Waste Forms for an Advanced Nuclear Fuel Cycle

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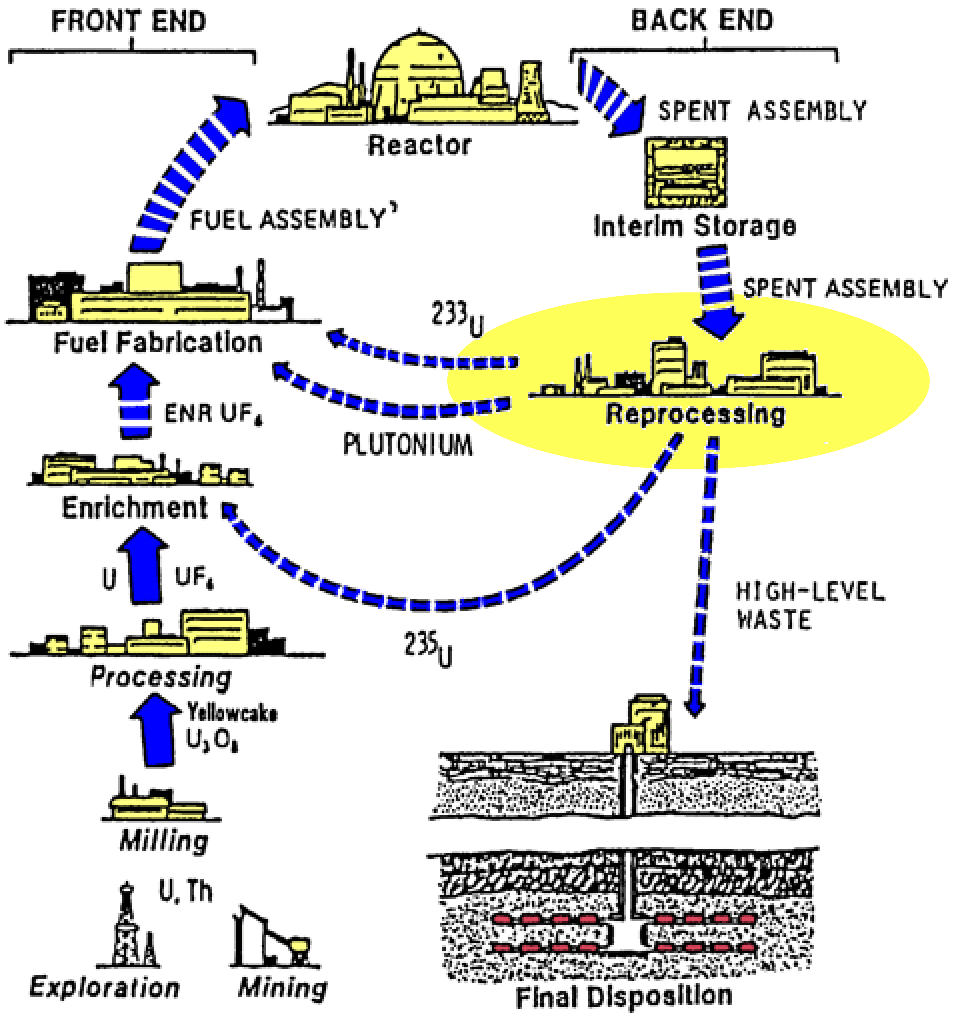
Background

- Vitrification is the process of choice for separated highly radioactive wastes in virtually every reprocessing nation
  - vitrification is: 1) a proven process, 2) tolerant to wide range of waste compositions, 3) a fast continuous process, 4) generates no fine particulates, and 5) the EPA best demonstrated available technology
  - produces a waste form of good performance that is reasonably well understood
- An unprecedented level of waste management control can be achieved through advanced separations
  - separate streams by waste chemistry
  - each stream can be immobilized separately or combined with others
  - the waste forms can be selected to match the waste and disposal environment chemistries

Challenge

- How would we manage wastes from a closed U.S. nuclear fuel cycle
- Need to consider full range of wastes
- This talk will focus only on reprocessing wastes



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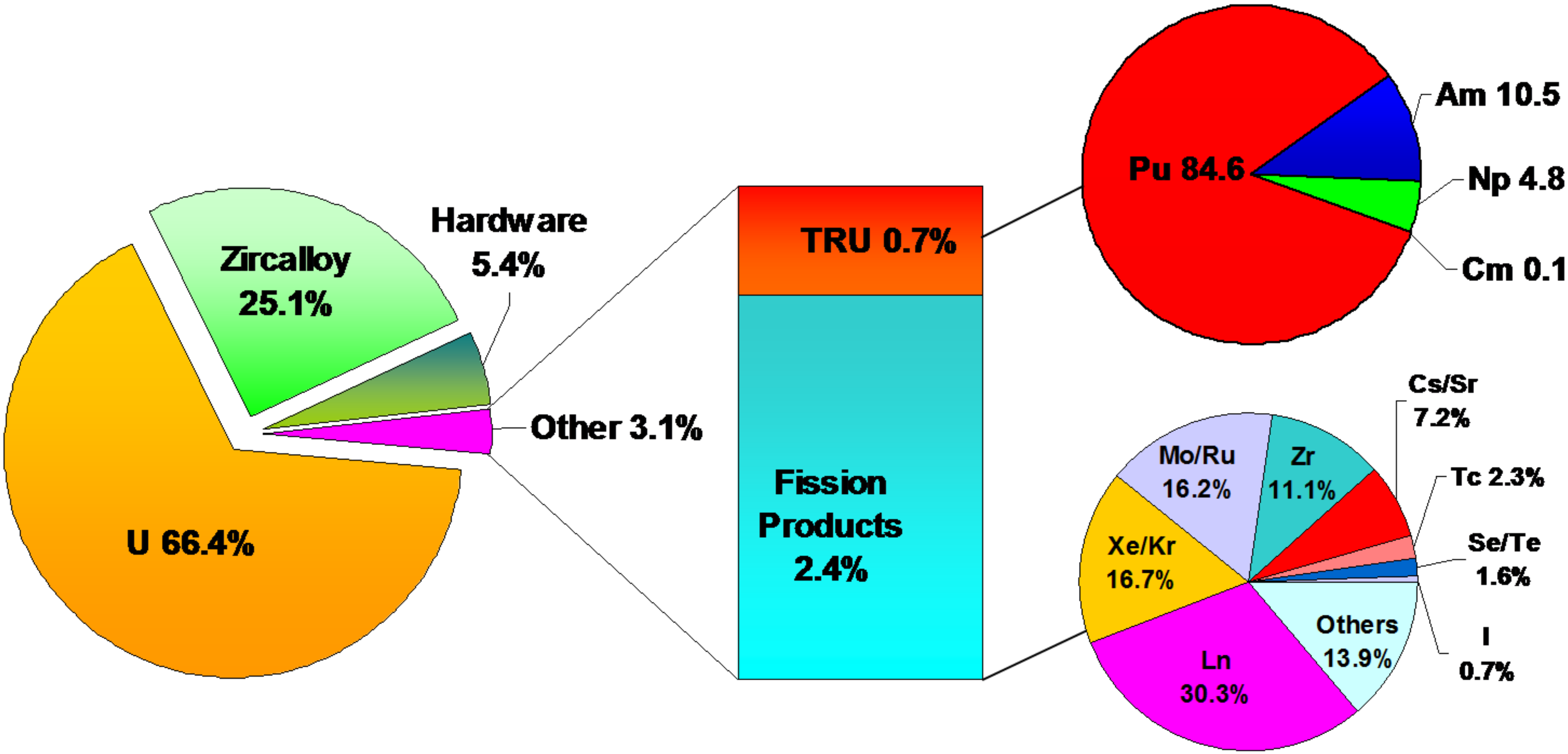
Average U.S. Fuel Composition



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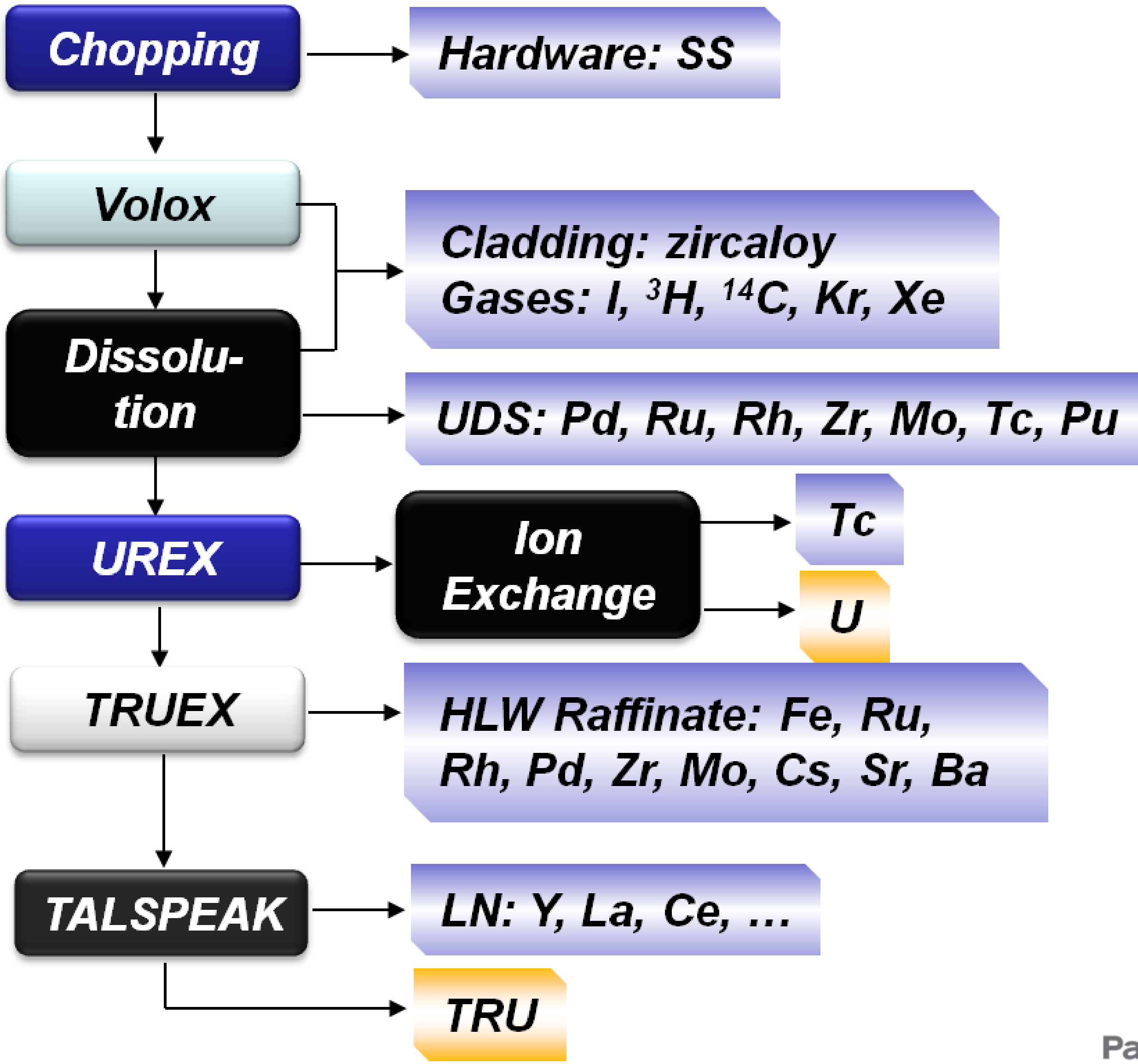
Waste Streams from Typical Aqueous Process



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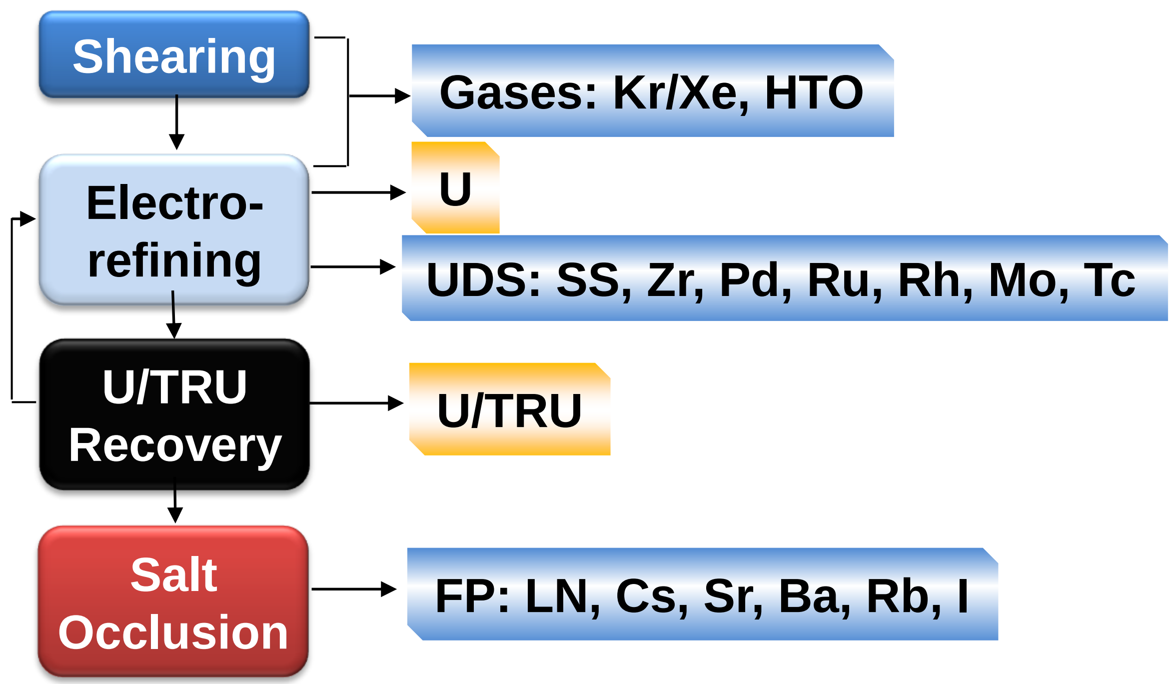
Waste Streams from Typical Pyrochemical Process

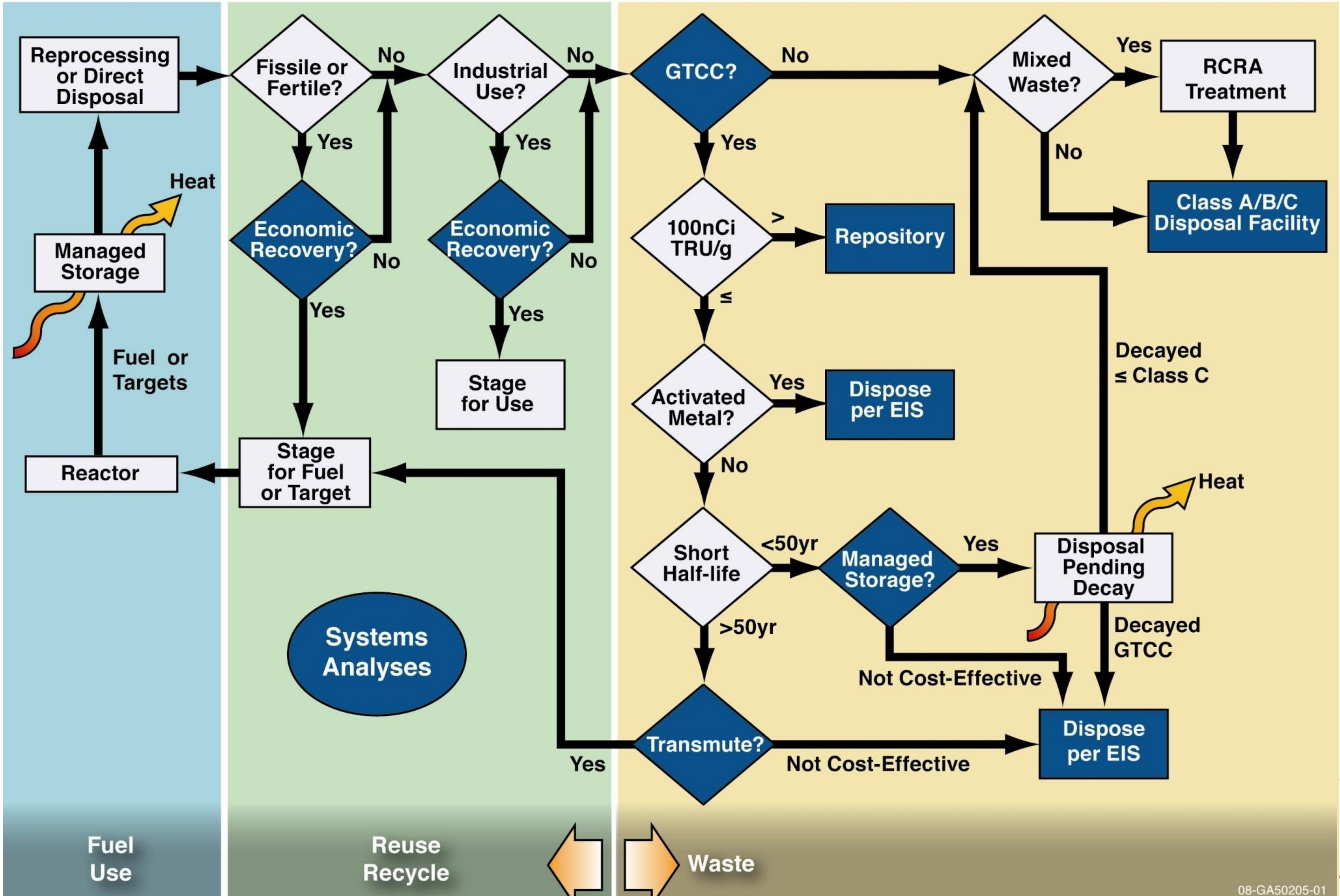


Typical Secondary Wastes

- wastes from each operation including: job control, maint., and operating
- amounts of these wastes are contingent on many factors including: plant capacity, treatment strategy, process complexity

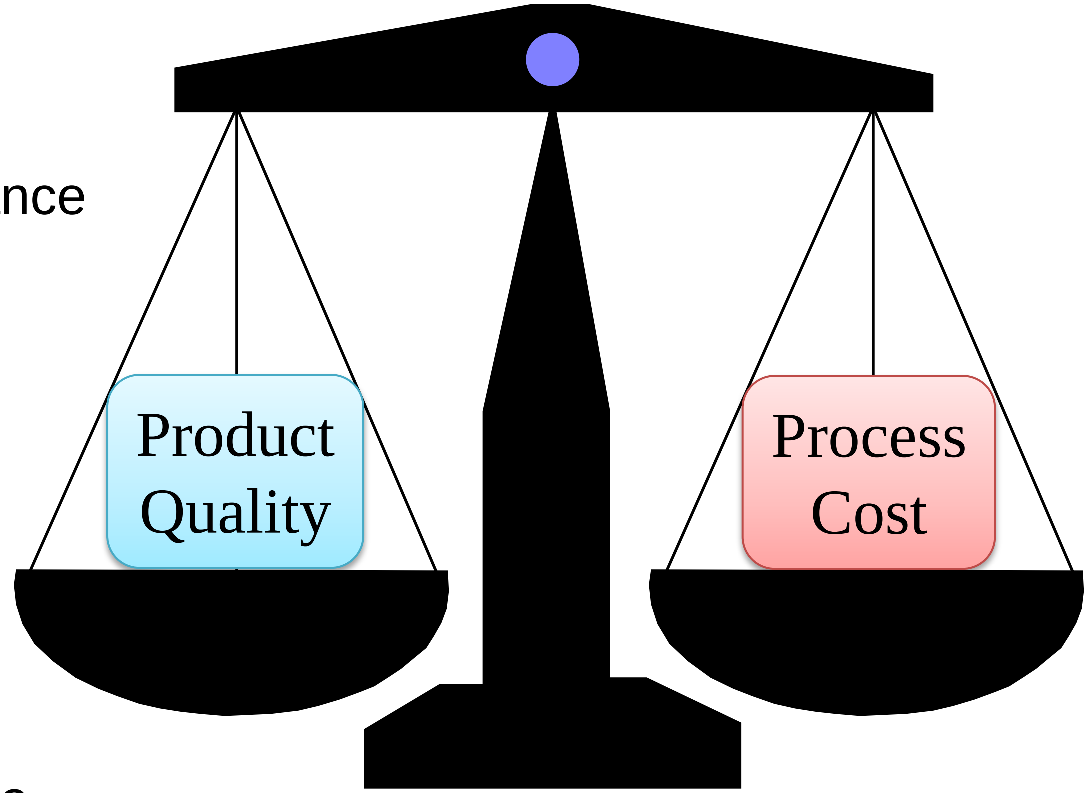
Absorber	Machining chips from MPCs
Containment hut material	Manipulator boots
Decon solution	Misc. wood, concrete, metal, and paint waste
Dewatered resin	Steam condensate
Disposable protective clothing	Off-gas scrub solution
Dust collection filters/bags	Outer containers
Electrical and instrument jumpers	Oxidizer
Evaporator condensate	Plastic suits
Filter cartridges	Pool sludge
Fuel cask and canister decontamination filters	Sample bottles
Fuel cask and canister decontamination wipes	Shear blades
Glovebox filters	Shielding window oil
Gloves	Shoe covers
Heater/heating coil	Spent equipment of every type
HEPA filters	Spent solvent
Inner container (bagless transfer) stub pieces	Step-off pads
Laboratory returns	Used Multi-Purpose Canisters (MPC)
Laundered protective clothing	Used oils
Light bulbs (for in-cell applications)	

Waste Management Strategy



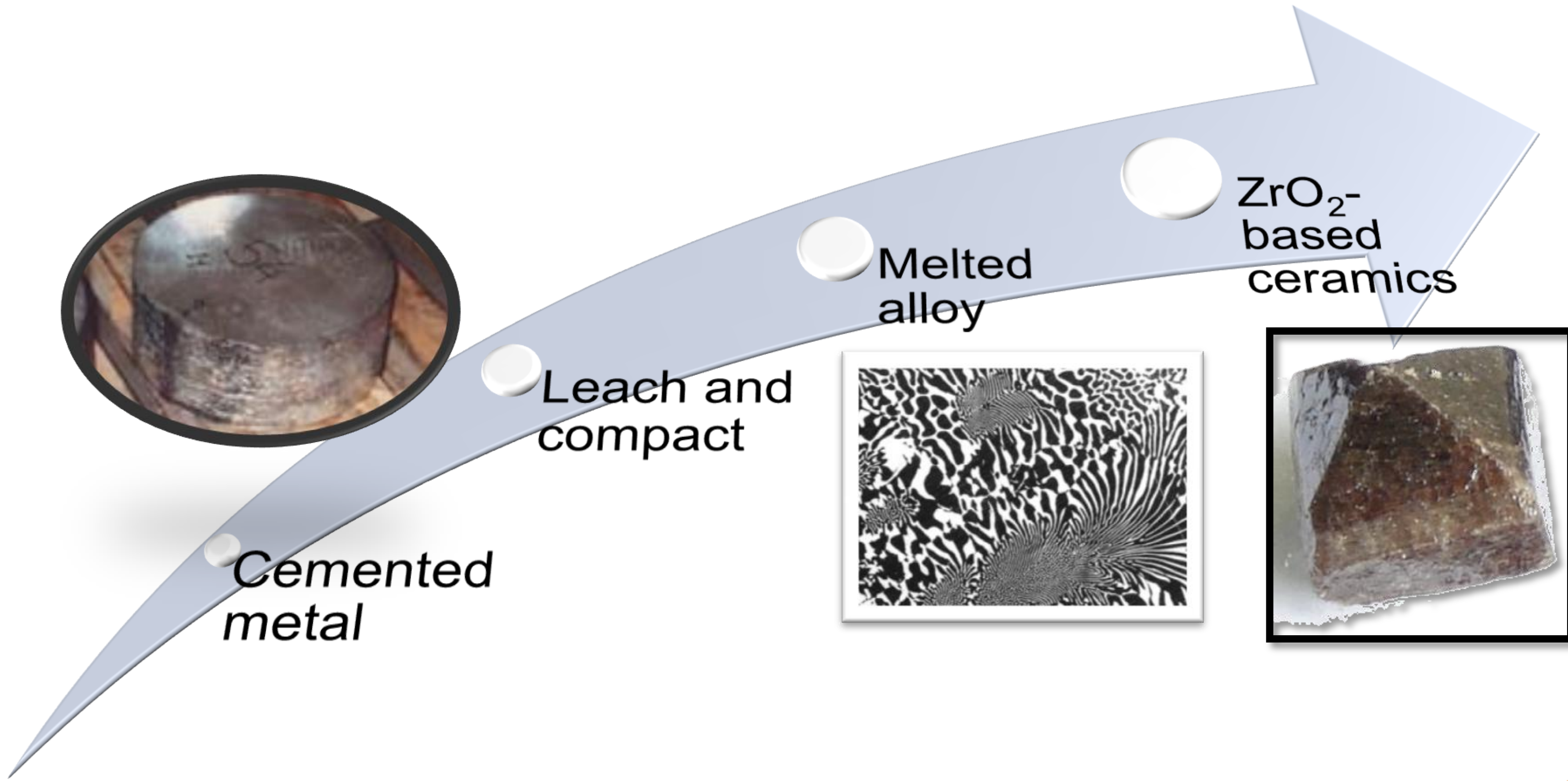
Waste Form Options

- Product quality
  - chemical durability
  - well understood performance
  - thermal stability
  - radiation stability
- Processing and cost
  - low waste form volume
  - small process footprint
  - continuous process
  - mature technology
  - minimum secondary waste
- Raises a critical question
  - how good is good enough?



Example - Hulls and Hardware

Product quality and process cost



Proposed Waste Forms for Aqueous Separated Fuel

Stream	Reference	Alternatives		
Hull, Hardware	Decon, Recycle	Compacted Metal WF	Melted Alloy	Cermets for combined wastes
UDS, Tc	Fe-Alloy	Oxide Ceramic	Epsilon Metal	Glass
HLW Raffinate	BS Glass	Glass Ceramics	PO_4 Glass	Oxide Ceramics
I	Glass Enc Ag-MOR	Collapsed Aerogel	Low-Temp Glass	SiC or other Ceramic
^{85}Kr	Release	Compressed Gas/MOF	Zeolite	SiC
^{14}C	Release	Cement		
^{3}H	Cement			

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Proposed Waste Forms for Pyrochemical Separated Fuel

Stream	Reference	Alternatives		
Hull, UDS	Fe-Zr Alloy	Zr-Fe Alloy		
Salt	Glass bonded sodalite	Alumino-silicates	Tellurite glass	Separate and treat
^{85}Kr	Release	Compressed Gas/MOF	Zeolite	SiC
^{14}C	Release	Cement		
^{3}H	Cement			

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Secondary Waste Treatments

- Blending
- Compaction
- Liquid adsorption
- Fluidized bed steam reforming
- Cementation
- Evaporation
- Incineration
- Polymer encapsulation
- Vitrification
- …

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Example Waste Forms

- Glass
- Metal
- Ceramic

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Potential Glass Streams

- HLW raffinate and its subparts (Cs/Sr, TM, LN, etc.)
- TRU
- Secondary Wastes
- Iodine (low-melting glass)

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Glass Waste Forms

Structure

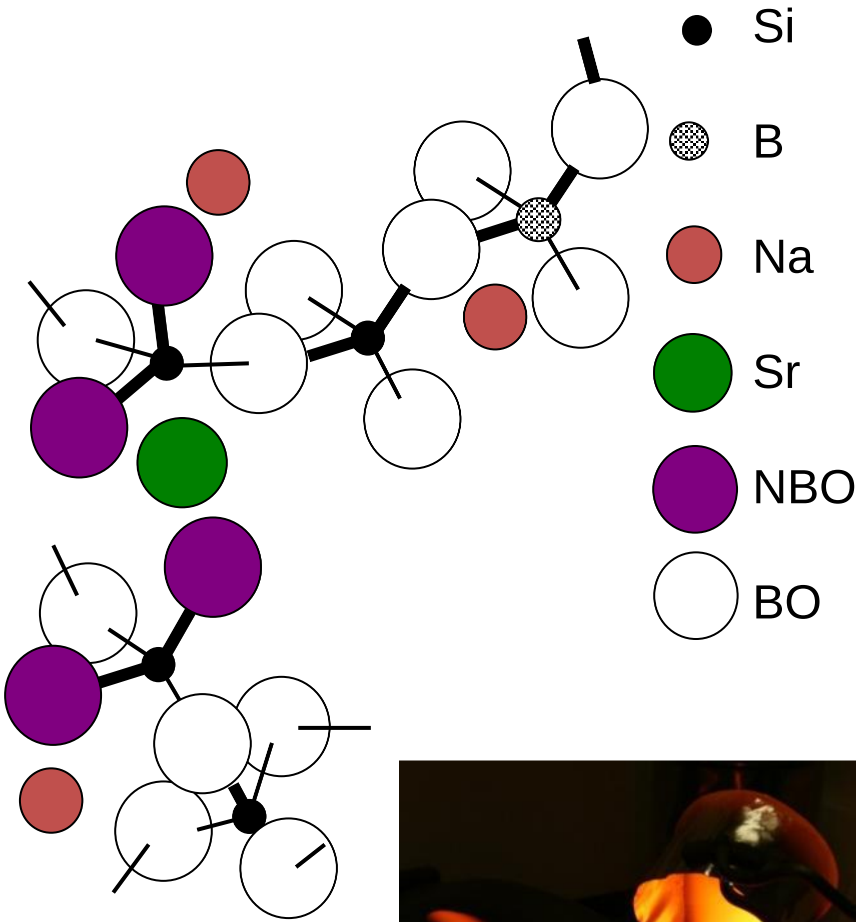
- Amorphous structure: more flexible than crystalline network
- SiO_4^{-4} tetrahedra form the continuous network
- B and Al are modified by waste elements to tetrahedral form
- Waste elements are integral part of glass structure… not simply contained or surrounded

Characteristics

- High flexibility to waste composition
- High speed continuous process

Primary options

- Alkali-borosilicate (ABS)
- Lanthanide-borosilicate (LaBS)
- Iron phosphate (FeP)



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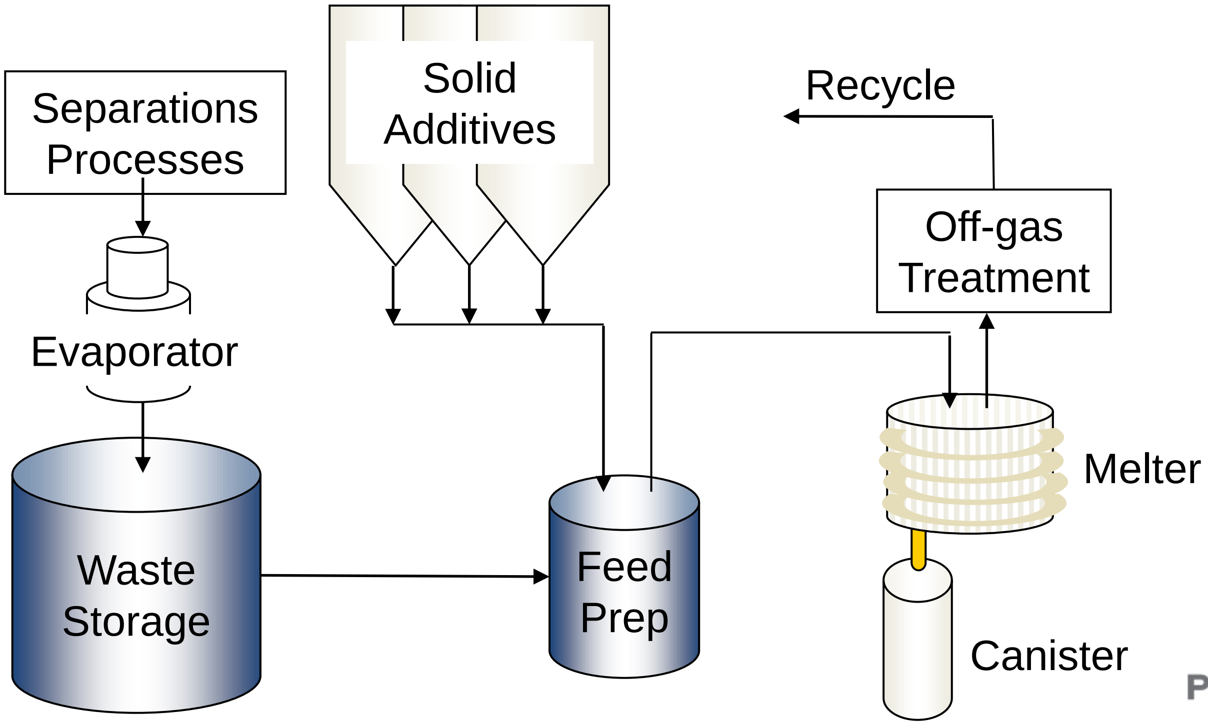
Vitrification Process

- Evaporate waste stream to heat, dose, solubility, etc. limits
- Blend with additives (e.g. aluminosilicates, reductant, …)
- Feed to melter (CCIM, HWIM, …)
- Cast into containers/allow to cool
- Seal, decontaminate or overpack, and store



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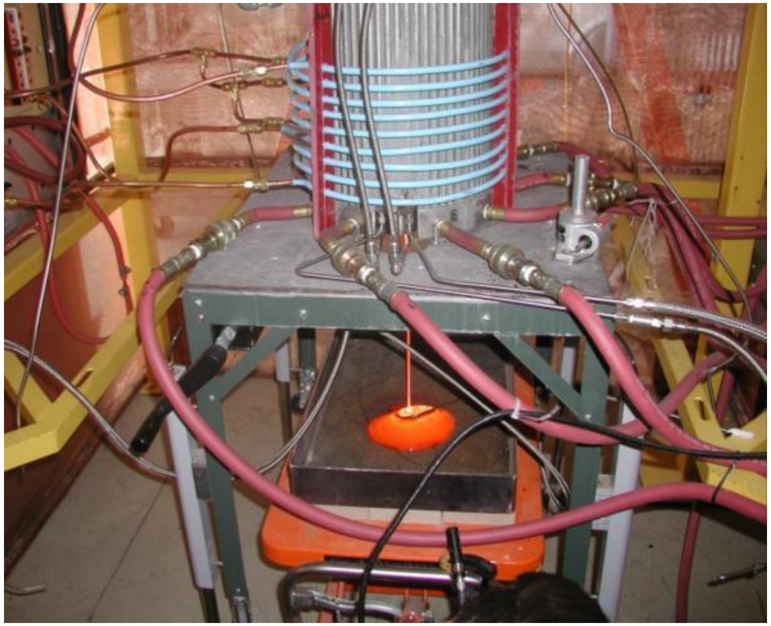
Melters



- A relatively small waste stream will be generated from a 800 MTIHM/y plant
  - from 200 to 400 MTG/y if all potential wastes are vitrified
  - translates to melter sizes of 0.6 m to 0.9 m diameter
- The CCIM and HWIM are thought to best meet this mission due to:
  - small in-cell size, high specific melting rate, tolerance to solid inclusions, ability to fully empty
- HWIM is better able to melt glasses with low alkali content (e.g., LNFP) since the induction couples to the crucible rather than the glass
- CCIM is better able to melt glasses with noble metals (e.g., TMFP or UDS) since the glass "scull" protects the melter

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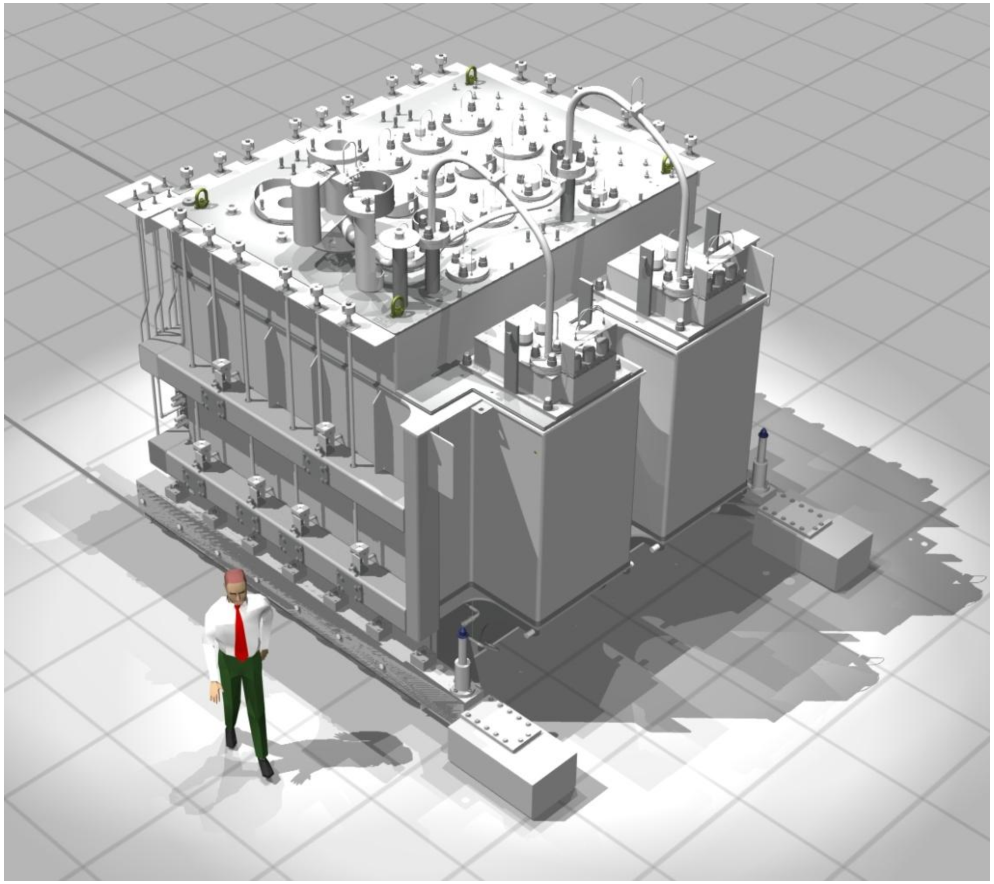
Melters – Joule-Heated, Ceramic-Lined

- Developed in the U.S. for vitrification of defense HLW
- Advantages of JHCM
  - large size capability (heat is deposited to volume rather than surface)
  - well demonstrated at WVDP, DWPF
  - relatively high design life
- Disadvantages
  - large size
  - temperature limits



- In short, well suited to tank waste, but, not for small scale new recycling plant

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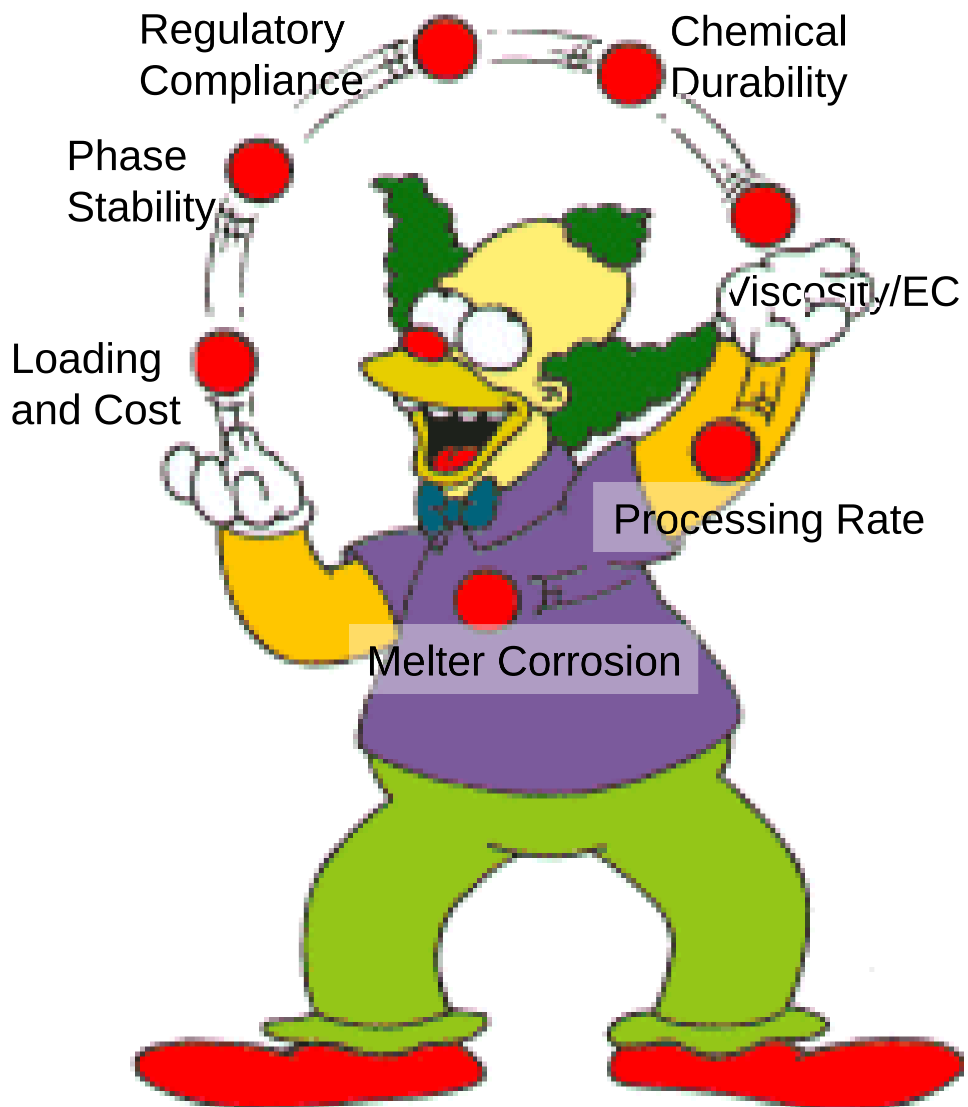
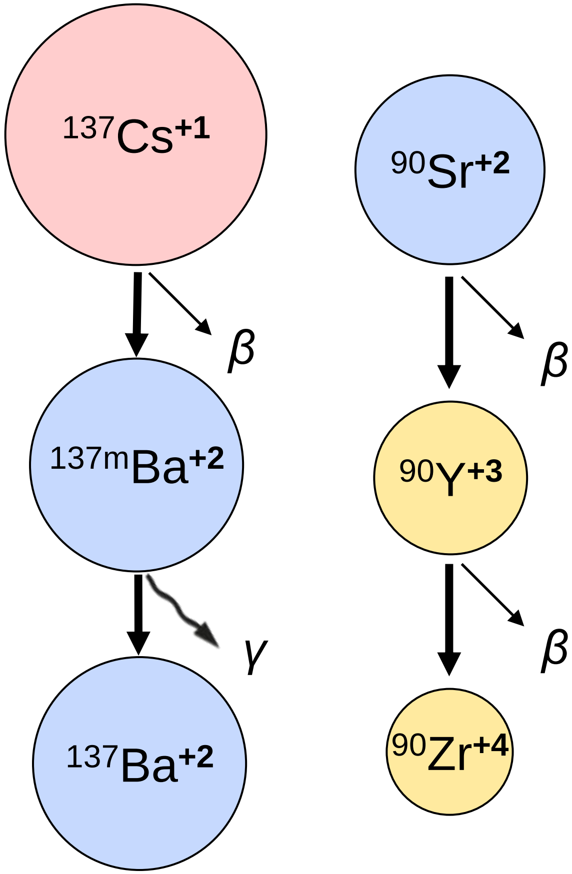
Glass Formulation

- Glass must meet a number of constraints:
  - product quality → chemical durability, thermal conductivity, radiation resistance, regulatory constraints, transition temperature, phase stability etc.
  - processability → melting temperature, crystal formation, inclusions, conductivity
  - economics → waste loading, processing rate, process TOE



Key Formulation Considerations for Advanced Closed Fuel Cycle

- Temperature
  - glass with high Cs/Sr, requires high T_g to ensure that the glass stays as a solid with self-heating
  - this tends to require high melting temp. (limiting melter technology)
  - high thermal conductivity is a plus
- Radiation and decay tolerance
  - radiation generates high β-γ dose
  - decay changes chemistry $Cs^{+} \rightarrow Ba^{2+}$ and $Sr^{2+} \rightarrow Zr^{4+}$
  - high mobility and multivalent oxides
- Volatility (primarily Cs and halides)



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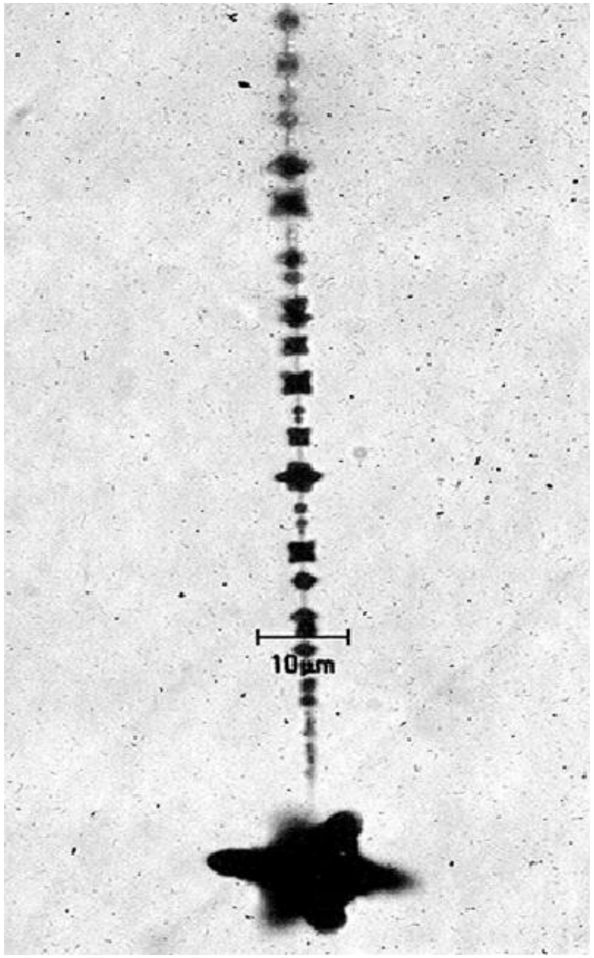
Key Formulation Considerations for Advanced Closed Fuel Cycle

- Solids
  - noble metals (Pd, Rh, Ru) are insoluble in most oxide glasses
  - need a melter technology that will tolerate solid inclusions
  - waste loadings may be set to maintain NM concentration below melter tolerance limit
- Waste solubility
  - many waste components are sparsely soluble in glasses
    - Mo, Cr, S in ABS, higher in FEP
    - AN, LN in FEP, higher in ABS, higher still in LaBS
- Chemical durability



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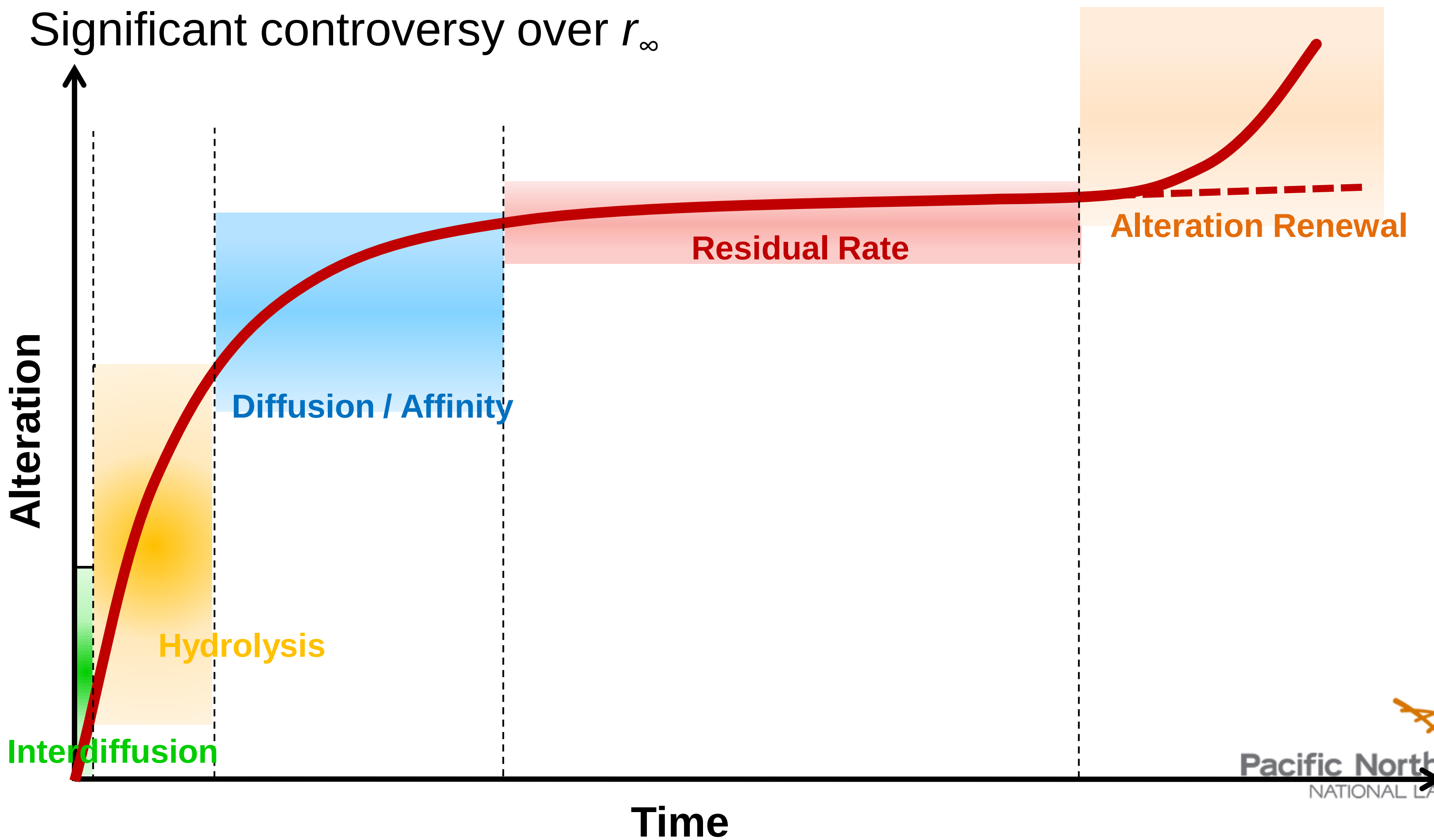
Glass Corrosion Rate

- Waste is incorporated in the glass – that is bound on a molecular scale within the solid
- During reaction with water, the release of most waste components from glass is determined primarily by the rate of glass corrosion
- Need to couple experiments and modeling to estimate release
- Significant controversy over r_∞



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Pros and Cons of Glass as a Waste Form

Pros	Cons
Mature technology	Thermal process (difficult to permit)
Flexible to composition and process variations	Low tolerance to some components (Noble metals, S, Mo, etc.)
Well understood properties including chemical durability	Lower durability than many ceramic phases (e.g., zirconates and titanates)
Continuous process with no respirable fines	Low temperature limit to withstand radiolytic heat ($400 < T_g < 750°C$)
High tolerance to radiation and transmutation	Volatility of Cs requires recycle
Qualified for repository disposal	
High waste loading (low disposal volume)	
Typically single phase waste form	

Potential Metal Waste Streams

- UDS
- Tc (aq)
- TMFP (if separated)

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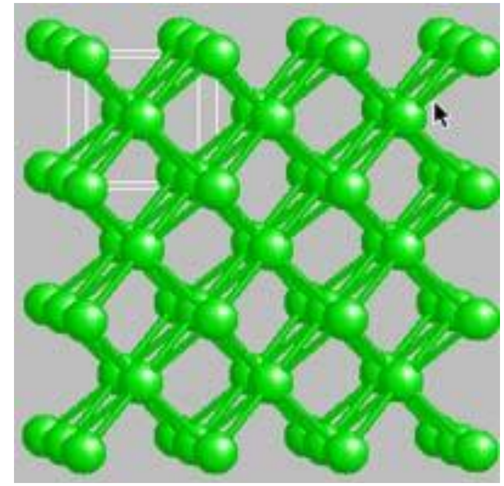
Metal Waste Forms



<u>Structure</u>

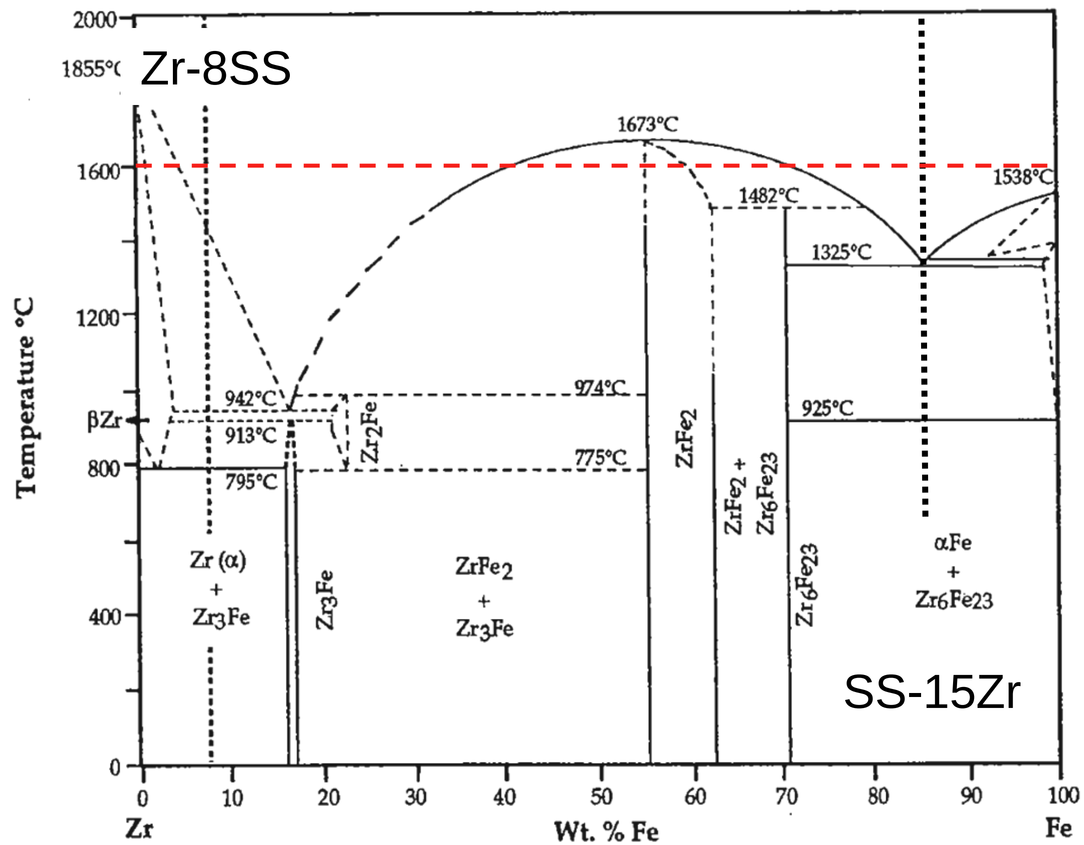
- Crystalline metals
- fcc, bcc, hcp, etc.

<u>Characteristics</u>

- Reduced waste form
- High density
- High thermal conductivity

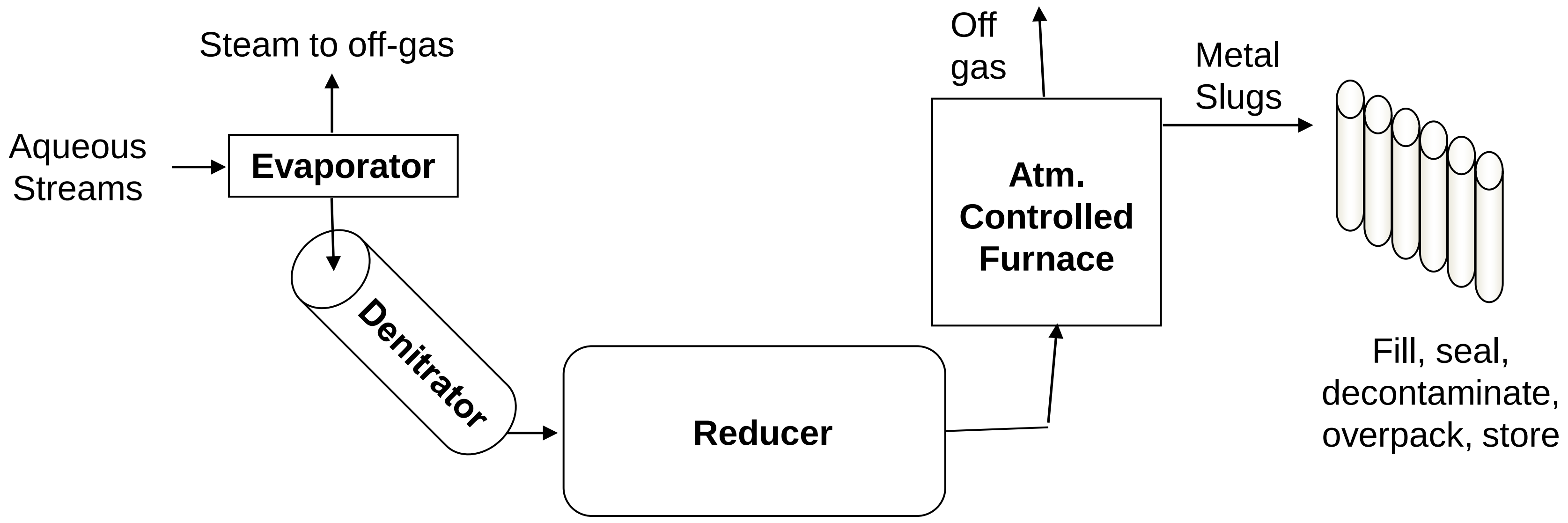
<u>Primary options</u>

- Zr
- Fe
- intermetallics



Metal Process

- Evaporation, calcination, and reduction to form metal
- Combine in crucible with coke and other metal streams
- Melt in crucible, move to canister in “slugs”
- Seal, decontaminate or overpack, and store



Metal Formulation

- Similar process to glass formulation
- Processing (temperature, microstructure development, slag formation, etc.)
- Product (phases formed, radionuclide partitioning, slag properties, corrosion rate)

	Maximum Solute Concentration, atomic%									
	Fe	Cr	Mn	Ni	Mo	Pd	Rh	Ru	Tc	Zr
γ-Fe	—	11.9	100	100	1.7	100	3	23	30	0.7
α-Fe	—	100	3	5.5	24	6.5	19	4	0	0.05
Fe_2M	—				33.3					66-73
FeM	—	45-50	0-100	0-100	43-57	0-100	0-100		15-66	
ZrM_2	66-73	64-69	60-80		60-67				No	—
ZrM								50	No	—
Zr_2M	32			33		66	33		No	—

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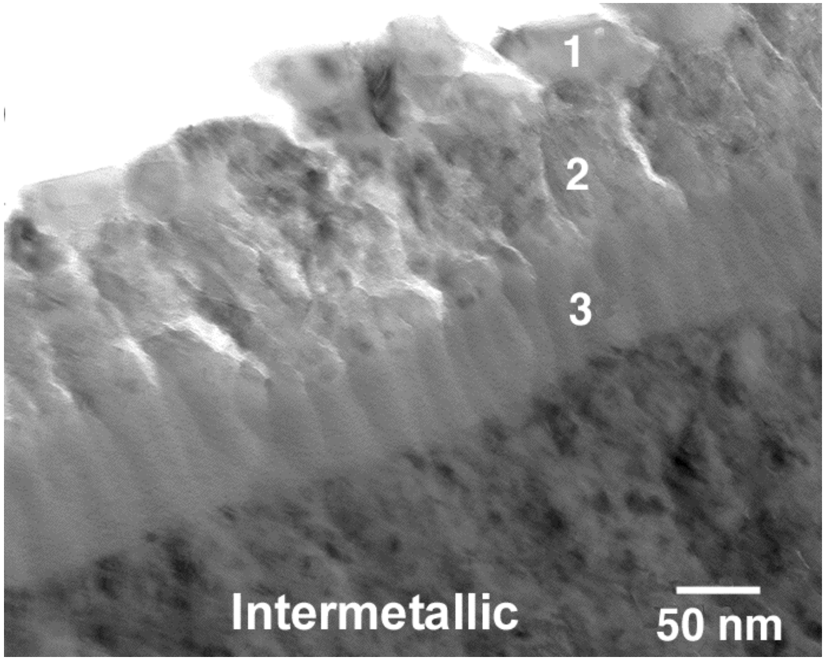
Metal Corrosion

- Metal corrodes by an oxidative process
  - electrochemical measurements are used to measure corrosion behavior
  - incongruent corrosion has been found for waste alloys (both Fe- and Zr-based alloys)
  - determining the phase preference of radionuclide is important
  - passivation layers may form and slow reaction
  - hydrogen embrittlement, SSC, and pitting are also key processes
- Rates can be comparable to oxide waste forms, particularly in reducing repositories



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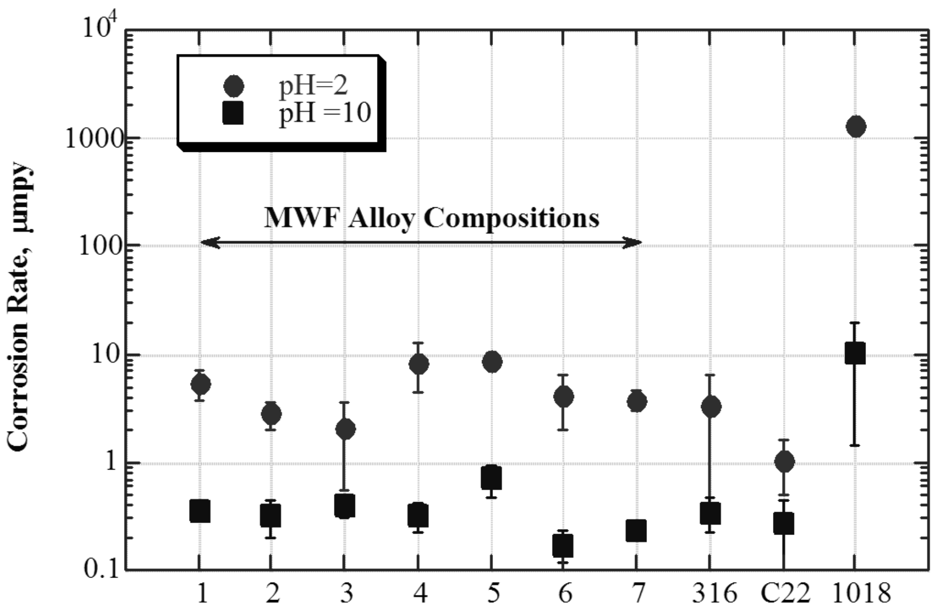
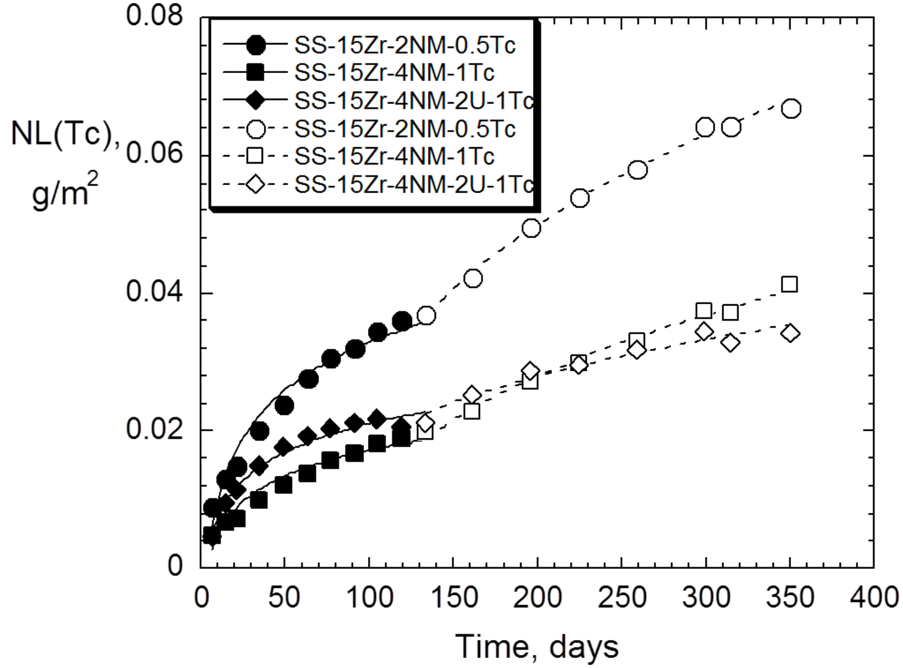
Metal Waste Form Corrosion





1: SS-15Zr-5U-2Tc
2: SS-15Zr-1Nb-1Pd-1Rh-1Ru-1Tc
3: SS-20Zr-1Nb-1Pd-1Rh-1Ru -1Tc
4: SS-5Zr-1Nb-1Pd-1Rh-1Ru -1Tc
5: SS-15Zr-0.6Ru-0.1Pd-11U-0.3Tc
6: SS-15Zr
7: SS-15Zr-1Nb-1Pd-1Rh-1Ru

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Pros and Cons of Metal as a Waste Form

Pros	Cons
Somewhat flexible to composition and process variations	Thermal process (difficult to permit)
High tolerance to radiation and transmutation	Requires reduction process when applied to Tc and TMFP
High waste loading (low disposal volume)	Lower durability than many ceramic phases (e.g., zirconates and titanates)
Maintains reducing environment, limiting Tc releases	Durability and processability not well understood
High thermal conductivity, allowing possibility of high storage temperatures	Multiphase waste form
	Handling of metallic slugs required
	Non-continuous (batch) process

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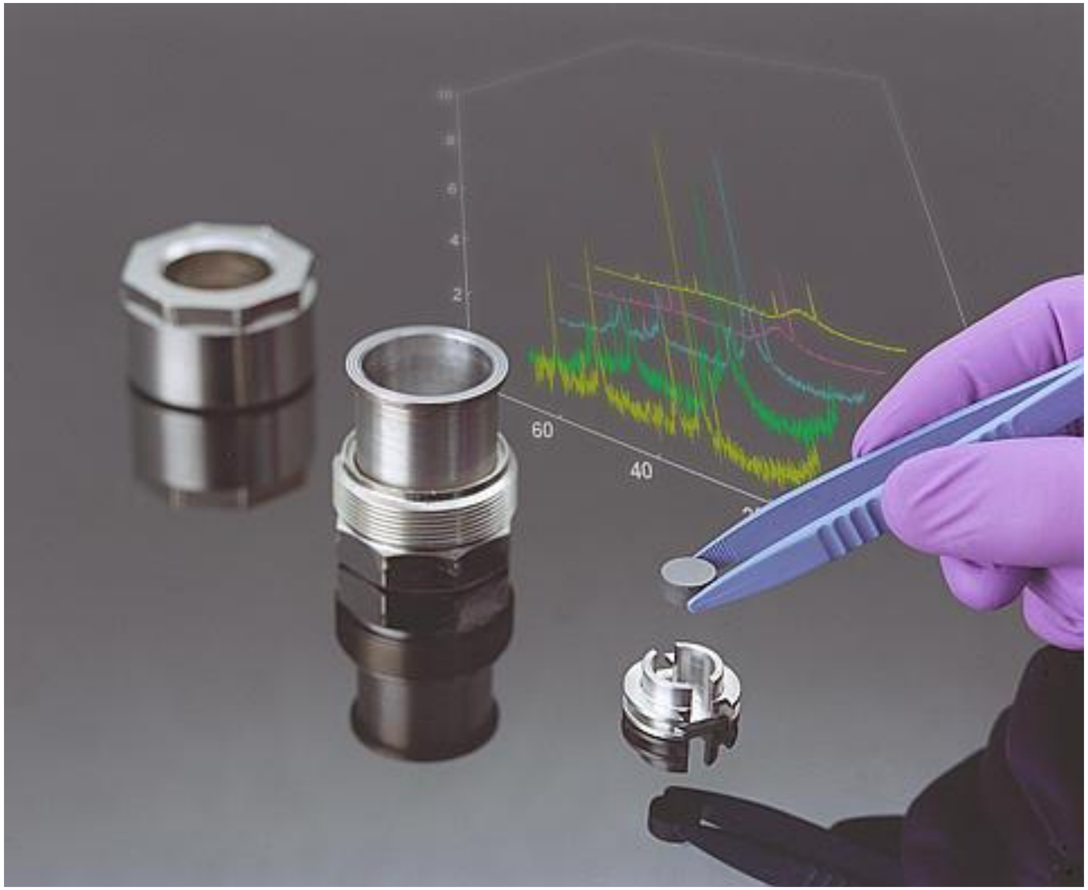
Potential Ceramic Streams

- Iodine
- HLW raffinate and its subparts (Cs/Sr, TM, LN, etc.)
- TRU



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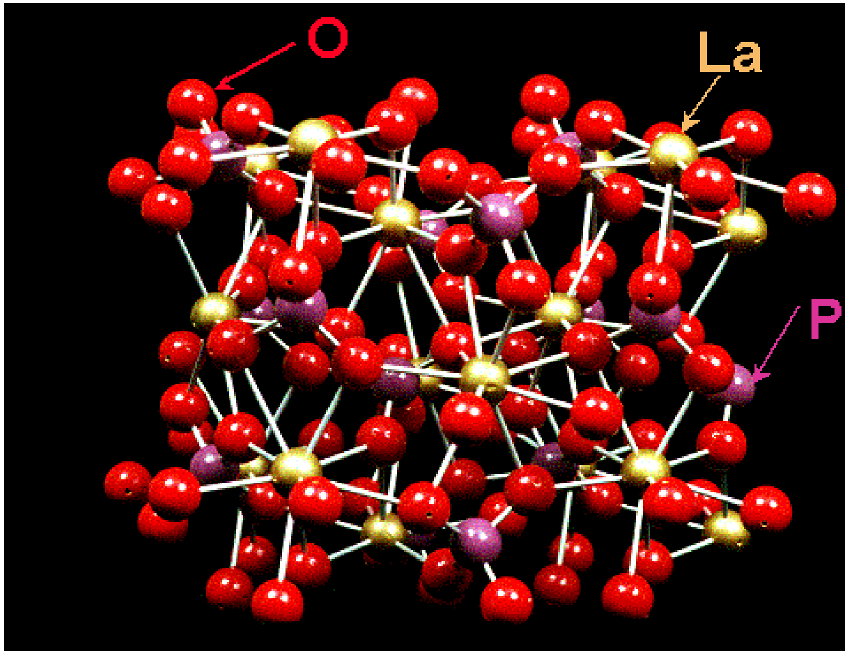
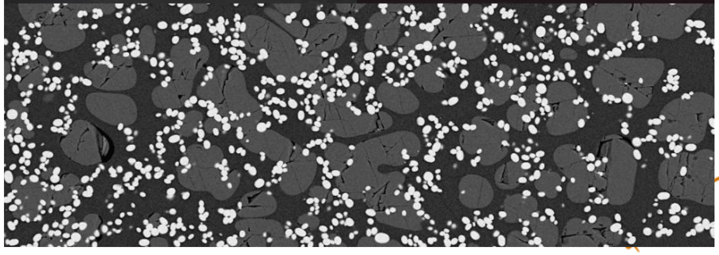
Ceramic Waste Forms





Structure

- Thermodynamically stable crystalline oxides
- Regular network with long-range order

Characteristics

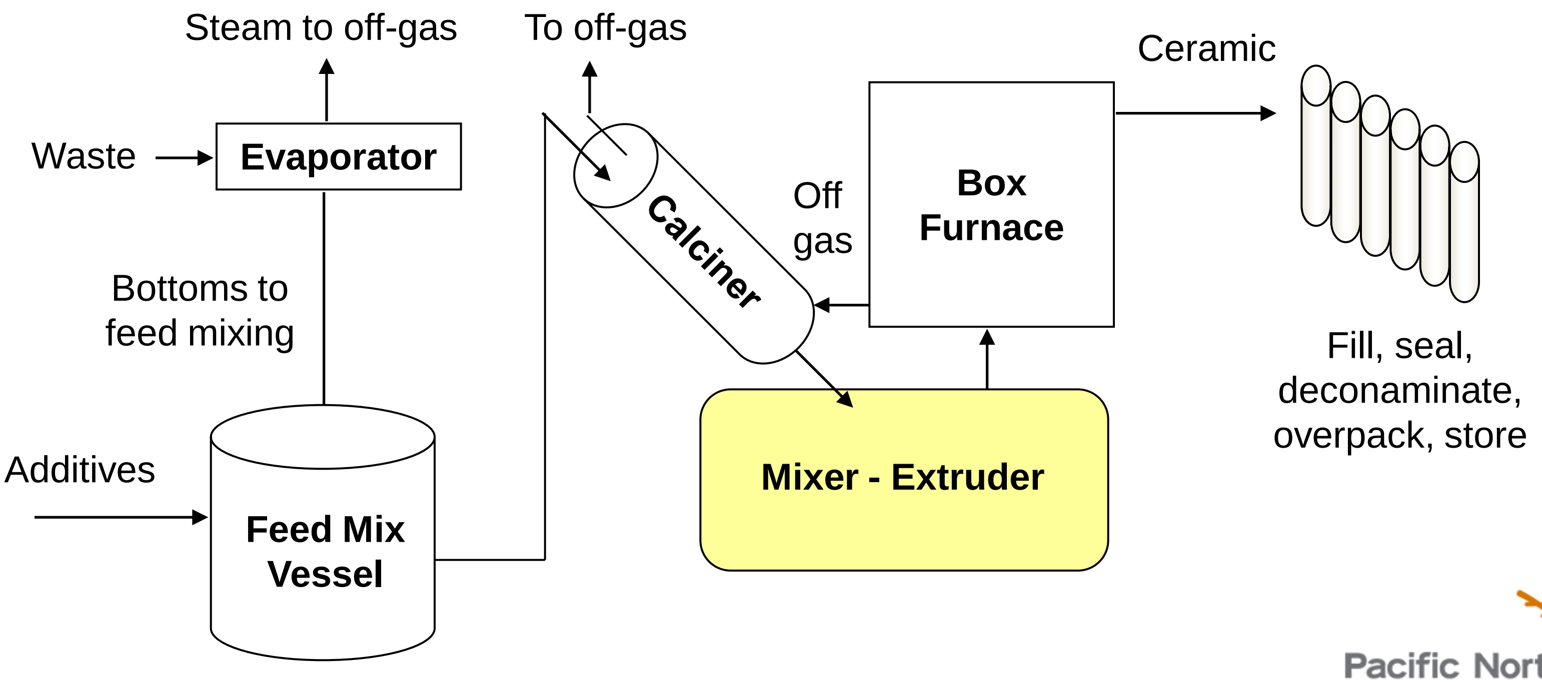
- Very high durability
- High thermal stability

Primary options

- Alumino-silicates
- Titanates
- Zirconates
- Phosphates

Example Ceramic Process

- Evaporate waste stream to heat, dose, solubility, etc. limits
- Blend with additives
- Calcine mixture to remove water and organics or nitrates
- Form green ceramic (press, extrude, etc.)
- Ramp heat in box furnace (dry, react, sinter, and slow cool)
- Load into canisters, seal, decontaminate or overpack, and store



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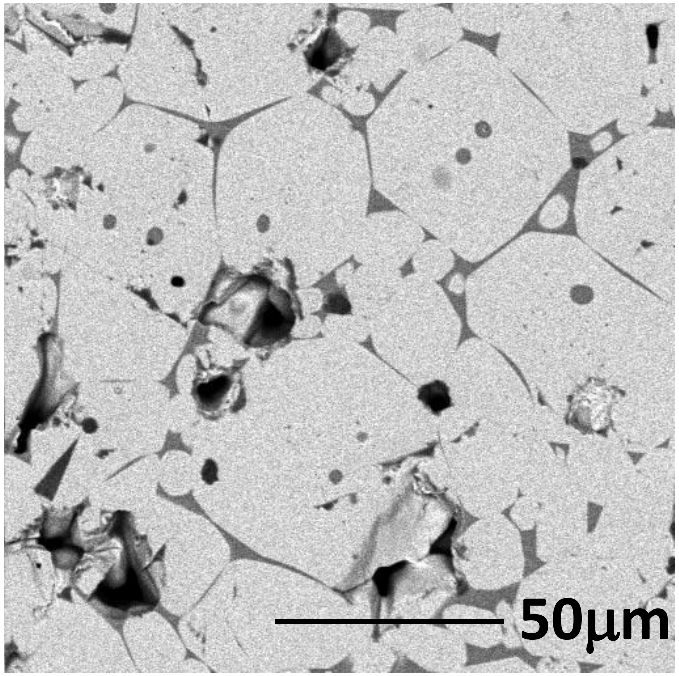
Ceramic Process Alternatives

- There is not a single ceramic process, but, many process steps that can be combined for an optimal total process
- Head end
  - absorption/adsorption
  - precipitation
  - calcine
  - sol-gel
- Forming
  - filter press
  - cold press
  - extrusion
  - casting
- Heating
  - furnace (tunnel or box)
  - hot isostatic press (HIP)
  - hot uniaxial press (HUP)
  - plasma-spark-sintering (PSP)

Ceramic Formulation

- Just as their isn't a single ceramic process, there isn't a single *ceramic*
- Typically, a target phase or phases are selected and additives are optimized to adjust processability and product quality
  - pyrochlore: $[Ru,Pd,Zr,Tc,Rh]_2[LN,AN]_2O_7$
  - zircon: $[Zr,AN,Th]SiO_4$
  - zirconolite: $[Ca,Ba,Sr][Zr,AN]Ti_2O_7$
  - monozite: $[LN,AN]PO_4$
  - pollucite: $[Cs,Rb][Al,Fe]Si_2O_6$
  - celcian: $[Ba,Sr][Al,Fe]_2Si_2O_8$



- Processing (phase formation, process temperature, densification rate, ripening or grain growth, shrinkage, etc.)
- Product quality (phase formation, grain boundary composition, microstructure, radiation damage, chemical durability)

Pros and Cons of Ceramic as a Waste Form

Pros	Cons
Very durable waste forms	Thermal process (difficult to permit)
Thermodynamically stable in disposal environment	Expensive relative to glass
High thermal stability	Potentially generates respirable fines
	Multiphase waste form
	Handling of ceramic parts required
	Non-continuous (batch) process

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Example Cost Analysis

- Three options considered for immobilizing five wastes
  - base-case uses five waste forms for the five primary aqueous waste streams
  - options 1 and 2 reduce to two waste forms
  - option 1 removes the need for Cs/Sr separation and has roughly the same waste volume as the base
  - option 2 requires TMFP reduction and has the lowest waste form volume

<table>
<tr><th>Case</th><th>UDS</th><th>Tc</th><th>TMFP</th><th>LNFP</th><th>Cs/Sr</th></tr>
<tr><td>Base</td><td>Fe-alloy</td><td>Zr-alloy</td><td>ABS glass</td><td>LaBS glass</td><td>ABS glass</td></tr>
<tr><td>Opt 1</td><td colspan="2">Fe-alloy</td><td colspan="3">ABS glass</td></tr>
<tr><td>Opt 2</td><td colspan="3">Fe-Alloy</td><td colspan="2">LaBS glass</td></tr>
</table>

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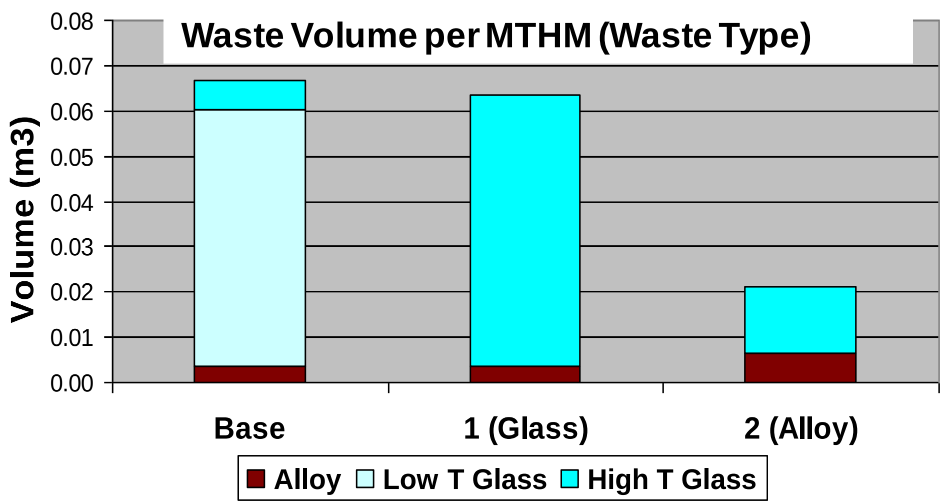
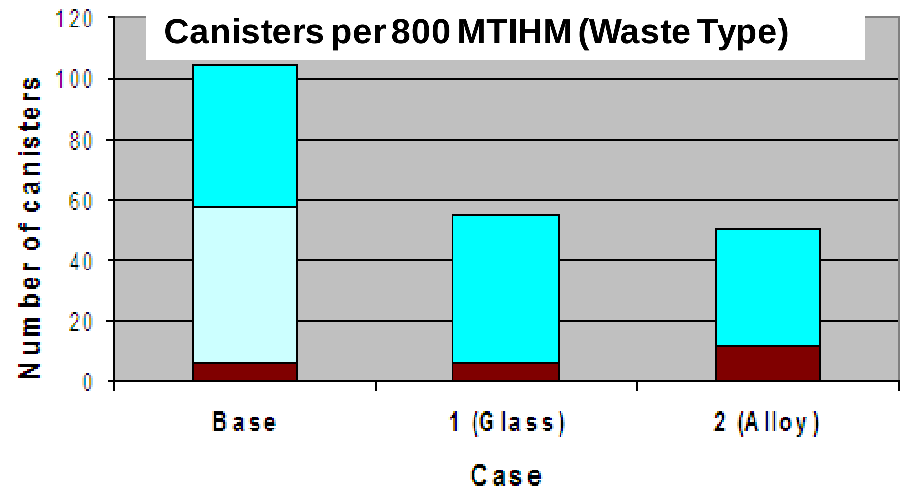
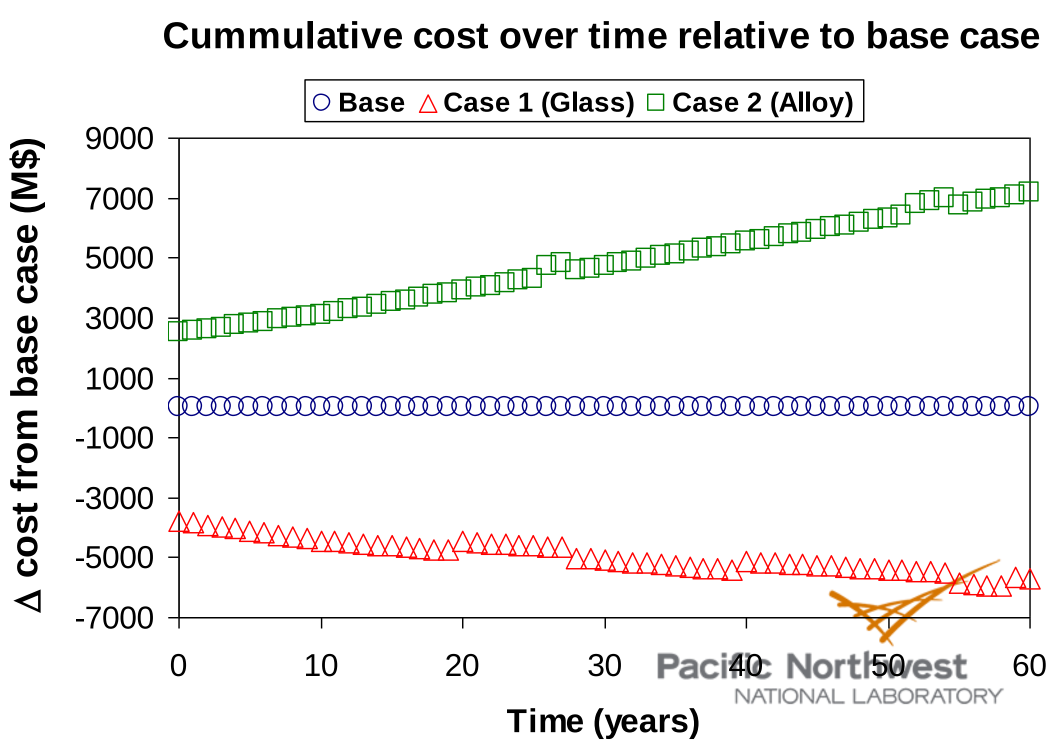
Trade Study Results





- Combining TMFP, Cs/Sr, and LNFP into a single glass waste form is the most cost effective option
  - many sensitivities evaluated
  - lines vary, but, order doesn't change
  - capital and operating costs of FPEX and TMFP reduction out weigh waste volume costs
- Only costs evaluated not other benefits



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Treatment of Secondary Wastes

- Near surface disposal in the U.S.
  - cost basis is by volume, by class
  - reducing volume may increase cost due to increase in class
  - no current disposal facility for GTCC
  - 10 CFR 61.55 dictates the class Ci concentration, is being changed

Site	*Barnwell*	*Clive*	Hanford	Andrews
Class	A, B, C	A	A, B, C	A, B. C
State	CT, NJ, SC	All	AK, HI, WA, OR, ID, UT, WY, MT, NV, CO, NM	TX, VT, all
Max volume	30Mft^3	165	35	59
Current volume	27		14	0
Est. closure	2050	2041	2056*	?

Radionuclide	***A***	***C***	
^{14}C	*0.8*	*8*	*Ci/m^3*
^{14}C in activated metal	*8*	*80*	*Ci/m^3*
^{59}Ni in activated metal	*22*	*220*	*Ci/m^3*
^{94}Nb in activated metal	*0.02*	*0.2*	*Ci/m^3*
^{99}Tc	*0.3*	*3*	*Ci/m^3*
^{129}I	*0.008*	*0.08*	*Ci/m^3*
TRU (α >5yr)	*10*	*100*	*nCi/g*
^{241}Pu	*350*	*3,500*	*nCi/g*
^{242}Cm	*2,000*	*20,000*	*nCi/g*

	Ci/m^3		
Radionuclide	***A***	***B***	***C***
Total > 5 yr half-life	*700*		
^{3}H	*40*		
^{60}Co	*700*		
^{63}Ni	*3.5*	*70*	*700*
^{63}Ni in activated metal	*35*	*700*	*7,000*
^{90}Sr	*0.04*	*150*	*7,000*
^{137}Cs	*1*	*44*	*4,600*

10 CFR 61.55

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Treatment of Secondary Wastes

- Compaction
  - std (~ 5 T) or super (~1000 T) press
  - applicable to compressible wastes
  - volume reduction factors 3-10x
  - each year 10s of 1000s of drums are compacted with an average of 5x vol
- Cementation
  - macro and micro encapsulation
  - aimed at immobilizing liquid or dispersible wastes and adding a barrier to release of rad/haz
  - waste mixed with OPC, sand, slag and other additives and set (micro)
  - increases volume of waste (1.4-5x)

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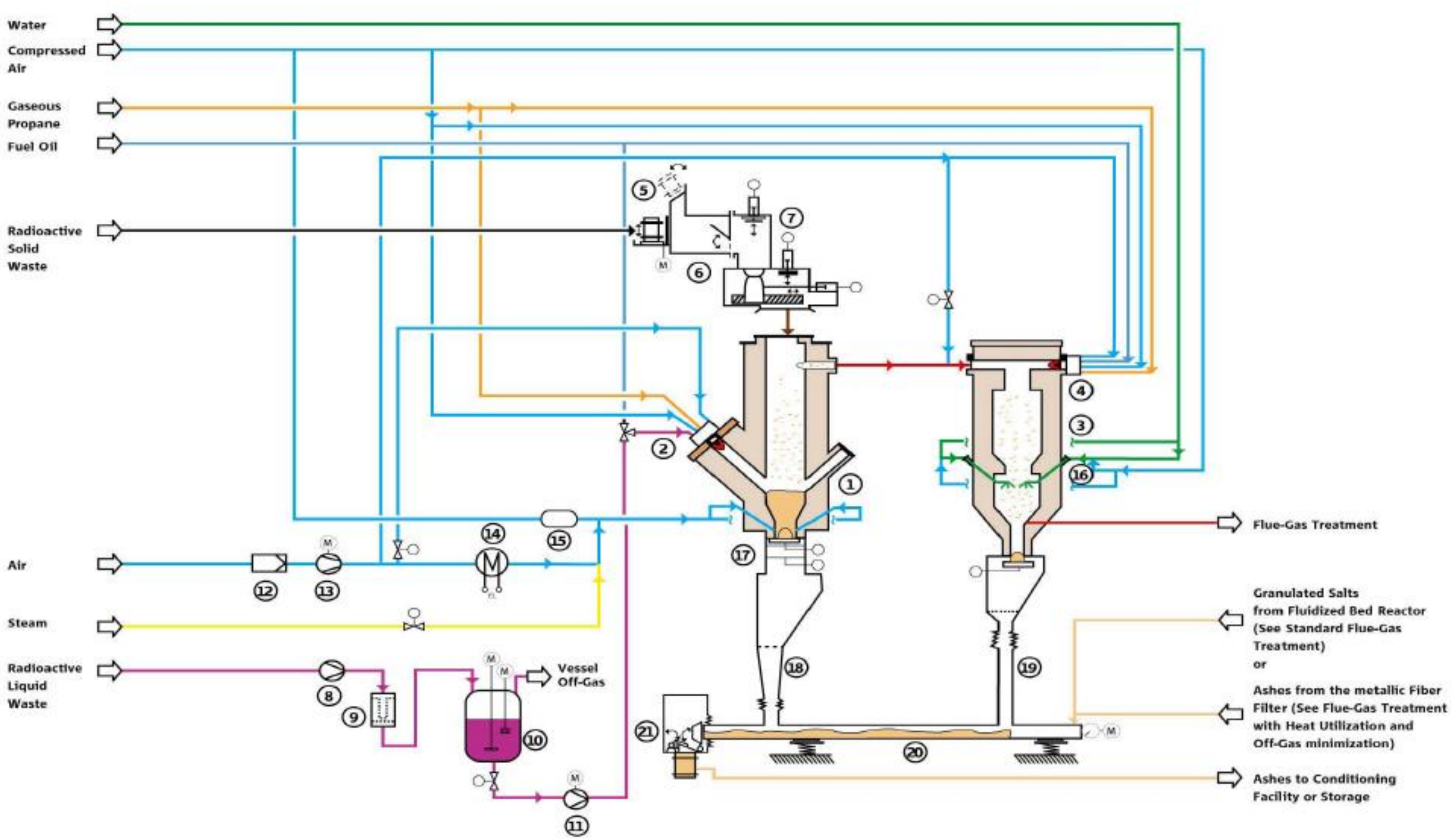
Treatment of Secondary Wastes

- Incineration
  - burn combustible wastes
  - ash is either further treated or disposed



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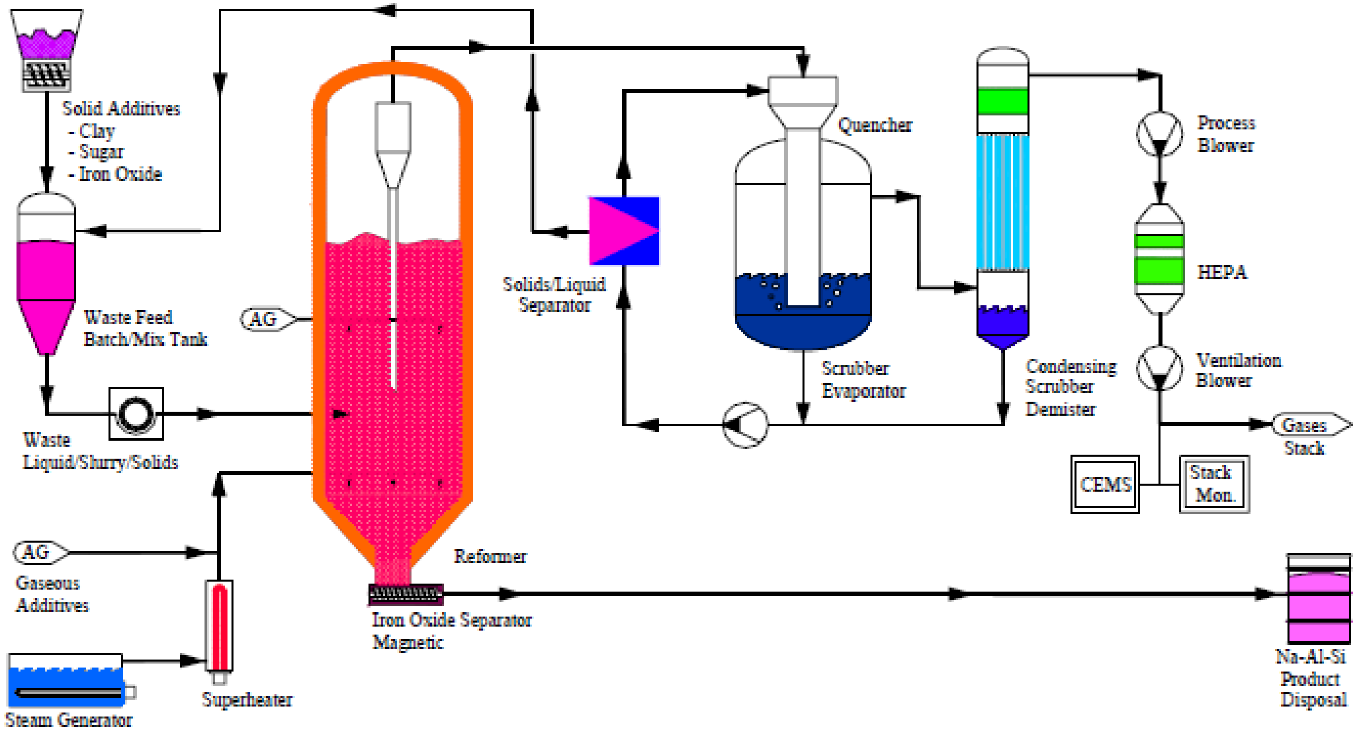
Treatment of Secondary Wastes

- Fluidized bed steam reforming
  - organic destruction by steam pyrolysis and dewatering



- other treatment technologies of note
  - Blending, Liquid adsorption, Evaporation, Polymer encapsulation

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Concluding Remarks

- There will be an opportunity to rethink the waste management strategy for U.S. commercial fuel
  - advanced separations flowsheets will allow for an unprecedented level of control over waste management
  - waste forms can be tailored to match waste chemistry and disposal environment
- Several options are available for each potential waste stream
  - need further development on each option (material and process)
  - selection depends on cost benefit analysis… cost is easy to estimate
- This presentation was aimed at giving a flavor for some of the waste stream and waste form option
  - many other separations flowsheets were not discussed
  - there are many other waste form options not discussed in detail (e.g., cement, glass-ceramic, composites, etc.)

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