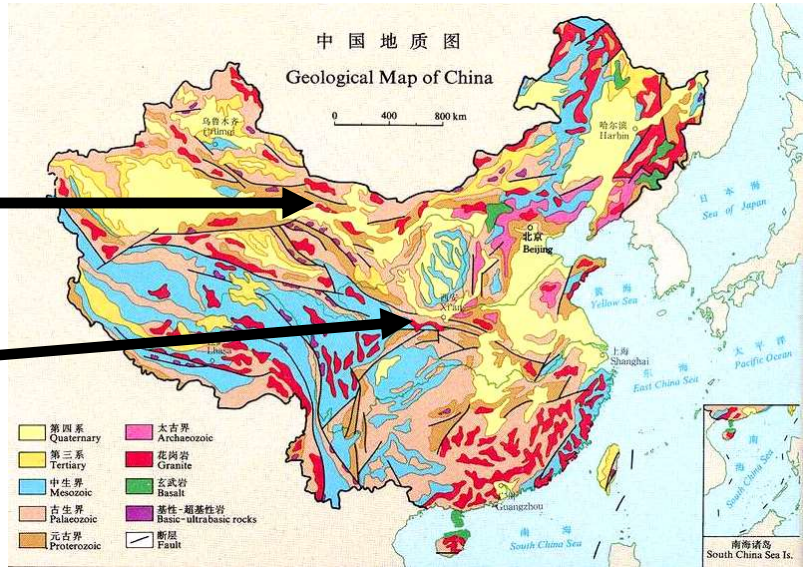
www.neimagazine.com/features/featuredelay-and-decay-7481278/

P. K. Wattal, *Progr. Nucl. Energy* 101 (2017) 133-145.

P. Sengupta, C.P. Kaushik & G.K. Dey "Immobilization of high level nuclear wastes: the Indian scenario", Chapter 2, in Mu. Ramkumar (ed.) *On a sustainable future of the earth's natural resources,* Springer-Verlag, Berlin, Heidelberg (2013) 25-51.

China HLW Thermal Treatment / Vitrification

- Following reprocessing, separated high-level waste will be vitrified, and placed into a geological repository 500m deep.
- Granite rock site, **Beishan area of the Gobi desert**. Beishan underground lab 400-560m deep, construction started 2021.
- **Vitrification Plant China (VPC)**, Guangyuan site, Sichuan province (https://solutions.iqony.energy/en/media/sliderstory/vitrification-plant-china)
- Began operations 2021. Technically very closely based on Karlsruhe vitrification facility (VEK) (https://ka-heidelberg.de/en/vitrification/)
- Liquid-fed JHCM (glass frit + liquid waste)
- For legacy defence waste, but the technology may be usable later for civil waste (https://world-nuclear.org/information-library/country-profiles/countries-a-f/china-nuclear-fuel-cycle.aspx)



- A large (800 t/yr) commercial reprocessing plant is planned to follow and begin operation about 2025 (Purex process)
- Actinides and fission products will become waste which is vitrified.
- STEAG Energy Services GmbH secured a long-term follow-up contract with a similar scope of services at the Diwopu site in the province of Gansu (DVP).

China HLW Thermal Treatment / Vitrification

Sampling (top), pouring (middle) and temporary storage (bottom) https://www.caea.gov.cn/n6760338/n6760342/c6831032/content.html

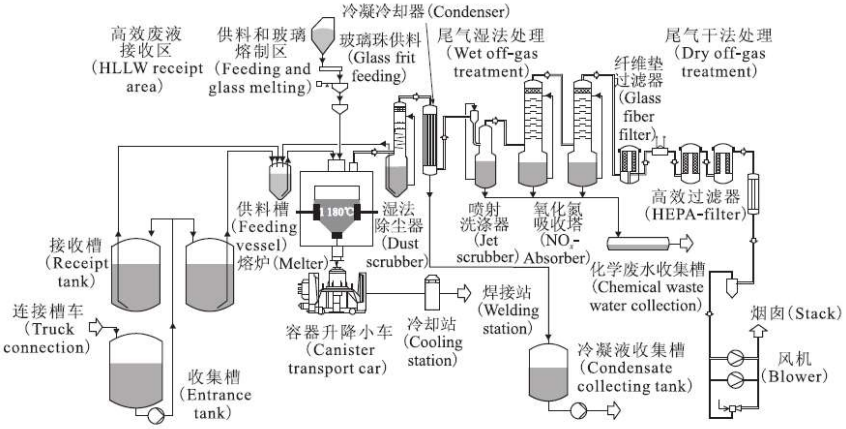


图 1　德国卡尔斯鲁厄研究中心 INE 的 PVA 冷台架工艺流程图

Fig. 1　Simplified flow diagram of the inactive prototype vitrification test facility PVA

Chemical composition of the recommendatory glass frit

组分(Compositions)	w/%	组分(Compositions)	w/%
SiO_2	53.44	CaO	8.00
B_2O_3	14.60	MgO	5.20
Na_2O	5.21	BaO	4.16
Li_2O	2.60	V_2O_5	1.79
Al_2O_3	4.40	Sb_2O_5	0.60

L-J. Liu et al., Verification Experiment Research of Glass Formulation for High Sodium and High Sulfur Bearing HLLW, *J. Nucl. & Radiochem*. 36 (2014) 163-168 (Chinese).

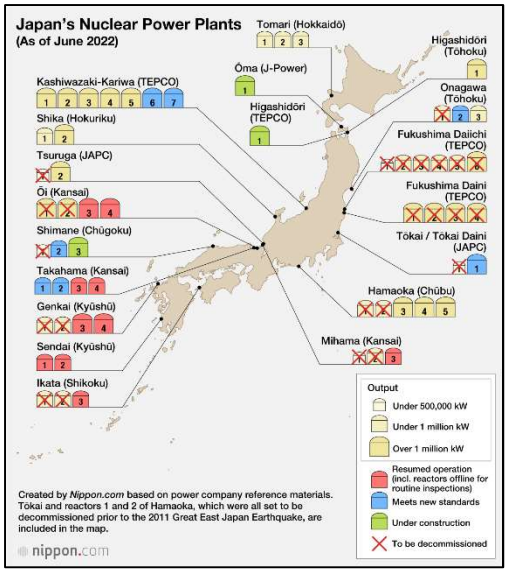
Also Used By: S. Tan et al., Influence of Radioactive Sludge Content on Vitrification of High-Level Liquid Waste, *Sustainability* 15 (2023) 4937.

Composition of simulated HLLW and glass[27]

模拟高放废液		基础玻璃	
组分	含量/(g·L^{-1})	组分	含量/%
U_3O_8	31.84	SiO_2	57.7
PuO_2	0.01	B_2O_3	16.8
Al_2O_3	11.43	Na_2O	5.0
NiO	0.51	Al_2O_3	3.1
Cr_2O_3	0.73	MgO	1.9
Fe_2O_3	35.3	CaO	3.1
Na_2O	32.89	TiO_2	6.2
稀土氧化物	5.03	ZrO_2	1.9
MnO_2	0.25	Li_2O	4.3
SO_3	10.48		
SrO	0.6		
Na_2O	1.27		
TiO_2	0.8		
ZrO_2	3.36		
K_2O	0.14		
总计	134.64	总计	100

Y. Li et al., Progress in Research and Development of Vitrification Technology for High-Level radioactive Liquid Waste at CIAE, *Atomic Energy Sci. Technol.* 54 (2020) 126-136 (Chinese).

HLW in Japan



- First nuclear reactor began operating in 1966.
- **Fleet:** Light Water Reactors (LWR) comprising Pressurized Water Reactors (PWR) and Boiling Water Reactors (BWR)
- Up until 2011, Japan was operating 54 nuclear reactors generating ~30% of the country's electricity. According to IAEA, it was 7% in 2021.
- **Reactors Currently Licensed to Operate:** 17 (licensed); 8 (license pending)
- **Resumed Operation:** 11 (As of July 2023)
- **Nuclear fuel cycle:** Closed

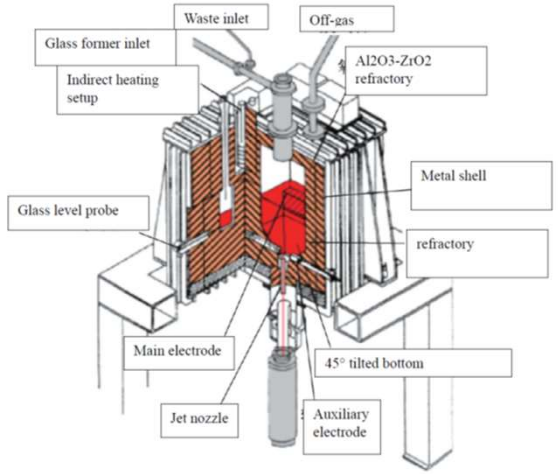
HLW treatment and reprocessing

- From 1969 to 1990, ~2940 tonnes of Japan's spent nuclear fuel was shipped to France (Cogema – now Areva) and ~4100 tonnes was shipped to the UK (BNFL) for reprocessing.
- Tokai has been the main site of JAEA's (Japan Atomic Energy Agency) R&D on the HLW treatment and reprocessing. At Tokai, 1140 tonnes of used fuel was reprocessed using PUREX process between 1977 – 2009. Since 2006, the plant has focused on R&D, including the reprocessing of MOx spent fuel. It was reported to have 40 t/year capacity to reprocess MOx fuel.
- In September 2014, the JAEA announced that it would close down the whole facility rather than spend JPY 100 billion to upgrade it to new safety, especially seismic, standards. The Rokkasho plant would take over further work.
- In June 2017, the JAEA presented decommissioning plans to the Nuclear Regulation Authority (NRA), with work to take 60 years and cost JPY 987 billion.

Ref: https://world-nuclear.org/focus/fukushima-daiichi-accident/japan-nuclear-fuel-cycle.aspx; Nuclear Fuel Reprocessing and Mixed-oxide fabrication services, US Arms Control and Disarmament Agency, September 1983.

HLW vitrification in Japan

The *Pacific Grebe*, carrying five large flasks holding 132 canisters of HLW borosilicate glass arrives in Japan from the UK in April 2014.
Ref: https://www.world-nuclear-news.org



Schematic diagram of vitrification facility at Tokai

Japan's HLW vitrification in Europe

- France and UK have vitrified Japan's HLW into borosilicate glass during 1980s and early 2000s.
- France shipped the first batch of 29 HLW glass canisters to Japan in 1995 and the last batch of 130 canisters in 2007. A total of 1310 HLW glass canisters were shipped from France to Japan in 12 years.
- UK shipped the first consignment of 28 HLW borosilicate glass canisters to Japan in 2010 and the last consignment of 132 canisters in 2016. A total of 520 canisters of HLW glass have been shipped from UK to Japan.

HLW Vitrification at Tokai in Japan

- Japan's policy, "Promotion of R&D on conditioning and disposal of high-level wastes" issued in 1980 recommended the vitrification of HLLW into borosilicate glass using JHCM.
- Tokai vitrification facility (TVF) officially started its operation in 1995.
- TVF employed liquid fed Joule heated ceramic melter (LFCM), which involved simultaneous additions of HLW and glass forming agents in to the melter. The melter operated between 1100 – 1250 ˚C with a melting rate of 9 kg/h. During its operation until 2007, the TVF had produced 247 canisters of HLW glass.
- The TVF resumed operation in 2016. Since then it has processed more than 400 m^3 HLW and produced 59 canisters of waste glass.

HLW vitrification in Japan

HLW vitrification at Rokkasho

- In 1993, JNFL (Japan Nuclear Fuel Ltd.) built the first radioactive reprocessing plant in Rokkasho to process the SNF produced by Japan's LWRs.
- The vitrification facility at Rokkasho, i.e., K-facility, adopts similar liquid fed ceramic melter (LFCM) technique as TVF. Borosilicate glass is first melted in the JHCM. HLW is then introduced into the melter. Finally, the molten mixture is poured into the container.
- The melter at Rokassho has two distinct features:
  - (1) the melter uses both the main electrodes (Joule heated) and indirect electrical heating to maintain the temperature of both the glass and gas phase in the target range;
  - (2) (2) based on the results from the mock-up vitrification facility at Tokai (KMOC), a melting process has been designed where the mixture of HLW and glass is heated at different temperatures at different stages of the process to avoid the precipitation of platinum group elements.
- After 13 years of construction and 28 months of trials, Rokkasho was planned to officially start in 2008. However, due to several technical and other issues, the vitrification facility has not been officially operated until now.
- The R&D efforts in Japan are focused on designing glasses with enhanced waste loadings by suppressing the formation of (moly-rich) yellow phase and precipitation of PGEs.
- Japan and France plan to collaborate for R&D of reprocessing of MOx fuel.

J. Lu et al., *Vitirification technologies of high level radioactive liquid waste in Japan,* Radiation Protection 40 (2020) 67-77; *T. Matsuda, Current Status of JNFL Rokkasho Nuclear Fuel Cycle Facilities, 7th Asian Nuclear Energy Briefing 2023; https://world-nuclear-news.org/Articles/France,-Japan-to-cooperate-on-MOX-fuel-recycling-s*

Glass composition for TVF vitrification

Oxide	wt.%	
SiO_2	46.7	Glass matrix: 75%
B_2O_3	14.3	
Al_2O_3	5.0	
Li_2O	3.0	
CaO	3.0	
ZnO	3.0	
Na_2O	10.0	Waste loading: 25%
P_2O_5	0.3	
Fe_2O_3	2.0	
NiO	0.2	
Cr_2O_3	0.1	
FP oxides	9.9	
Actinides	2.5	

HLW vitrification in Russia

- In 2011, 16% of used fuel was reprocessed, from VVER–440s, BN-600, research reactors and naval reactors. By 2030 Rosatom hopes to close the fuel cycle.
- Commercial reprocessing started 1977 at 2 sites:
- Mayak Production Association, Ozersk.
- Mining and Chemical Combine (MCC), Zheleznogorsk.

Mayak Vitrification Facility:

- 1969–1971: Creation of laboratory facilities for the solidification of solutions in a glass furnace using direct electrical heating
- 1973–1977: testing of pilot facilities using model radionuclide-labeled solutions
- 1986–1988: start-up of the complex and regular operation of the first electric furnace EP500/1
- 1991–1997: Operation of the 2nd electric furnace EP500/2
- 2001–????: Operation of the 3rd electric furnace EP500/3
- ???? –????: Operation of the 4th electric furnace EP500/4
- 2016–2020: Operation of the 5th electric furnace EP500/5

- In 2021 Mayak developed design documentation for 2 new unique types of melter to provide radiochemical production with modern high-level waste vitrification units. These are:
- An EP-250/6 type melter for producing aluminophosphate glass; and
- A small-sized EPM type melter for producing borosilicate glass

https://world-nuclear.org/information-library/country-profiles/countries-o-s/russia-nuclear-fuel-cycle.aspx
An International Spent Nuclear Fuel Storage Facility: Exploring a Russian Site as a Prototype: Proceedings of an International Workshop. Washington, DC: The National Academies Press. https://doi.org/10.17226/11320.
https://www.neimagazine.com/news/newsmayak-to-start-reprocessing-of-fuel-from-beloyarsk-amb-reactors-9896420

HLW vitrification in Russia

- Mayak EP-500/x JHCM melters use single-stage vitrification process
- Phosphoric acid (H_3PO_4) is added directly to melter together with aqueous waste
- Sodium aluminophosphate glass is produced
- Phosphate glasses believed to exhibit high capacity to incorporate sulphate*
- Iron present as few % as impurity
- 7700 tonnes glass produced since 1980's
- Similar mass to US total glass production and French total glass production
- Radon Institute also used borosilicate glasses to vitrify LILW

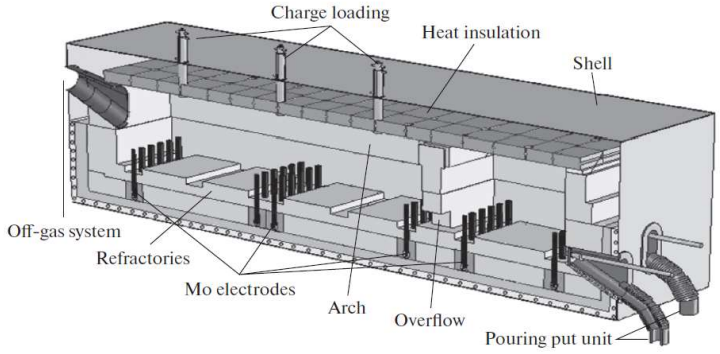


Fig. 3. Scheme of HLW vitrification furnace EP-500/5, "Mayak" Facility (Dubkov and Remizov, 2015).

Oxide compositions of HLW glasses, wt.% [30].

Country	Facility	SiO_2	P_2O_5	B_2O_3	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	PbO	MnO	Na_2O	Misc.
Belgium	Pamela	–	70.7	–	7.1	22.2	–	–	–	–	–	–	–
Belgium	Pamela	52.7	–	13.2	2.7	–	–	4.6	2.2	–	–	5.9	18.7.
France	AVM	46.6	–	14.2	5.0	2.9	–	4.1	–	–		10.0	17.2
France	R7/T7	54.9	–	16.9	5.9	–	–	4.9	–	–		11.9	5.5
Germany	VEK	60.0	–	17.6	3.1	–	–	5.3	–	–		7.1	6.9
India	WIP	30.0	–	20.0	–	–	–	–	–	25.0		5.0	20.0
India	AVS	34.1	–	6.4	–	–	6.2	–	–	–	9.3	0.2	43.8
Japan	TRP	46.7	–	14.3	5.0	–	–	3.0	–	–	–	9.6	21.4
Russia	EP500	–	53.3		15.8	1.6	–	–	–	–	–	23.5	5.8
UK	WVP	47.2	–	16.9	4.8	–	–	–	5.3	–	–	8.4	17.4
US	DWPF	49.8	–	8.0	4.0	–	–	1.0	1.4	–	–	8.7	27.1
US	WVDP	45.8	–	8.4	6.1	11.4	–		1.4	–	–	9.1	17.8
US	WTP	50.0	–	20.0	5.0	–	–		–	–	–	25.0	–

Misc. – Miscellaneous, including oxides of radioactive waste.

Glass/Country Oxide (wt%)	SiO_2	P_2O_5	B_2O_3	Al_2O_3	CaO	MgO	Na_2O	Misc	Waste Oxides
R7/T7, France	47.2	–	14.9	4.4	4.1	–	10.6	18.8	28
DWPF, USA	49.8	–	8.0	4.0	1.0	1.4	8.7	27.1	33
SRNL, USA	30.5	1.1	15.2	25.0	6.1	0.1	9.6	13.5	45[a]
WVP, UK	47.2	–	16.9	4.8	–	5.3	8.4	17.4	25 (up to 35–38)
Pamela, Germany–Belgium	52.7	–	13.2	2.7	4.6	2.2	5.9	18.7	30
Mayak, Russia	–	52.0	–	19.0	–	–	21.2	7.8	33[b]
Radon K-26, Russia	43	–	6.6	3.0	13.7	–	23.9	9.8	35[c]
P0798, Japan	46.6	–	14.2	5.0	3.0	–	10.0	20.2	
GC-12/9B, China	46.2	–	13.4	4.2	2.5	1.5	9.1	23.1	

DWPF – Defence Waste Processing Facility, Savannah River Site, US; SRNL – Savannah River National Laboratory, US; WVP – Waste Vitrification Plant, Sellafield, UK.
[a]This glass has been developed to host Hanford high-Al radioactive waste.
[b] ≤10 for fission products and minor actinide oxides.
[c]This glass is designed for sodium-containing LLW and ILW.

S. V. Stefanovsky et al., Chemical-Technological and Mineralogical-Geochemical Aspects of the Radioactive Waste Management, Geochem. Int. 54 (2016) 1136–1156. M. I. Ojovan & W. E. Lee, An Introduction to Nuclear Waste Immobilisation, Elsevier, 2nd Ed., 2013; M. I. Ojovan & W. E. Lee, New Developments in Glassy Nuclear Wasteforms, Nova Publishers, 2007; M. I. Ojovan & S. V. Yudintsev, Open Ceramics 14 (2023) 100355.

HLW Vitrification: Global Summary and the Future?

- HLW vitrification is a mature technology, with decades of accumulated operational experience across many countries
- Wastes differ between countries and within countries, and each country has tailored its selection of vitrification technologies and its glass formulations to its own situation
- Consequently, a wide range of vitrification technologies, glass formulations and wastes exists
- In the main, alkali borosilicate glasses have been selected globally
- However, “the devil is in the detail”
  - Students and postdocs: look deeper and understand why there is such variety!

- Future prospects?
  - Some HLW vitrification programs are running down (e.g., UK has closed reprocessing facilities)
  - Other HLW vitrification programs will soon come online (e.g., WTP, USA)
  - Other HLW vitrification programs will continue / evolve (e.g., France, India, Russia, Japan)
  - ...and other HLW vitrification programs may grow (e.g., China)

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Thanks for your attention!