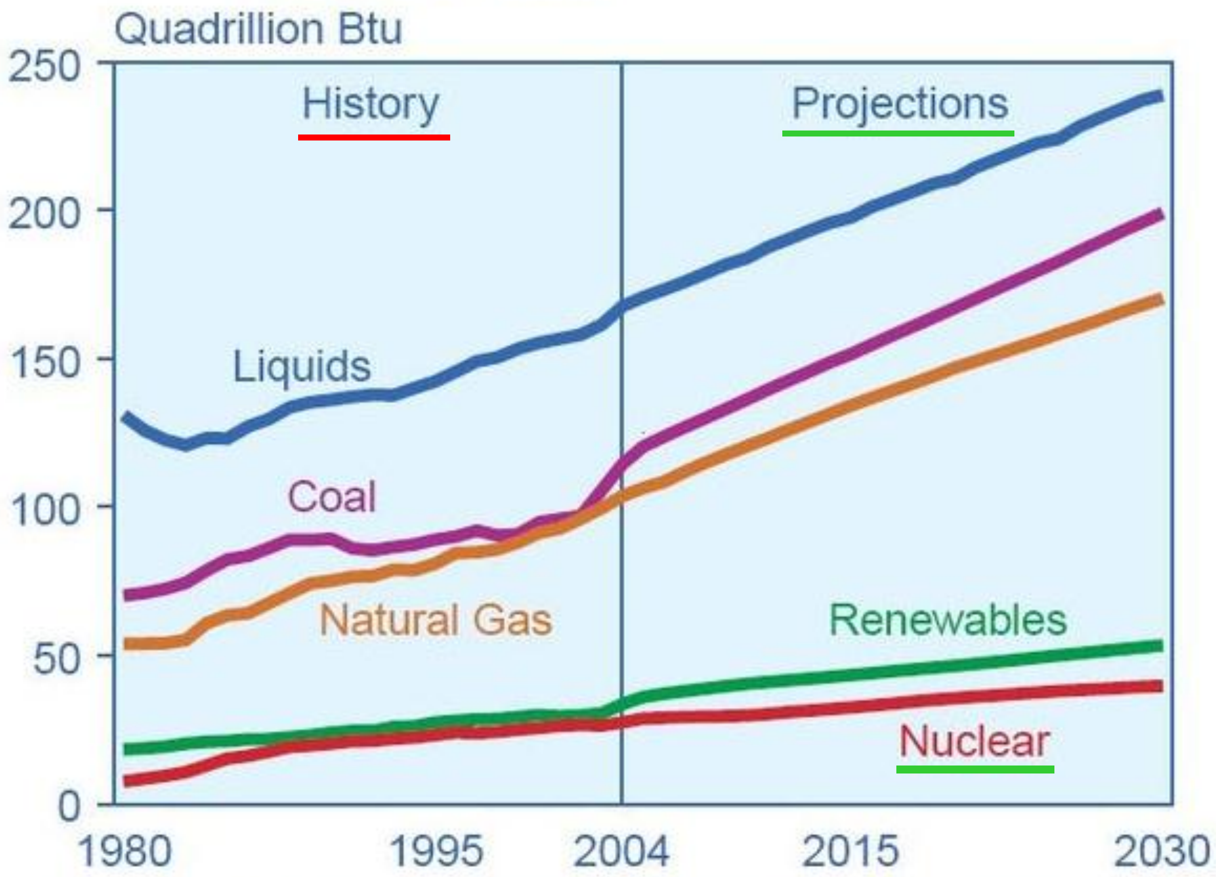
Glass in energy

Glasses for nuclear waste vitrification

MAT 498

Lehigh University

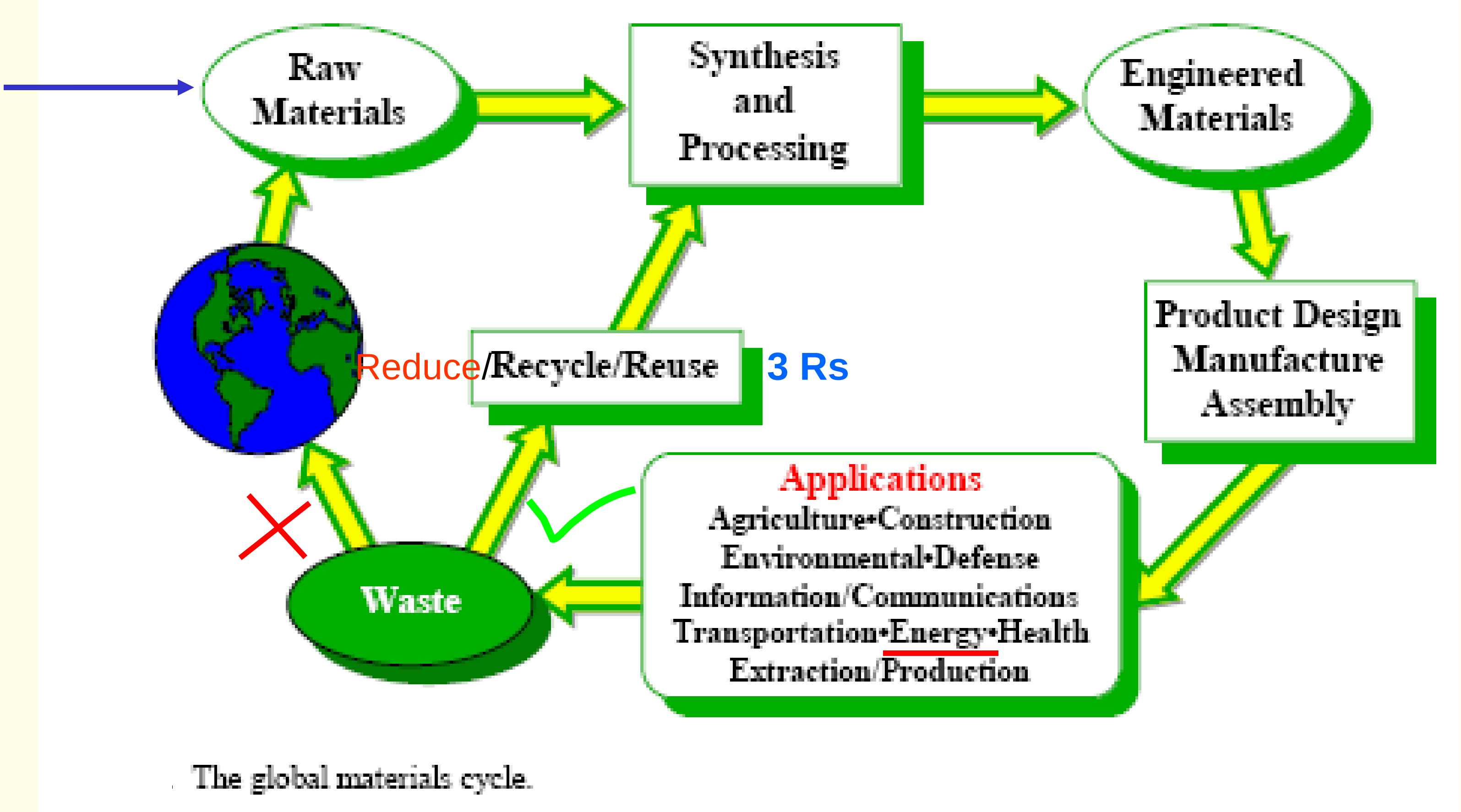
World Marketed Energy Use by Fuel Type, 1980-2030



Sources: **History:** Energy Information Administration (EIA), *International Energy Annual 2004* (May-July 2006), web site www.eia.doe.gov/iea. **Projections:** EIA, System for the Analysis of Global Energy Markets (2007).

Adapted from: http://en.wikipedia.org/wiki/Nuclear_power (3 March 2012)

Global materials cycle



The global materials cycle.

Adapted from: Carol M. Jantzen et al. WSRS-MS-2000-00105, Rev. 0

Nuclear power plants for electricity generation

and

waste management

Susquehanna steam electric station (boiling water reactor)

Adapted from: http://en.wikipedia.org/wiki/Nuclear_power (3 March 2012)

Approximately 15% of the electrical power in the world is generated in nuclear power plants, without significant CO_2 emissions.

However, there are radioactive wastes produced, in particular high level wastes, which must be properly isolated and stored.

High-level waste (HLW) arises from the 'burning' of uranium fuel in a nuclear reactor and it is the most toxic waste form of the nuclear industry.

HLW accounts for over 95% of the total radioactivity produced in the process of electricity generation. There are two distinct kinds of HLW:

- Used fuel itself (direct disposal)

- Separated waste from reprocessing the used fuel (liquid HLW from reprocessing, which must be solidified)

Each year, nuclear power generation facilities worldwide produce about 10,000 m^3 of HLW, including used fuel designated as waste.

But the volume of waste produced by the nuclear industry is still very small when compared with other toxic wastes generated. E.g. in the OECD countries, some 300 million tons of toxic wastes (very roughly ~ 50 million m^3) are produced each year, whereas the total conditioned radioactive wastes, including low and intermediate level forms, amount to only 81,000 m^3 per year (it is roughly 50 million vs. 80 thousand m^3 only).

Used fuel gives rise to HLW, which may be either the used fuel itself in fuel rods, or the separated waste arising from its reprocessing. But in either case, the amount is modest and a typical reactor generates about 27 tons (~ 2 m^3) of spent fuel per year, yielding ~ 75 m^3 of encapsulated disposal volume if it is treated as waste and vitrified as such, or only 3 m^3 per year of vitrified waste if the fuel is reprocessed.

Nuclear fuel processing

Uranium oxide concentrate from mining, essentially *yellowcake* (U_3O_8), is not significantly radioactive – barely more so than the granite used in buildings. It is refined and then converted to uranium hexafluoride gas (UF_6). As a gas, UF_6 undergoes enrichment to increase the U-235 content from 0.7% to about 3.5%. It is then turned into a hard ceramic oxide (UO_2) for assembly as reactor fuel elements.

Highly radioactive fission products and also transuranic elements are produced from uranium and plutonium during reactor operations and are contained within the used fuel.

Any used fuel will also contain some of the original U-235 as well as various plutonium (Pu) isotopes formed inside the reactor core, and U-238. Where countries have adopted reprocessing to recycle material from used fuel, the fission products and minor actinides are separated from uranium and plutonium and treated as HLW (while **U** and **Pu** are **re-used** as fuel in reactors). In countries where used fuel is not reprocessed, the used fuel is considered a waste itself and therefore classified as HLW.

HLW is the major issue arising from the use of nuclear reactors to generate electricity.

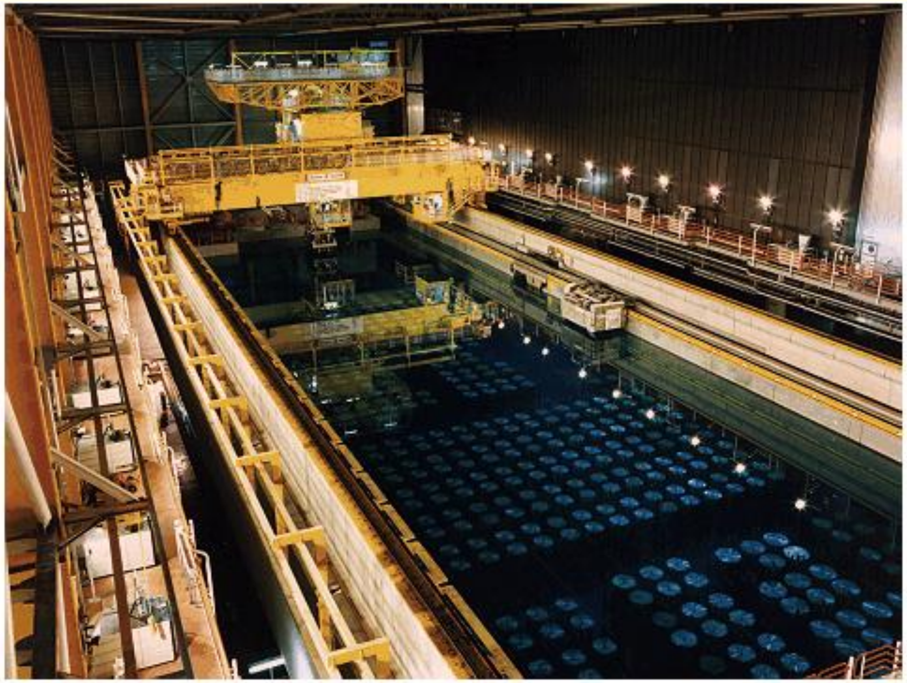
HLW storage and disposal

For the encapsulation of HLW, **glass** is the material of choice, due to its good chemical durability and superior radiation and thermal stability. The compositional variability of glass is also highly convenient for the storage of different nuclear waste materials and its well established processing techniques ensure large scale storage.

Storage occurs mostly in ponds at reactor sites, or occasionally at a central site. Some 90% of the world's unreprocessed used fuel is stored like this and some of it has been there for decades. The ponds are at least 7 m deep, to allow at least 3 m of water over the used fuel to fully shield it. However, since the **vitrified** used fuel largely consists of uranium (with a little plutonium), it still represents a potentially valuable resource for possible future use.

Direct disposal of used fuel has been chosen by the USA and Sweden among others, although evolving concepts lean towards making it recoverable if future generations see it as a resource.

The largest-scale nuclear waste central vitrification facility in the US is the Savannah River Site (DoE, SC), where over 4 million kgs of radioactive waste have been produced for the past 15 years.



Storage pond for used fuel at the Thermal Oxide Reprocessing Plant at the UK's Sellafield site

Adapted from: Radioactive waste management (World Nuclear Association, July 2011).

Storage pond
with **used fuel**

If the used fuel is reprocessed, HLW must be solidified first and it comprises highly-radioactive fission products and some transuranic elements with long-lived radioactivity. These are separated from the used fuel, enabling the U and Pu to be recycled. The HLW is vitrified, encapsulated into heavy stainless steel cylinders about 1.3 metres high and stored for eventual later disposal deep underground. This material has no conceivable future use.

France has two commercial plants to vitrify HLW left over from reprocessing oxide fuel, and there are also plants in the UK and Belgium. Some of these plants have been operating for more than three decades.

Loading silos with canisters containing vitrified HLW in the UK. Each disc on the floor covers a silo holding ten canisters.

Adapted from: Radioactive waste management (World Nuclear Association, July 2011).

After 40-50 years, the heat and radioactivity of the stored HLW have fallen to one thousandth (0.1 %) of the level at removal and the used fuel assemblies are ready for encapsulation or loading into casks, for indefinite storage or permanent disposal underground.

To ensure that no significant environmental releases occur over tens of thousands of years, “multiple barrier” geological disposal is necessary. This immobilizes the radioactive elements in HLW and some ILW and isolates them from the biosphere. The main barriers are:

- Immobilizing waste in an insoluble matrix like glass
- Sealing it inside a corrosion-resistant container, such as stainless steel
- Locating it deep underground in a stable rock structure

The process of selecting appropriate deep geological repositories is now underway in several countries. Finland and Sweden are well advanced with plans for direct disposal of used fuel. Both countries have selected their sites in Sweden. The USA has opted for a final repository at Yucca Mountain (Nevada), though this is now pending political decision.

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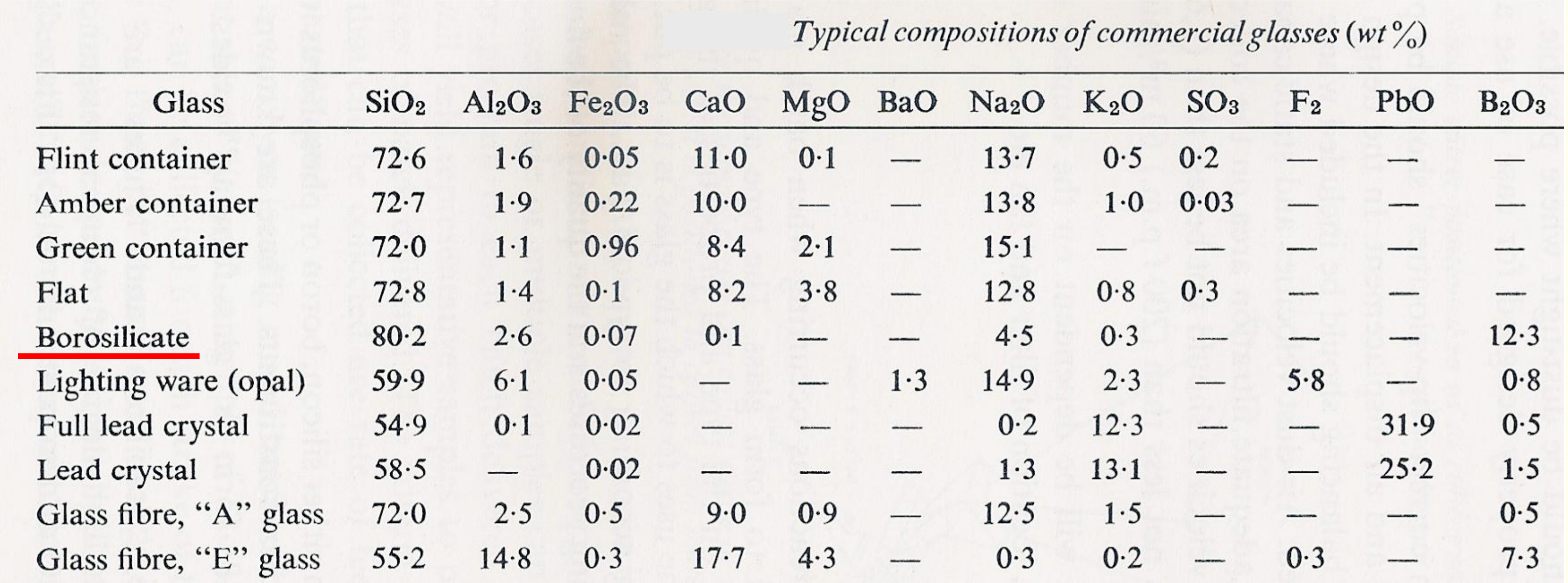
Vitrification process

Nuclear waste vitrification, a process in which the waste forms are melted together with stable glass compositions, has several advantages, namely: a large number of radioactice elements can easily be incorporated into the glass, producing highly durable and mechanically strong small-volume waste products.

Silicate glasses, in particular borosilicate (high silica) compositions (like those used in Pyrex and other commercial glasses), have very good chemical stability and are normally used at present.



Typical compositions of commercial glasses (wt %)

Glass	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	BaO	Na_2O	K_2O	SO_3	F_2	PbO	B_2O_3
Flint container	72·6	1·6	0·05	11·0	0·1	—	13·7	0·5	0·2	—	—	—
Amber container	72·7	1·9	0·22	10·0	—	—	13·8	1·0	0·03	—	—	—
Green container	72·0	1·1	0·96	8·4	2·1	—	15·1	—	—	—	—	—
Flat	72·8	1·4	0·1	8·2	3·8	—	12·8	0·8	0·3	—	—	—
Borosilicate	80·2	2·6	0·07	0·1	—	—	4·5	0·3	—	—	—	12·3
Lighting ware (opal)	59·9	6·1	0·05	—	—	1·3	14·9	2·3	—	5·8	—	0·8
Full lead crystal	54·9	0·1	0·02	—	—	—	0·2	12·3	—	—	31·9	0·5
Lead crystal	58·5	—	0·02	—	—	—	1·3	13·1	—	—	25·2	1·5
Glass fibre, "A" glass	72·0	2·5	0·5	9·0	0·9	—	12·5	1·5	—	—	—	0·5
Glass fibre, "E" glass	55·2	14·8	0·3	17·7	4·3	—	0·3	0·2	—	0·3	—	7·3

(Adapted from: Glass-making today, P.J. Doyle, Portcullis press, 1979)

Vitrification of radioactive and/or hazardous wastes into glass is also an attractive option because it atomically bonds the hazardous and radioactive species in a solid glassy matrix. The waste forms produced are, therefore, very durable and environmentally stable over a long period of time. The Environmental Protection Agency (EPA) has declared vitrification the Best Demonstrated Available Technology (BDAT) for high-level radioactive waste (HLW) disposal.

The radioactive waste material is mixed with borosilicate glass frit (powdered BS glass) and melted at ~ 1200 ºC, usually in Joule heated melters. The molten waste glass is **cast** into large stainless steel canisters, holding approximately 1700 kg each. These cannisters are then welded shut and stored at the vitrification facility, in ponds, before being eventually moved into a more definitive geological site.

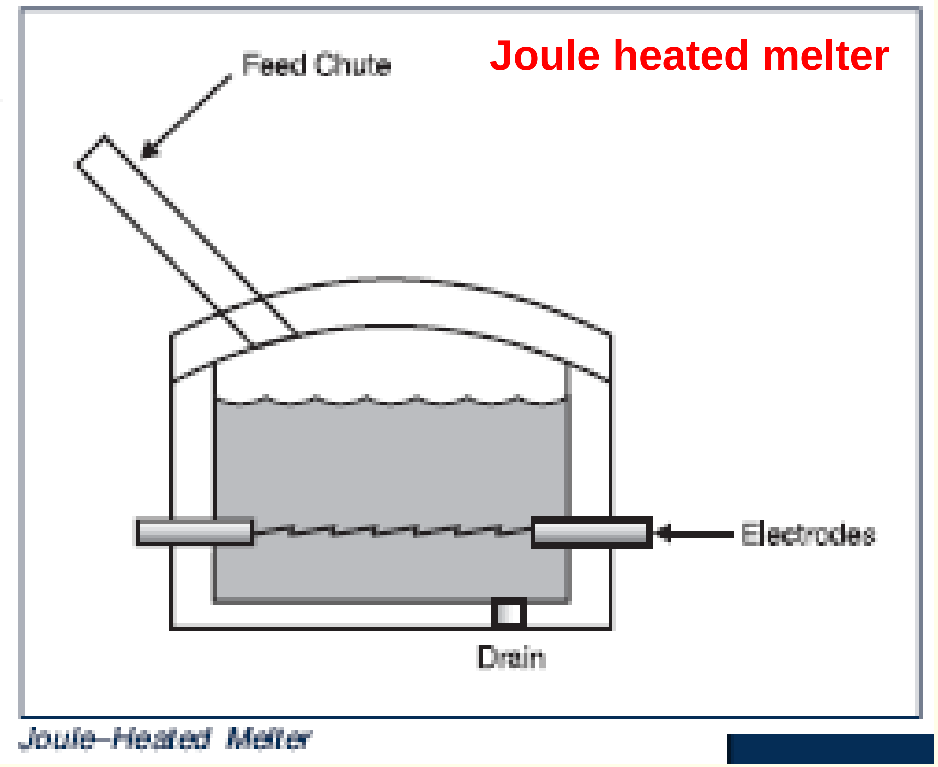
Melting techniques

- Joule heated melting, including compact melter technology

- Induction melting

- Plasma arc vitrification

A new generation of high throughput **Joule heated melters**, available from the commercial glass industry, allow for rapid **vitrification** of large volumes of waste.
The electrical current which passes through the melt heats it due to the Joule effect.



Joule heated melter

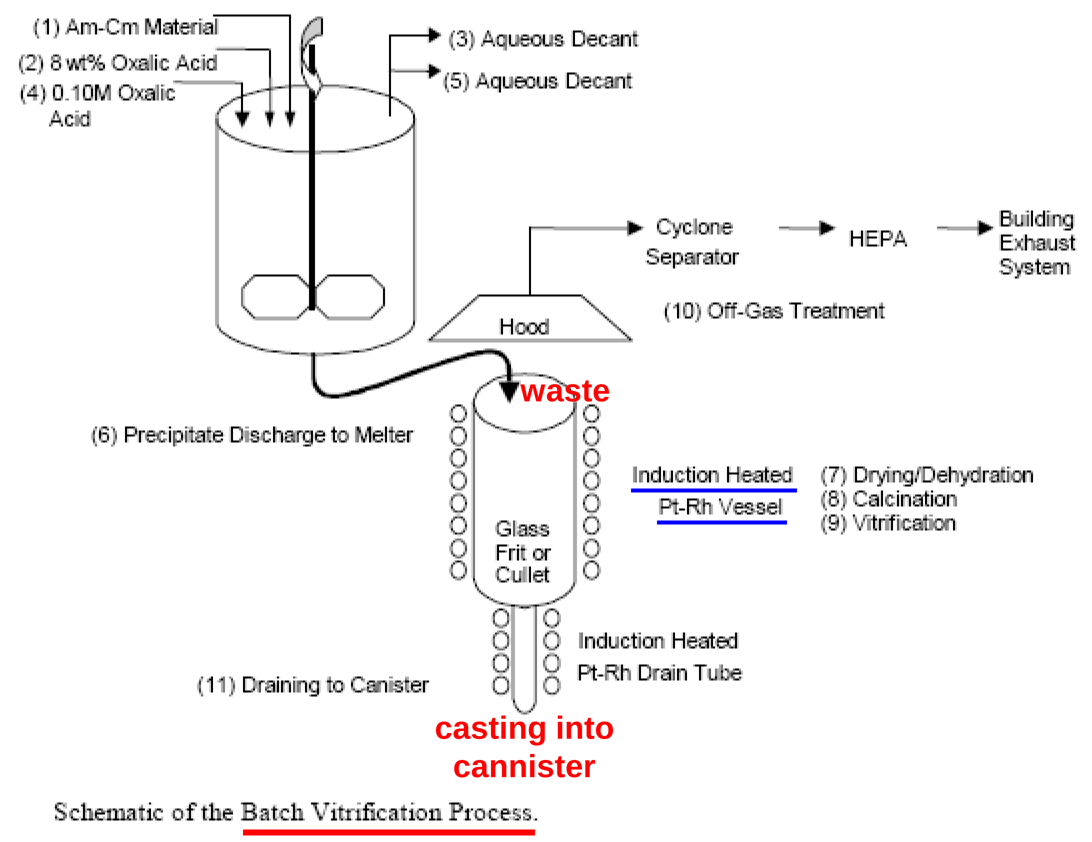
Adapted from: Waste vitrification systems: lessons learned (US DoE Report, March 1999).

Compact melter technology minimizes capital and operating costs, making vitrification cost effective on a life cycle basis, compared to other stabilization technologies which do not support recycle uses. The compact, modular Joule heated melter can be transported from waste site to waste site.

Transportable Vitrification System (TVS) in the field. Composed of 5 modules, a feed batch preparation module (left) with an exterior waste tank or hopper, a melter module (center double story), an off-gas module (along front face of concrete pad with a 40 foot tall off-gas stack), a control/power supply module (behind the off-gas and melter module). Co-designed by EnVitco Corporation and SRTC [24].

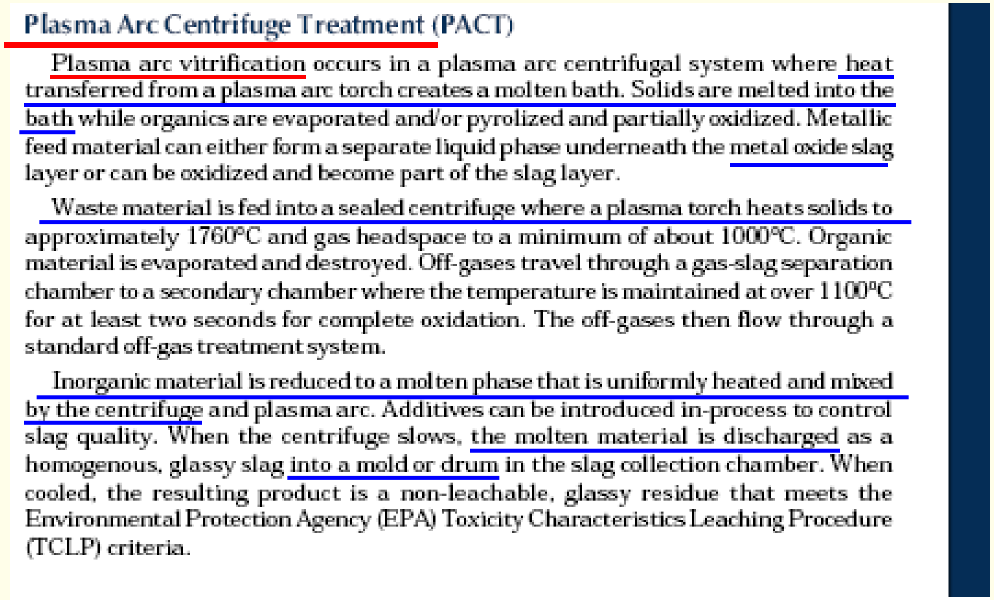
Adapted from: Carol M. Jantzen et al. WSRS-MS-2000-00105, Rev. 0

Induction melters with high throughput, also used in the commercial glass industry, are robust and compact enough to handle high throughput vitrification of TRU (transuranic, containing PU) wastes.



Schematic of the Batch Vitrification Process.

Adapted from: Carol M. Jantzen et al. WSRS-MS-2000-00105, Rev. 0

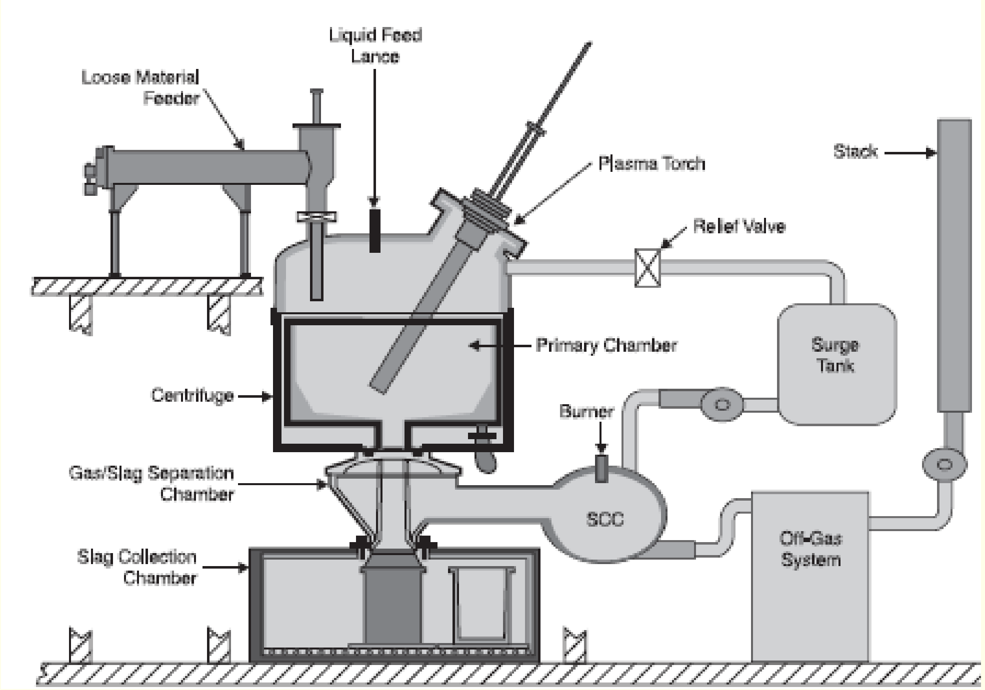


Plasma Arc Centrifuge Treatment (PACT)

Plasma arc vitrification occurs in a plasma arc centrifugal system where heat transferred from a plasma arc torch creates a molten bath. Solids are melted into the bath while organics are evaporated and/or pyrolized and partially oxidized. Metallic feed material can either form a separate liquid phase underneath the metal oxide slag layer or can be oxidized and become part of the slag layer.

Waste material is fed into a sealed centrifuge where a plasma torch heats solids to approximately 1760°C and gas headspace to a minimum of about 1000°C. Organic material is evaporated and destroyed. Off-gases travel through a gas-slag separation chamber to a secondary chamber where the temperature is maintained at over 1100°C for at least two seconds for complete oxidation. The off-gases then flow through a standard off-gas treatment system.

Inorganic material is reduced to a molten phase that is uniformly heated and mixed by the centrifuge and plasma arc. Additives can be introduced in-process to control slag quality. When the centrifuge slows, the molten material is discharged as a homogenous, glassy slag into a mold or drum in the slag collection chamber. When cooled, the resulting product is a non-leachable, glassy residue that meets the Environmental Protection Agency (EPA) Toxicity Characteristics Leaching Procedure (TCLP) criteria.



Adapted from: Waste vitrification systems: lessons learned (US DoE Report, March 1999).

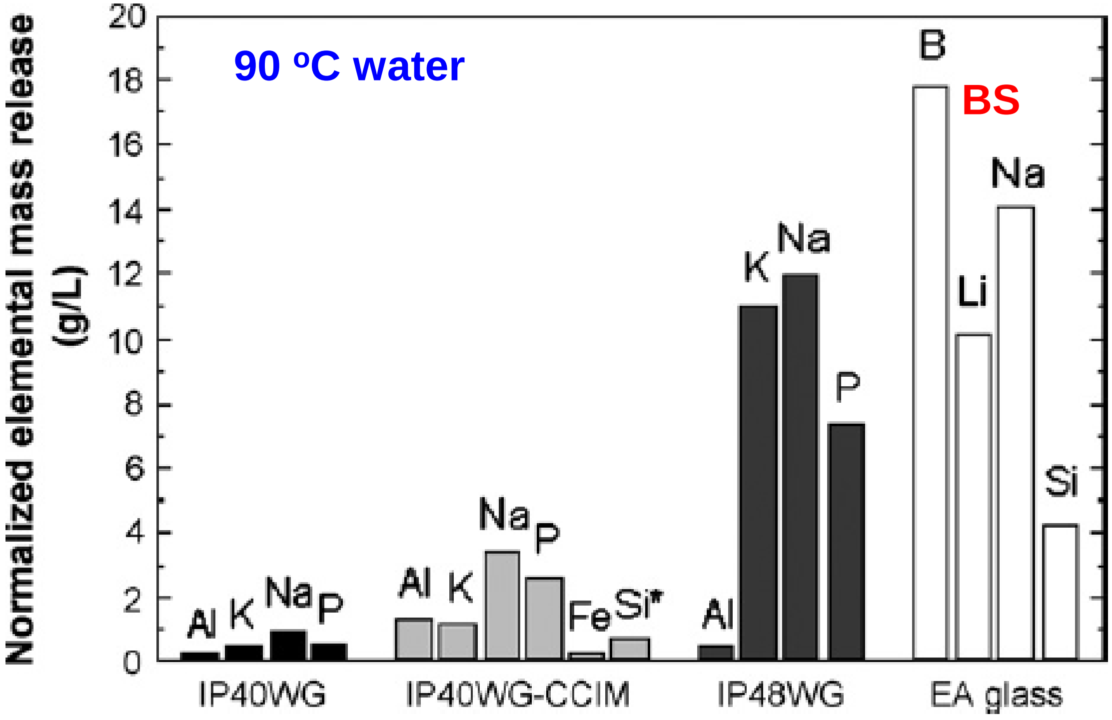
Another possible alternative to the melting of borosilicate glasses involves sol-gel processing of high silica glasses, which has the advantage of low temperature sintering compared to high temperature melting.

Deptula et al. [2] have proposed the use of gels which were heat treated, either as powders or as sintered monoliths.

Cs- Sr-, Co- and Nd- heavy metal (HM)-doped (10 mol%) silica gels were prepared and heat treated. Subsequent leaching tests in water were also performed.

It was found that all the HM elements were fully incorporated into the glass network structure. However, sintered powders and agglomerates were not found to be sufficiently stable against leaching in room temperature water. The final gel-derived forms need to be properly densified, with or without the use of pressure.

Non-silicate glasses have also been investigated, namely phosphate-based compositions, by Delbert Day and co-workers [4,5] and other researchers for the past ~ 15 years. These glasses have excellent chemical durability, with some compositions being ~ 1,000 times more durable than conventional borosilicate waste glass. The figure below compares the leaching of different **Fe phosphate glasses** with a standard borosilicate glass in water at 90 ºC for a fixed number of days. These glasses have also lower melting T than borosilicates, in the range of 950 – 1150 ºC.



Normalized elemental mass release (g/L) from three sodium waste-loaded iron phosphate glasses (IP) and a standard borosilicate glass (EA); from Kim et al.[54]

Adapted from: Richard K. Brow and Melodie L. Schmitt, J. Eur. Cer. Soc. 29 (2009) 1193.

Iron phosphate glasses have also potential for vitrifying nuclear wastes with high contents of phosphorus, fluorite and heavy metal oxides (e.g. Bi_2O_3 and CsO_2), which are not well suited for borosilicate glasses.

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