The Vitrification of Sustainable Nuclear Fuel Cycle Radwastes

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Why commit to "waste forms"?

"… but eventually the anti-nuclear groups found the soft underbelly of the industry. It was something that had remained in the engineering background for decades. It was not nearly as exciting as striving for plutonium breeder reactor configurations or ceramic cores for jet engines, but it was there, and it was a distant bother. It was a nag. It was the long-term disposal of all the radioactive byproducts of nuclear fission."

James Mahaffey, "Atomic Awakenings", p 304
Pegasus, 2009

Assumptions

- **Waste immobilization will be a integral part of the overall LFTR system**
- **It will be completed within ~5 years after waste is generated**
- **Disposal form(s) must meet current stakeholder expectations; i.e., be water leach resistant, not “dispersible”, & readily transportable**
- **No “great leaps of faith”***
- **Disposal forms will be stored onsite until a geological repository materializes**

* In particular, “magic box” chemical separations

Characteristics

Product

- Non dispersible - neither particulate nor liquid
- Durable – more leach resistant than EA glass
- Minimal volume - easy to store/transport/bury

Process

- Minimize “incidental” waste volumes/streams
- Maximize recycle
- Simple, Cheap, & Low Risk as Possible

IFR radwaste

- **Spent "electrorefiner" salt: mostly Li, K, & Na chloride salts (~95% mole-wise) containing "salt seeking" FP chlorides (~1/2 of total FP)**
- **Metallic dross: mostly Zr & stainless steel accompanied by noble metal FP (readily consolidated to a good quality waste form)**

LFTR radwaste

- thermal/epithermal reactors – primarily mixtures of fluoride salts
- “fast” reactors – primarily mixtures of chloride salts (similar to IFR electrorefiner waste)

Basis LFTR Waste Streams

(1 GWe, 2 salt, C/FLiBe moderated breeder, ORNL 3791)

- **~4 tonnes/year of NaF & MgF_2 pellets ("mostly NaF") from the $^{233}UF_6$ separation/purification system - initially contains about 200 kg of Ru, Tc, Nb, Mo, Sb, Te along with some I & Cs**
- **~one tonne each of LiF + involatile FP fluorides plus ~ 400 kg Na/KF eutectic/year from the "still bottoms"***
- **Aqueous waste from the caustic offgas scrubber - mostly KF plus residual KOH with traces of volatile FP ("smaller than the other waste streams")**

FP represent only ~5 mole% of the total

*A relatively small amount of still "tops" comprised of Cs/Rb fluorides plus some BeF_2 will probably also be generated

Why Vitrification?

- **Candidate crystalline waste form materials for anionic species (e.g. fluorapatite) don't accommodate much halide***
- **Candidate crystalline materials for cationic species (e.g., "SYNROC" & hollandite) don't accommodate much alkali**
- **Glasses are relatively "omnivorous" (fewer atomic size/chemistry constraints than crystalline materials)**
- **Glasses are simpler/cheaper to fabricate than hot-pressed ceramics***
- **World-wide acceptance**

* e.g., fluorapatite is 3.7wt% fluoride

Halide Recycle

Halide (F & Cl)-based glasses aren't very durable, but...

- **Halides are readily separated via distillation as hydrohalic acids (HF & HCl)**
- **Conversion of dehalogenated salt wastes to durable glasses should be simple/cheap**
- **Halide recycle should also be simple/cheap**
- **Recycle is politically correct**

Radwaste Glasses

Borosilicate (“bsg”, alkali+borate+silica)

- Universally accepted (BDAT for YM)
- Exhaustively characterized

Aluminophosphate(alkali+Al_2O_3+H_3PO_4)

- Russia’s choice – easier to produce than bsg

Iron phosphate (alkali+Fe_2O_3+H_3PO_4)

- More durable than aluminophosphate glasses
- Much recent DOE-funded R & D

Why Fe-P glass might be a better choice than borosilicate (bsg) glass

- **Easier/simpler/cheaper to produce (lower mp & viscosity)**
- **Higher waste loadings for especially problematic FP (e.g., Mo)**
- **Especially well suited for REEs/actinides (higher waste loading & intrinsically insoluble phosphates)**
- **Simpler/cheaper because H_3PO_4 facilitates halide removal/recycle (it's far more acidic than SiO_2/H_3BO_3)**

Hobby-Style R&D

- Totally focused upon "proving the principle"
- Based solely upon scientific principles/observables

Which means that it's also

- Unconstrained
- "Unconventional"
- Inexpensive (total cost to date ~$500)
- Fun!

Experimental

- ~50, mostly Fe-P-type glass/glass ceramic specimens made with chloride & fluoride-based salt waste simulants
- Specimens subjected to a simplified version of DOE's PCT leach test protocol
- Leachates compared to those similarly generated from DOE's HLW benchmark "Environmental Assessment" glass

Steel mortar (made from 2” pipe cap)

glass

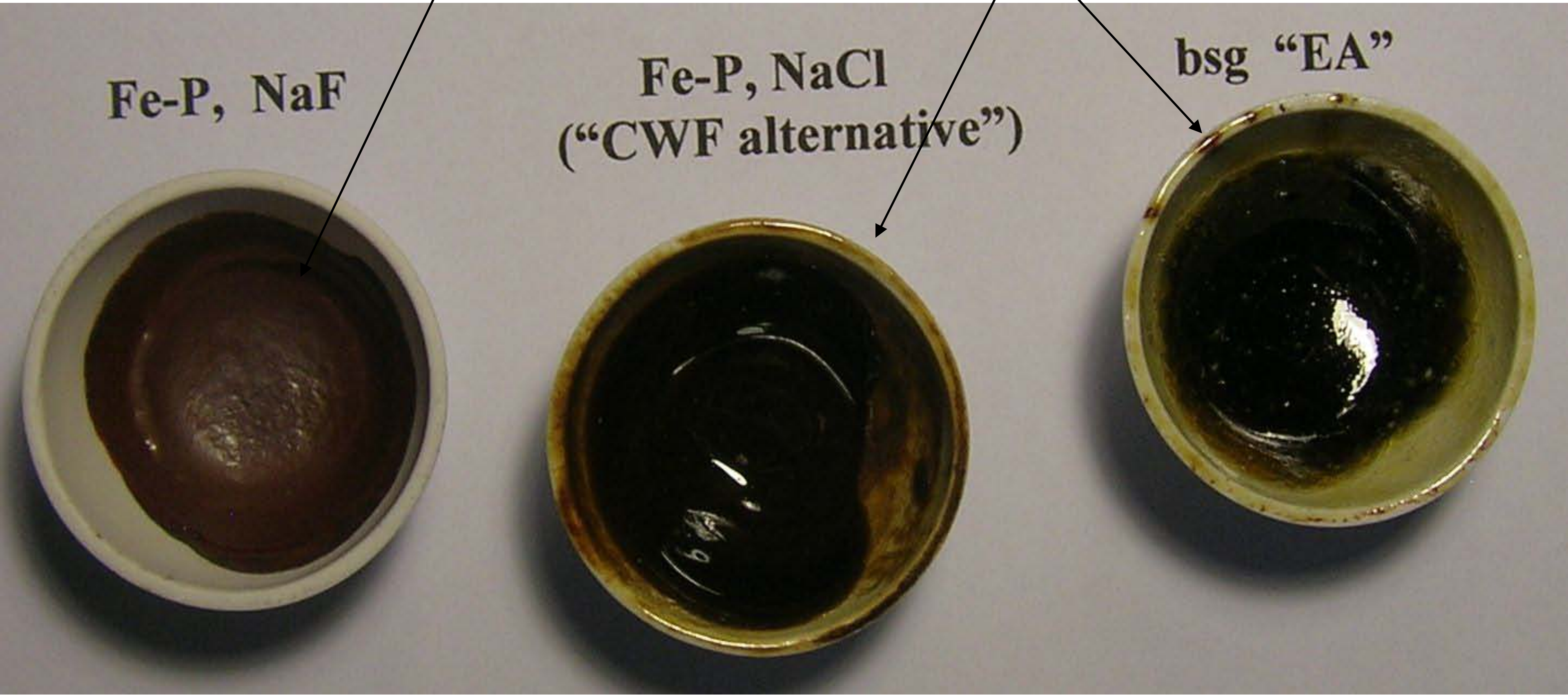
15 cc porcelain crucible

First pour!

“Direct VIT” Products

Glass-ceramic*

Glasses



*For the purposes of this discussion, “glass ceramic” means any combination of glass plus other solid phase(s)

Product Characterization

- **APPEARANCE (clear or crystalline?)**
- **MASS (consistent with expectations?)**
- **PCT LEACH TEST**
  1. Crush & isolate 75-150μ size fraction
  2. Rinse off dust
  3. Flush the particles into HDPE bottle with 10x as much distilled water
  4. Loosely cap that bottle, put into a canning jar containing water & a bit of NaOH, & put that jar into a 90ºC oven for 7 days
  5. Occasionally remove portions of the leachate, dilute with water, & measure conductivity

Observations

Chloride-based salt wastes*

- Simple to convert to durable Fe-P glass because H_3PO_4 quantitatively displaces chloride (HCl) during the melt
- Monophasic products (true glass) – not salt(s) mixed with and/or encapsulated by glass
- Waste loading up to ~8 moles alkali/kg - 4-5x higher than that of ANL's glass bonded sodalite "Ceramic Waste Form"
- Chlorine capture/recycle should be simple

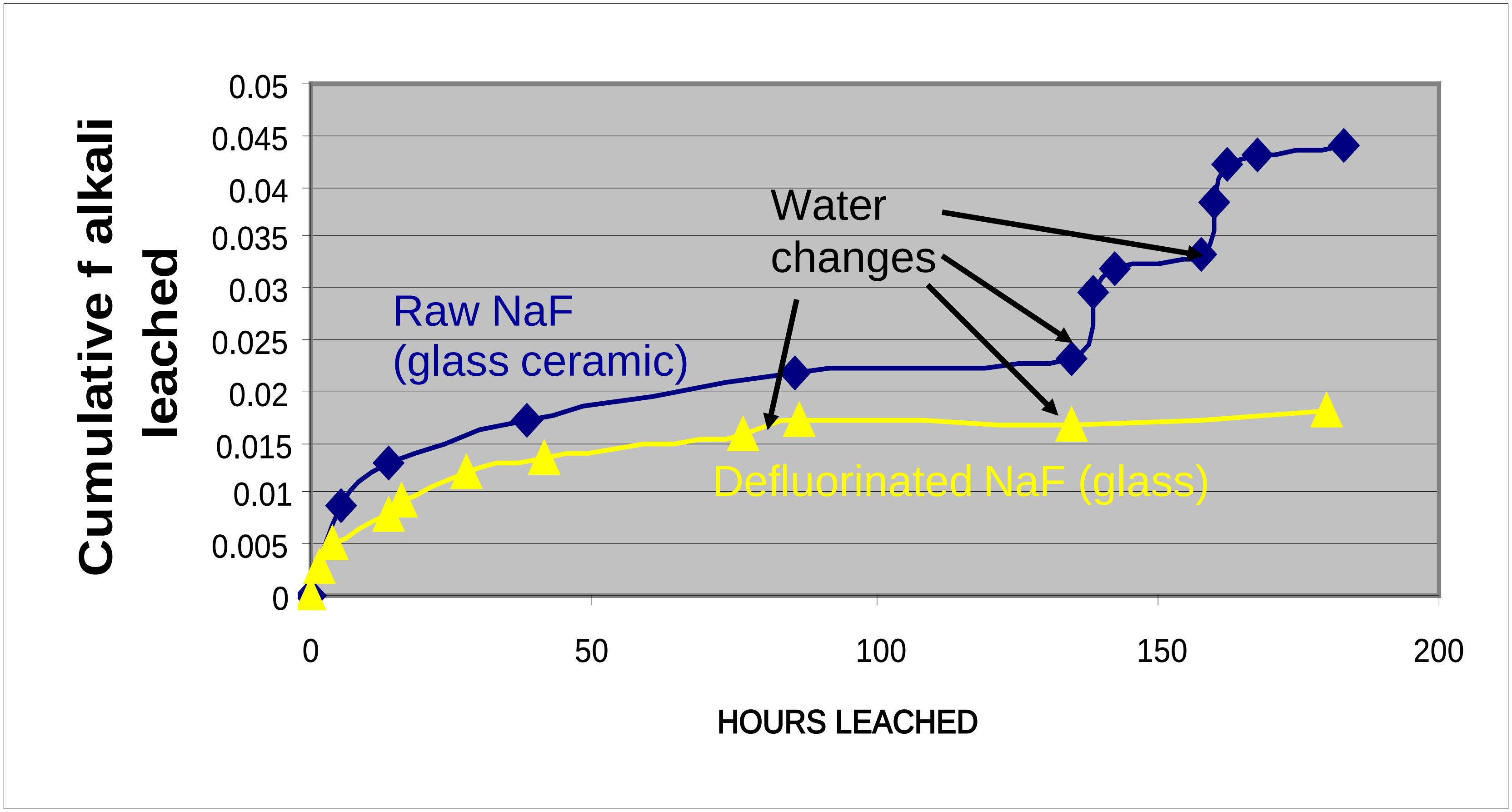
* **D. D. Siemer, "Improving the Integral Fast Reactor's Proposed Salt waste Management System", Nuclear Technology / Volume 178 / Number 3 / June 2012 / Pages 341-352**

Observations

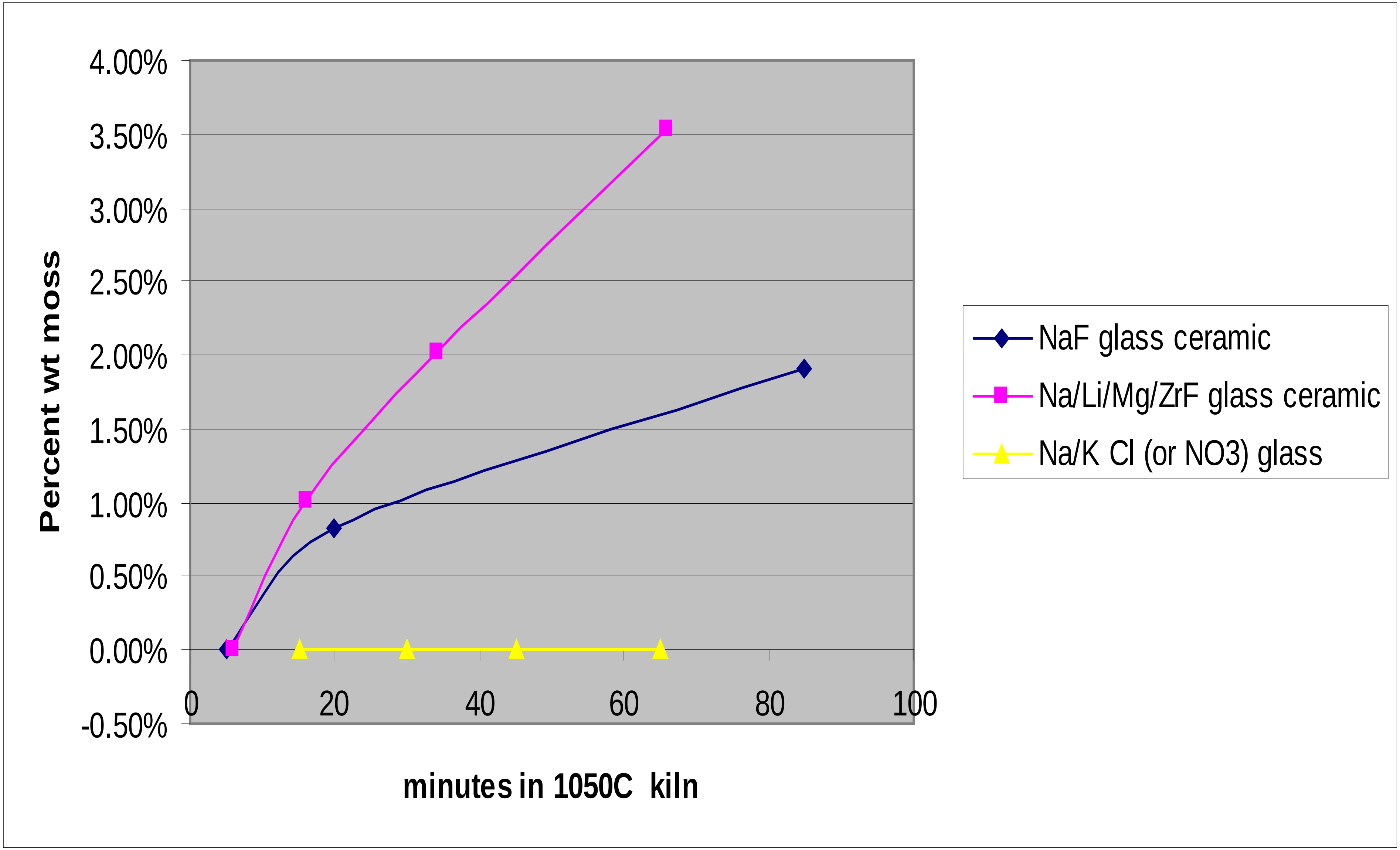
fluoride-based salt wastes

- **“Direct Vit” generates an inferior product because H_3PO_4 doesn’t displace enough of the F - the product is a multiphasic “glass ceramic” containing F salts which would rapidly leach in moving groundwater**
- **Consequently, most of the fluoride should be removed before vitrification**
- **A practical way to accomplish this would be to boil the waste salt(s) to dryness with dilute nitric acid**

PCT Leach "curves" indicate why most of the fluoride should be removed



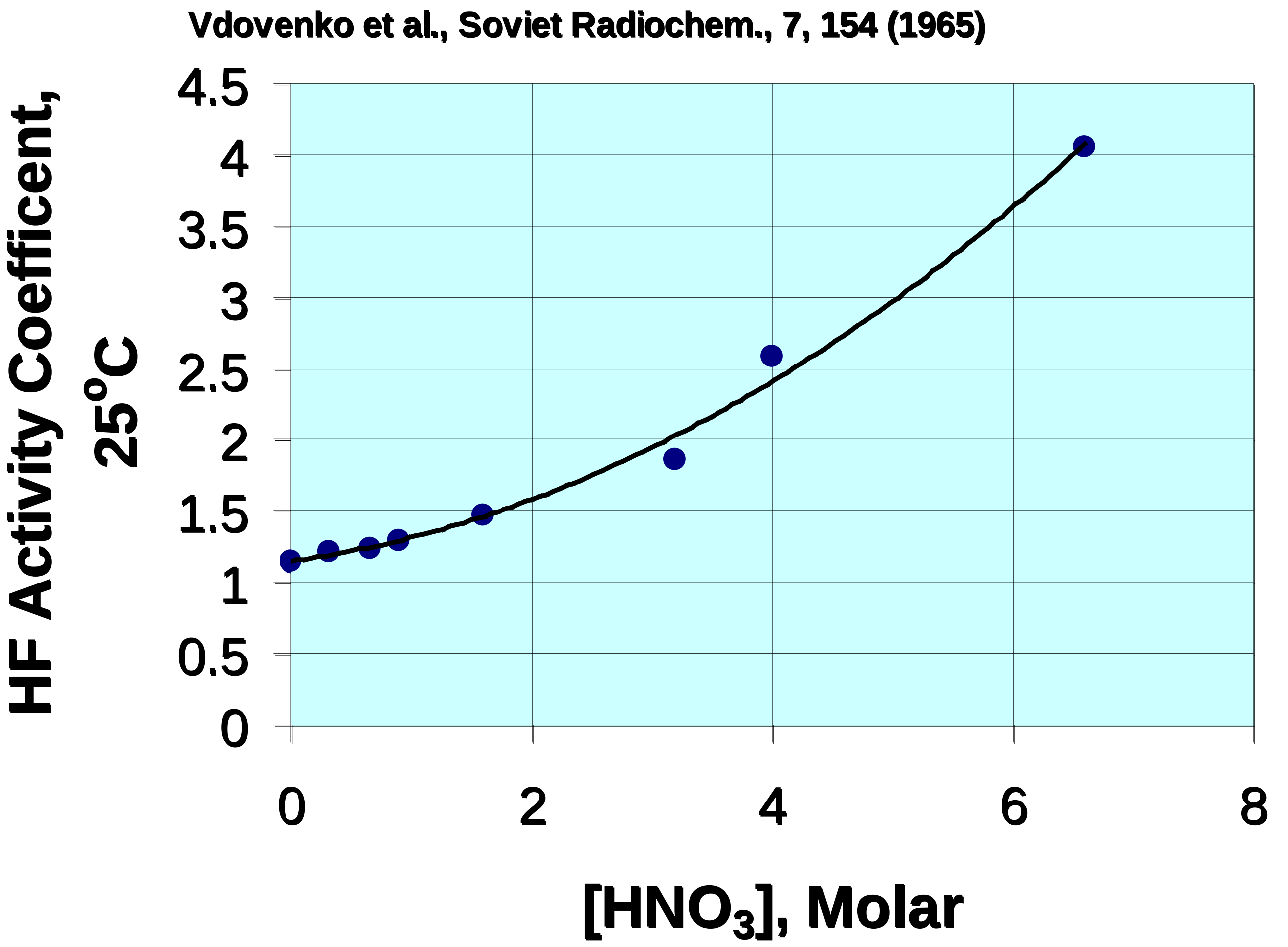
So do mass loss vs heating time plots



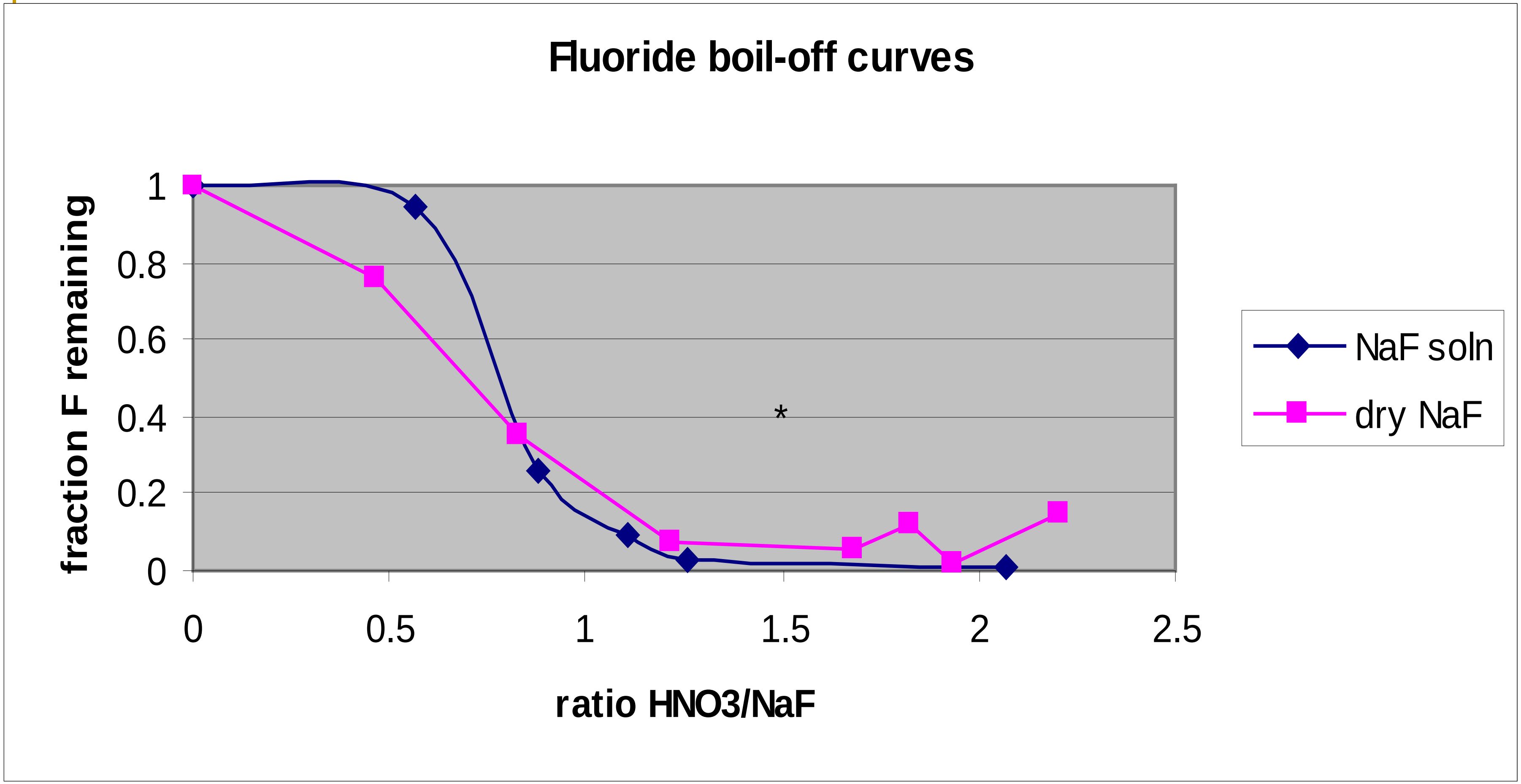
Why use nitric acid?

- Increases the vapor pressure of HF
- Experimentally verified – a single boil-down of AlkF salts with a slight stoichiometric excess of dilute nitric acid invariably volatilized most of the fluoride
- Nitrate-based salts would be compatible with any sort of vitrification process (glass)
- HNO_3 and NO_x are readily converted to elemental nitrogen
- Recovery/recycle of the fluoride in a deNOxed off gas should be simple/cheap

Activity Coeff of 4 Molar HF in HNO_3*



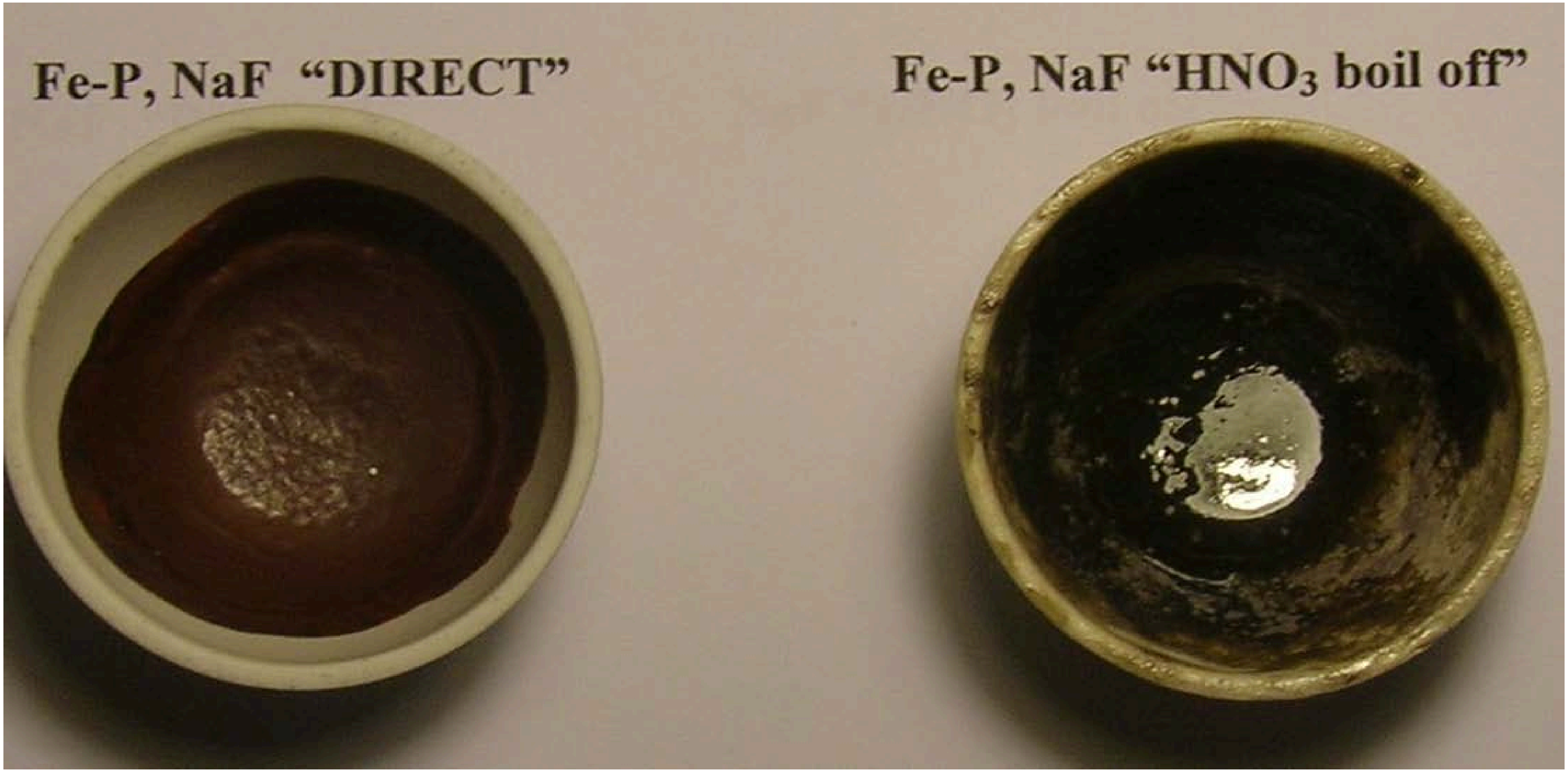
*Jerry Christian, 14Mar12

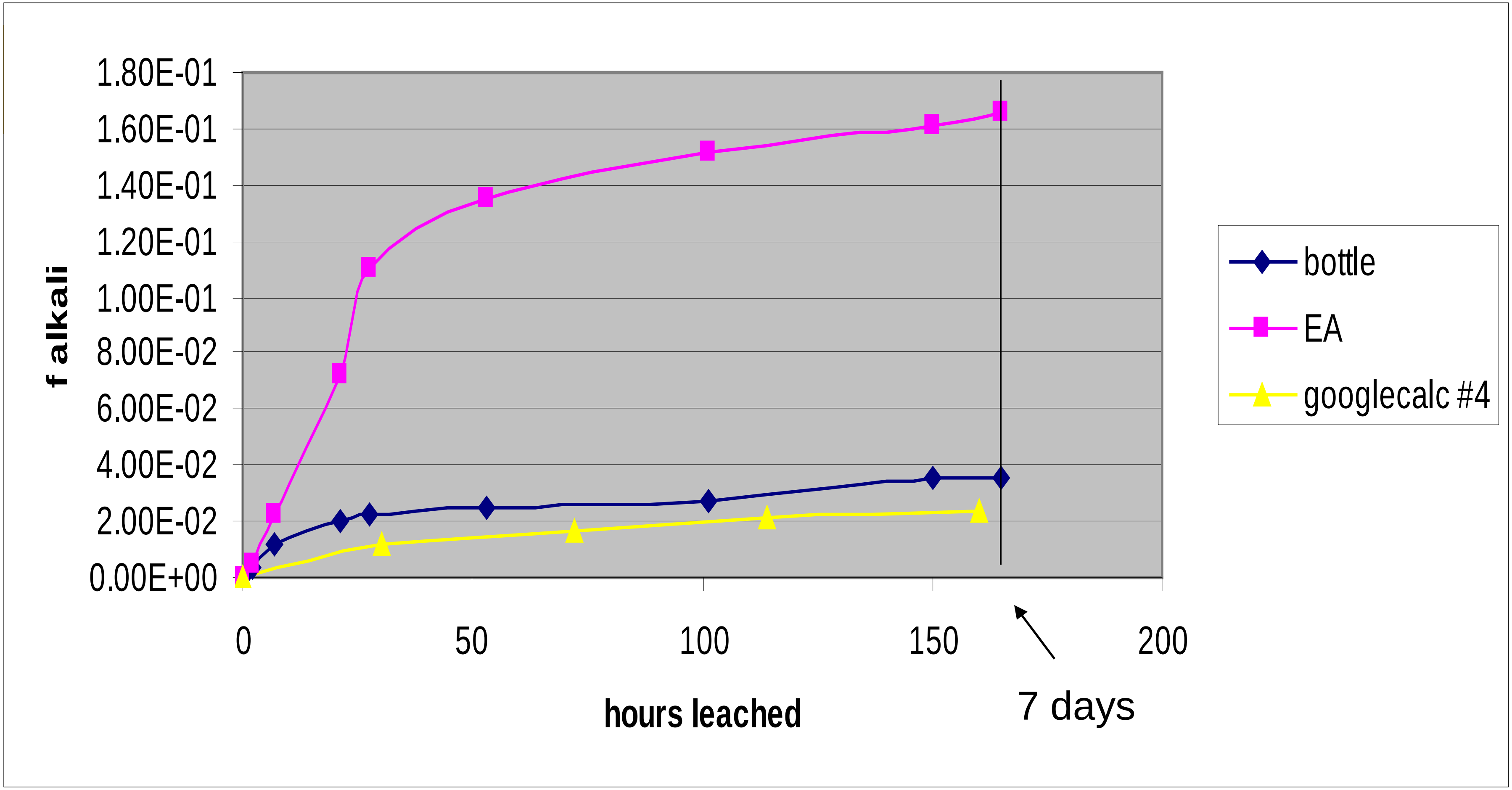


- **Teflon beaker/hotplate boil-offs with ~3M HNO_3 and ~20 mg NaF either dry or pre-dissolved in ~ 0.5 cc water**

- **Get better results with pre-dissolved salt - the downside is that ~5x as much water vapor is co-evolved**

"Large scale" conversion of NaF to $NaNO_3$


Fe-P, NaF "DIRECT"
Fe-P, NaF "HNO3 boil off"



Leach test (PCT) results

“EA” = DOE’s HLW benchmark BSG (∑alk = 8.3 meq/g)

“bottle” = soda-lime beer bottle glass (∑alk ≈ 4.3 meq/g)

GOOGLECALC #4 = Fe-P glass made with NaCl (∑alk = 6.8 meq/g)

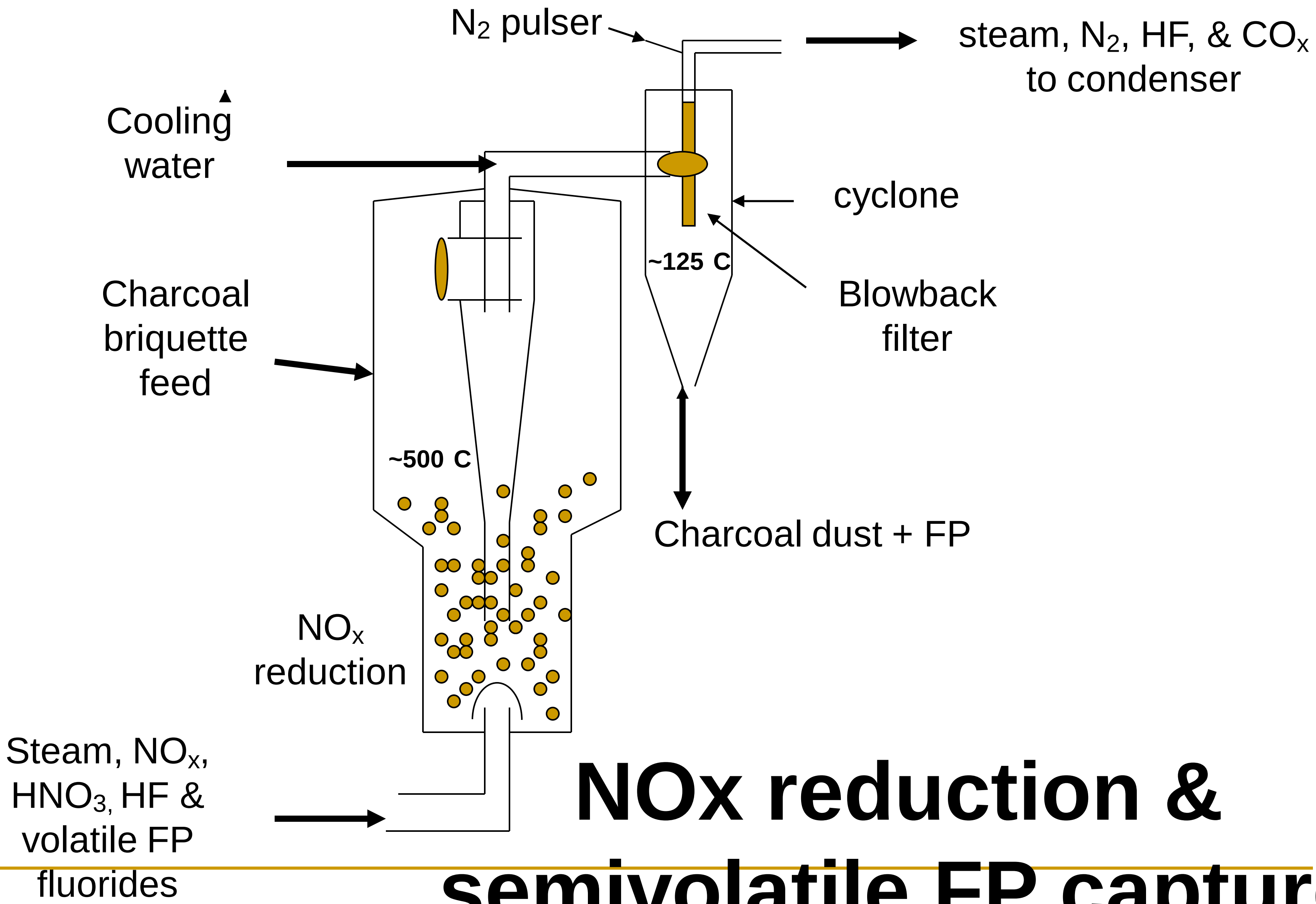
Off gas treatment

- Capture/recycle particulates & F
- Trap semivolatile FP (e.g. ^{129}I, Ru, Tc, etc.) for subsequent immobilization
- Destroy NO_x

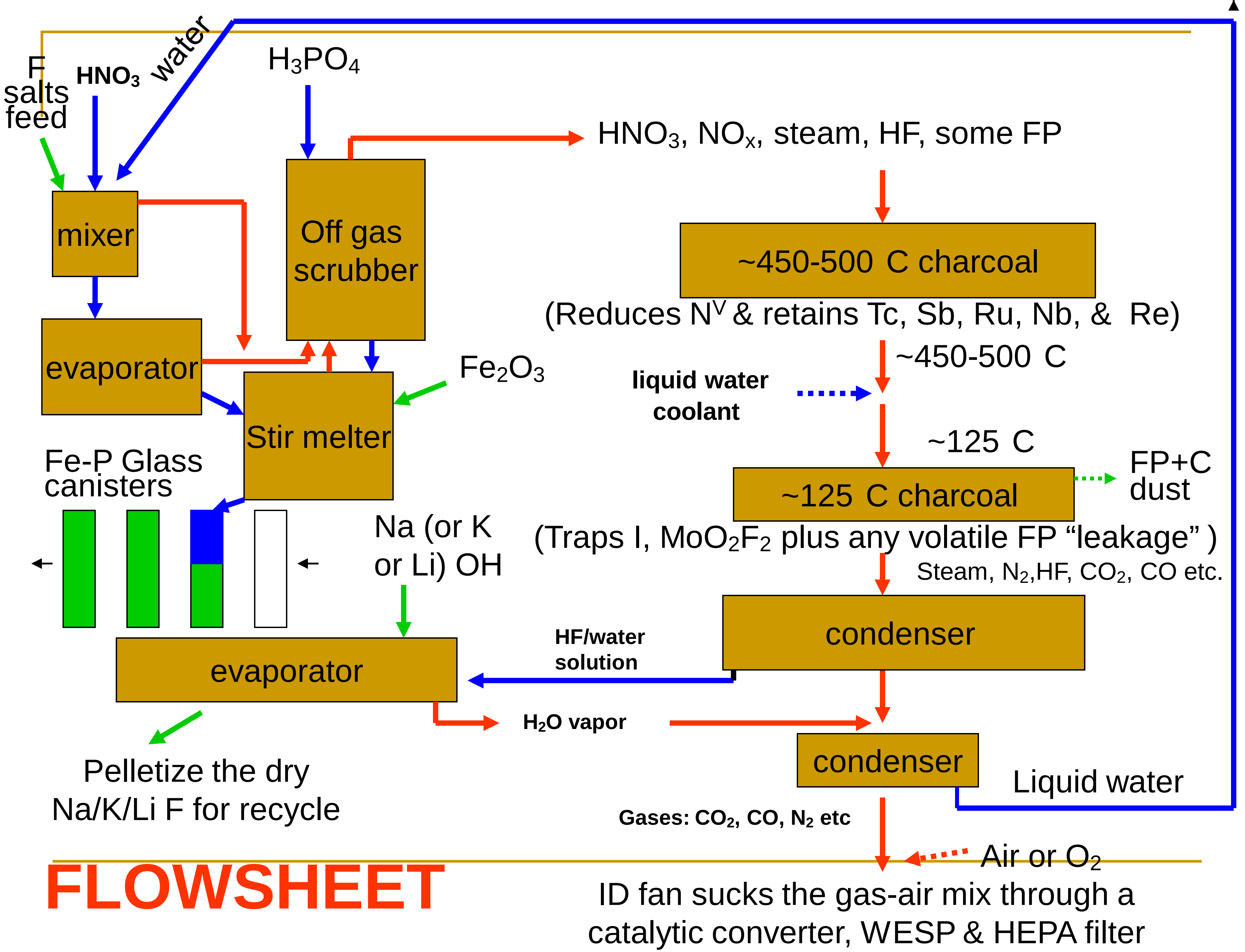
One way to achieve these goals would be to utilize charcoal as a “reactive” absorber

(hot C + NO_x → N_2 + CO_x)

(hot C + gaseous FP → solid FP)



NOx reduction & semivolatile FP capture


F salts feed
HNO_3
water
H_3PO_4
mixer
Off gas scrubber
HNO_3, NO_x, steam, HF, some FP
~450-500 C charcoal
(Reduces N^V & retains Tc, Sb, Ru, Nb, & Re)
~450-500 C
liquid water coolant
~125 C
evaporator
Fe_2O_3
Stir melter
Fe-P Glass canisters
~125 C charcoal
FP+C dust
(Traps I, MoO_2F_2 plus any volatile FP "leakage")
Steam, N_2, HF, CO_2, CO etc.
Na (or K or Li) OH
condenser
HF/water solution
evaporator
H_2O vapor
condenser
Liquid water
Pelletize the dry Na/K/Li F for recycle
Gases: CO_2, CO, N_2 etc
Air or O_2
FLOWSHEET
ID fan sucks the gas-air mix through a catalytic converter, WESP & HEPA filter

Semivolatile FP immobilization

Charcoal dust + semivolatile FP could be ...

Grouted (simplest, cheapest & probably good enough) or...

Mixed with zeolite powder, the C burned off, the FP trapped on Ag-loaded (or cold) zeolite, and then either...

- **recycled to the melter*, or...**
- **autoclaved with hydroceramic-type cement in sealed canisters, or...**
- **mixed with a low melting frit glass & HIPed in sealed canisters**

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*http://www.srs.gov/general/srnl/techex_2010/pdfs/S02-03.pdf

Summary

- **We can’t keep kicking the waste can down the road**
- **Vitrification is the most practical & generally accepted HLW immobilization technology**
- **Halide recycle would render the vitrification of sustainable nuclear fuel cycle HLW practical/affordable**
- **A GWe-yr’s worth of 2-salt* LFTR power corresponds to ~6.5 m^3 of HLW glass (or ~26 m^3 of HIPed glass-bonded fluorapatite)**
- **A GWe-yr’s worth of IFR power corresponds to ~6.5m^3 of HLW glass (or ~40 m^3 of HIPed glass-bonded sodalite)**

***The HLW invoked by a typical DMSR scenario[ORNL3791] corresponds to ~60 m^3 of glass-bonded fluorapatite plus ~24 m^3 of graphite/GWe-yr**

QUESTIONS?

EXTRA SLIDES

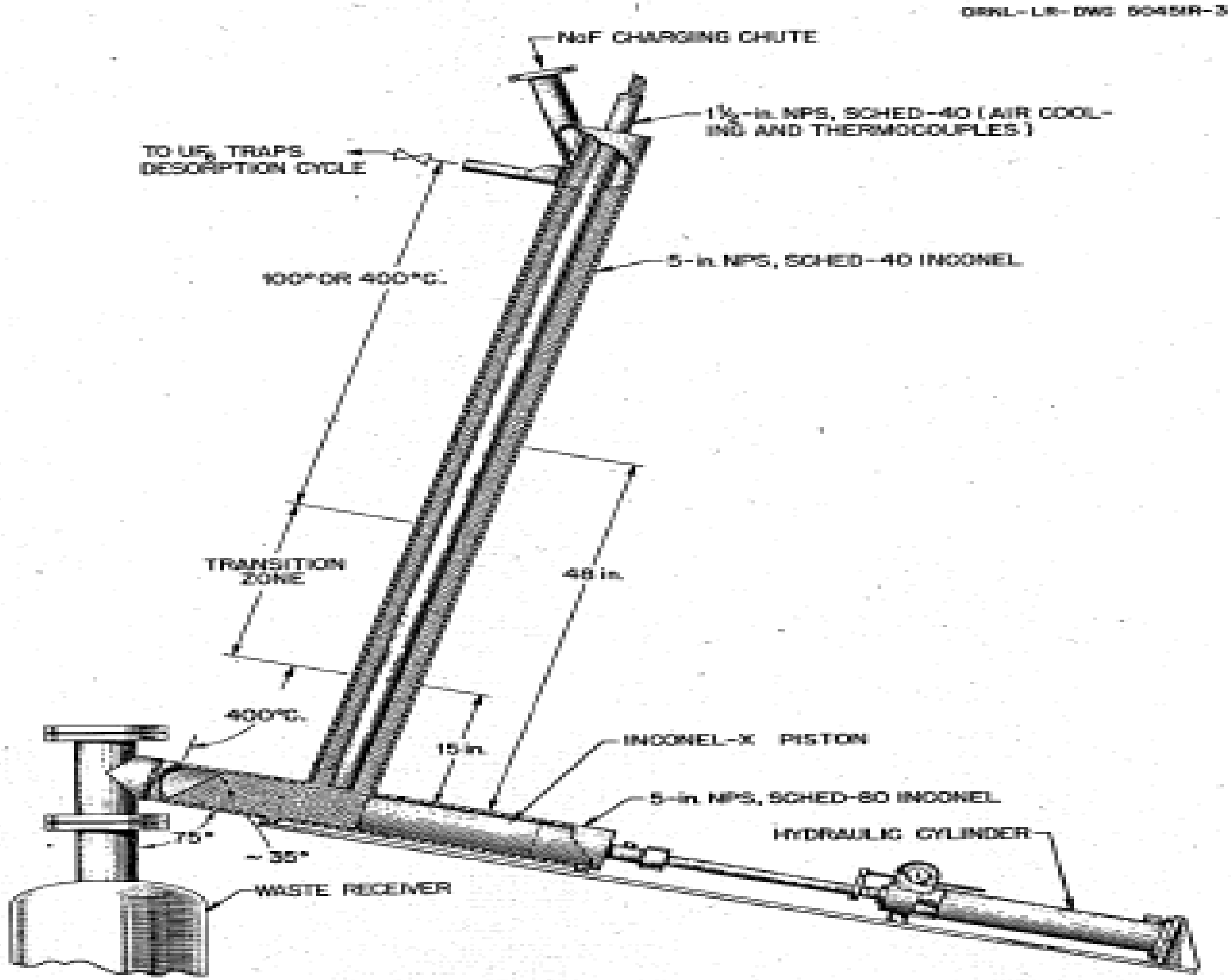


Fig. 7. Movable-Bed Temperature-Zoned Absorber. When the lower zone of the bed becomes loaded with fission products, the hydraulic cylinder operates the piston to discharge that portion of the bed into the waste carrier. Fresh NaF is added at the top. This apparatus has already been tested in the ORNL pilot plant.

ORNL 3791

One Plate Still

ORNL DWG 65-1802R2

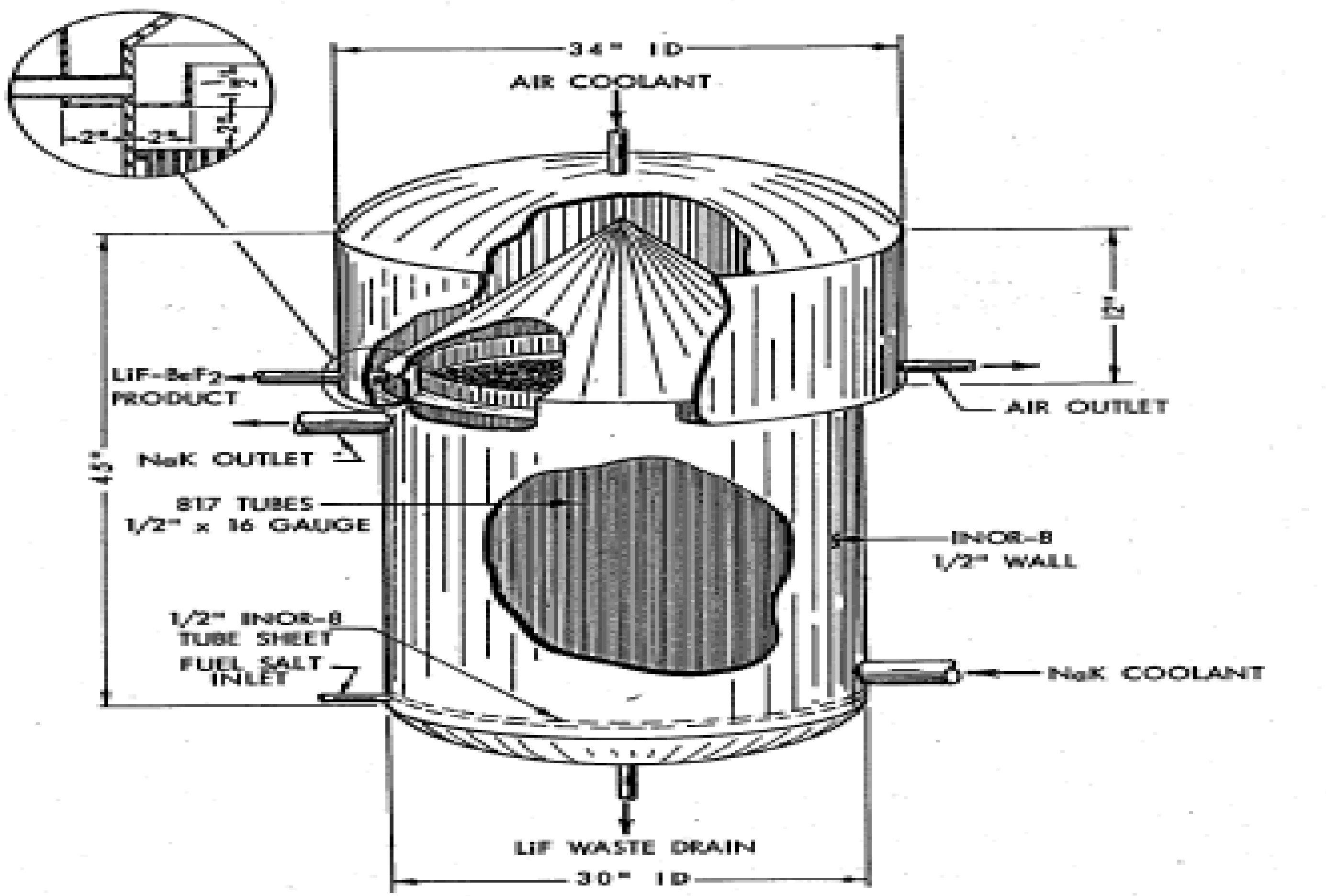


Fig. 9. Vacuum Still for MSBR Fuel. Barren fuel-carrier flows continuously into the still, which is held at about 1000°C and 1 mm Hg. LiF-BeF$_2$ distillate is removed at the same rate that salt enters, thus keeping the volume constant. Most of the fission products accumulate in the still bottoms. The contents are drained to waste storage when the heat generation rate reaches a prescribed limit. This concept of the vacuum still has not been tested.

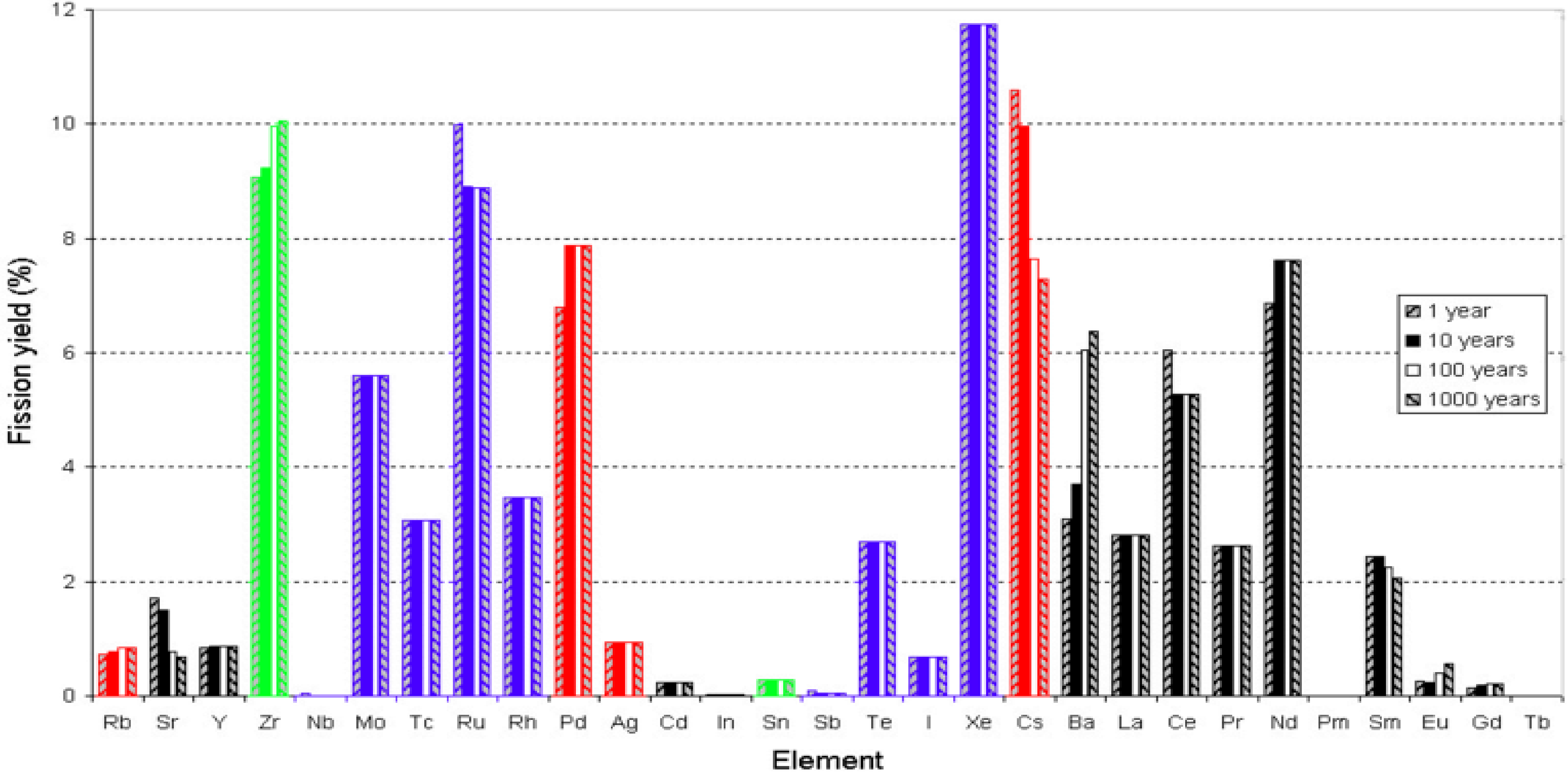
Designing a multi-plate still should be a primary R&D goal

~450 C charcoal should reduce/capture most FP fluorides

boiling points C

	$SALT_{nF_{max}}$	Metal
I	5	184
Ru	227	4150
Mo	34	4639
Tc	55	4265
Sb	141	1587
Nb	234	4744
Te	-39	988
Cs	1251	671
Se	-46	685

http://en.wikipedia.org/wiki/Fluoride_volatility



Blue - Definitely volatilized but vitrifiable (except Kr & Xe)

Black - Definitely separable & vitrifiable (one-plate still)

Red (Pd?) & **Green** – Separable/vitrifiable (multi-plate still)

Pelleted Salt Wastes

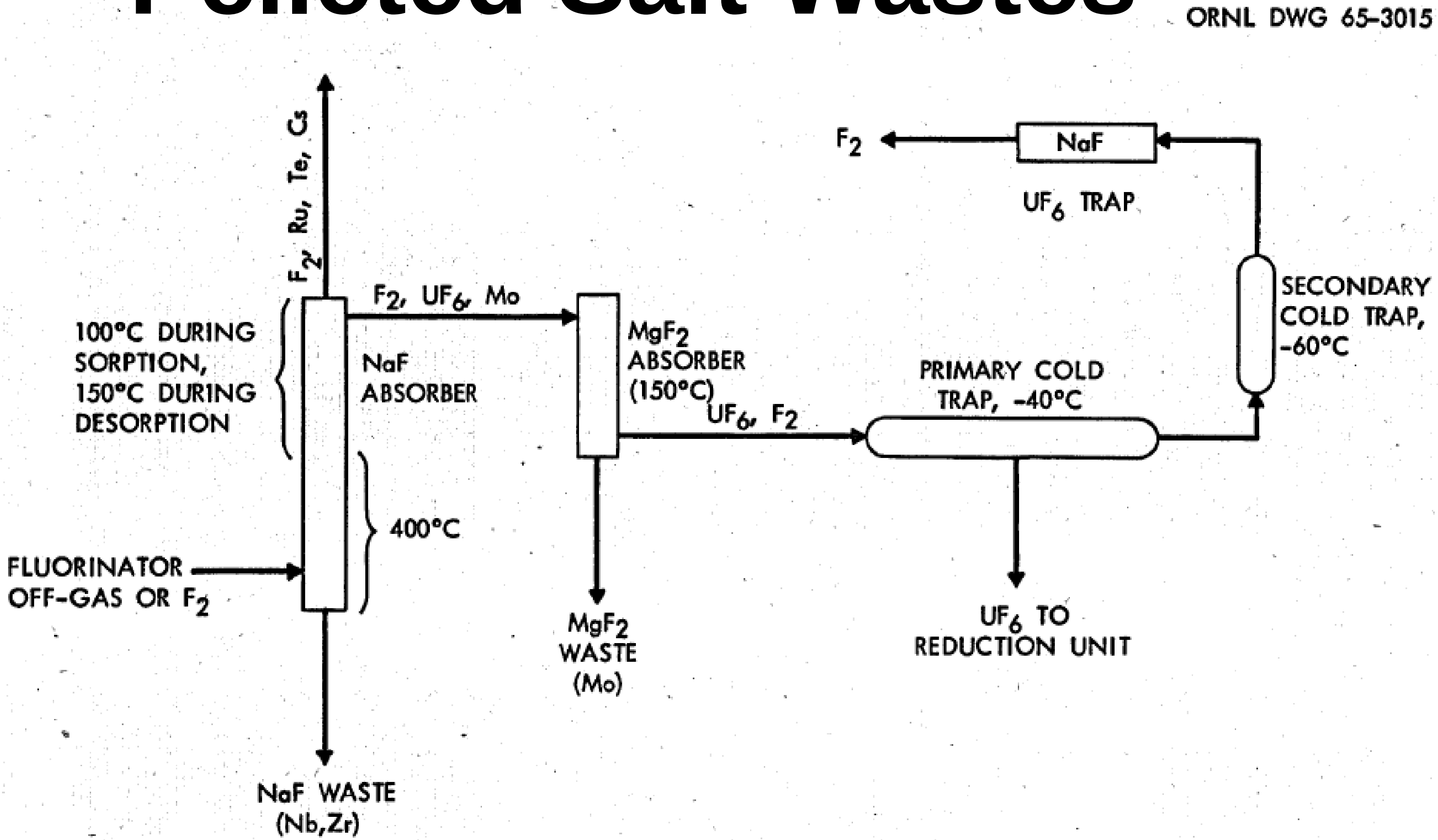
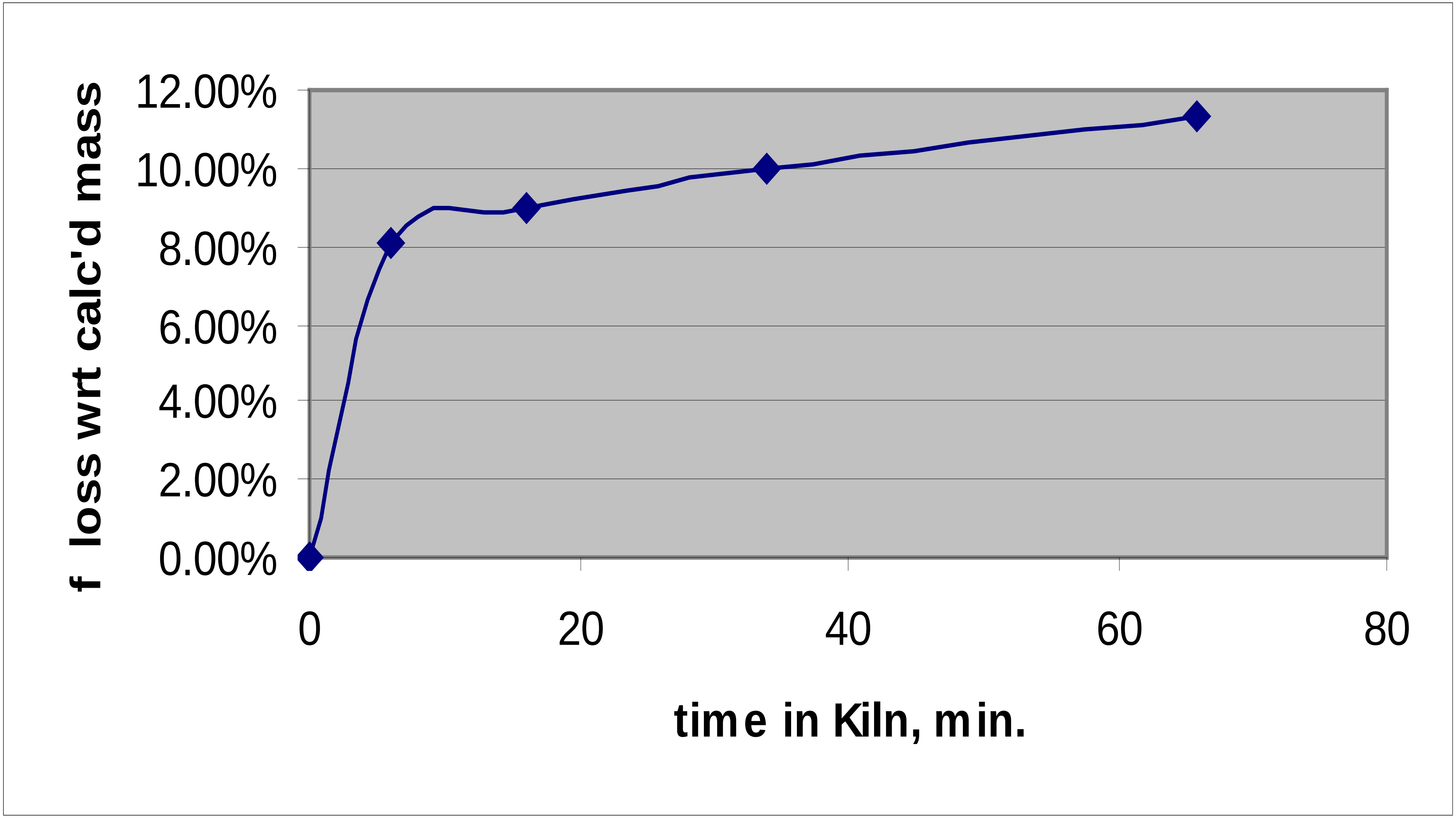


Fig. 6. Purification System for UF_6 with Disposition of Volatile Fission Products. Two such systems are used, one for the fuel stream and one for the fertile.

Fractional Mass Loss vs Post Melt Time @1100C

(mix of Na, Li, Mg, & Zr fluorides: ∑alkali=11 meq/g)



GLASS KILN (nichrome wire, steel paint can, alumina cement, vermiculite insulation, fan, light dimmer….)

PCT oven: **a light bulb-heated, "blue board" box, with diode T sensor/op amp/SCR temp controller**

PCT sample screens: 150 & 75 µ NITEX™, silicone glue, & 2” PVC pipe fittings

Why commit to "waste forms"?

1967: "... (because MSBR) waste disposal is not a critical problem...bulk storage procedures like those used (at Hanford) for aqueous wastes can be used for the near term while R&D effort is applied in more-critical areas." ORNL TM-1852, p. 37 (1967)

2012: I'm convinced now that after learning about the failures of project management, the neglect of nuclear safety quality assurances and the uncontrollable costs we will hear about today that this (Hanford clean up) project is on a fast road to failure," said Rep. David Hobson, R-Ohio.

Substituted fluorapatite (SFA) scenario

(analagous to ANL's glass bonded sodalite "CWF")

- **Often proposed for DMSR[ORNL 7207] scenarios invoking the periodic disposal of entire cores; i.e., of ~1300 tonnes of graphite plus ~100 m^3 of mixed F salts/GWe**
- **Keyed to the disposition of fluoride; e.g.,**

$$Li_2BeF_4 + 6Ca_3(PO_4)_2 \rightarrow 4(Li_{0.5}Be_{0.25}Ca_{4.5}(PO_4)_3F)$$

- **Translates to periodically making/HIPing a mix of ~4100 tonnes of SFA with ~800 tonnes of powdered glass**
- **Which, over 30 years, corresponds to an average HLW (C + SFA) production rate of ~78 m^3/GW_e-yr**
- **A modern LWR/PUREX-based nuclear fuel cycle generates ~3 m^3 of HLW glass /GW_e-yr**

Major LFTR Waste Streams

(2 salt, C/FLiBe moderated breeder, ORNL 3791)

- NaF & MgF_2 pellets from the $^{233}UF_6$ separation/purification system - initially contains most of the Ru, Tc, Nb, Mo, Sb, Te & some of the I & Cs FP
- Still bottoms* - LiF + involatile FP fluorides
- Aqueous waste from caustic offgas scrubber - mostly KF and residual KOH with traces of volatile FP

*A relatively small amount of a "still tops" product containing Cs/Rb fluorides plus some BeF_2 will probably also be generated

Quantities*

ORNL 3791, 1 GW_e

- **NaF/MgF_2 pellets ("mostly NaF"): ~ 4 tonnes per year containing about 200 kg semivolatile FP**
- **Still bottoms: roughly one tonne each of LiF and FP fluorides plus ~400 kg NaF/KF eutectic per year**
- **Aqueous: "smaller than the other waste streams" (mostly KF)**

FP fluorides comprise about 5 mole% of the HLW (it's mostly <u>alkali</u> fluorides)

* one salt MSRs/DMSRs are apt to be much more "wasteful"