VITRIFICATION OF *IFR* ELECTROREFINER SALT WASTE

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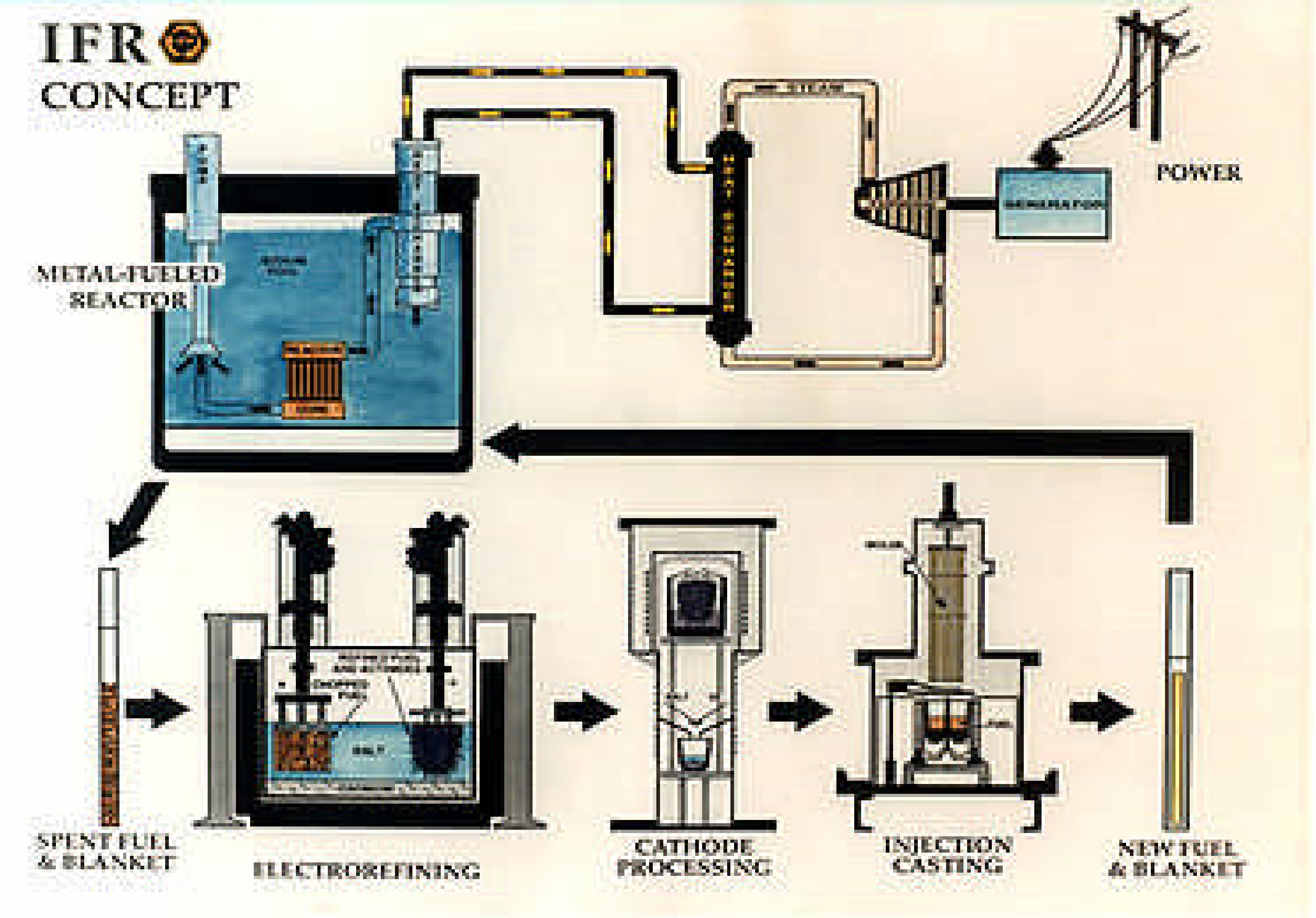


A genuinely “sustainable” nuclear fuel cycle

HOWEVER…

“… 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”,
Pegasus, 2009

Assessment of Partitioning Processes for Separation and Transmutation of Actinides

IAEA TECDOC 1648, March 2010

Section 9.5.3: 10) “Waste from pyro-process contains more corrosive and toxic chlorides, so a fabrication of a high integrity waste form is more limited. Waste form with a high durability and leach-resistance might lighten the cost to meet the disposal criteria….

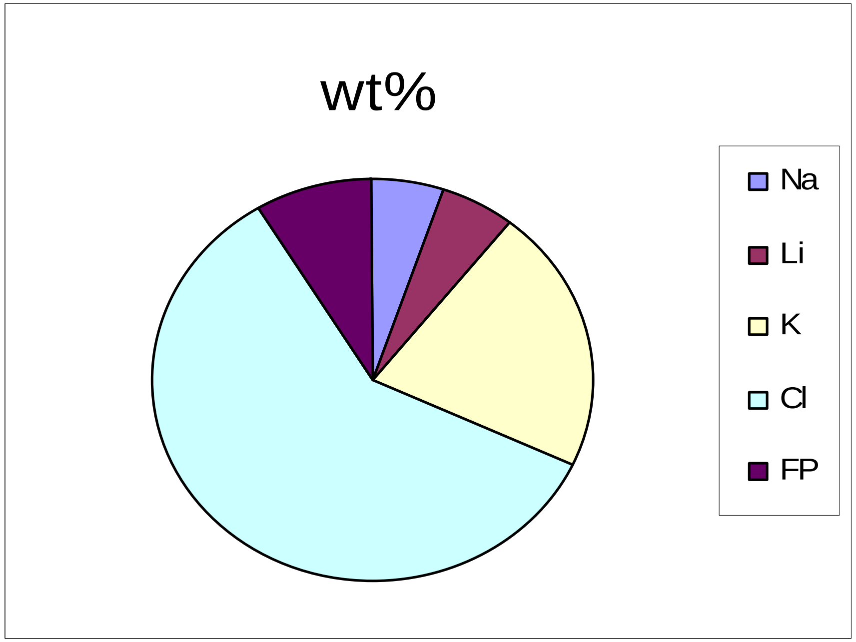
…a reduction of waste generation, which can be achieved by purification and recycle, may promote the usefulness of P&T. Therefore, efforts to fabricate a high-integrity waste form, as well as to reduce the waste generation are essential.”

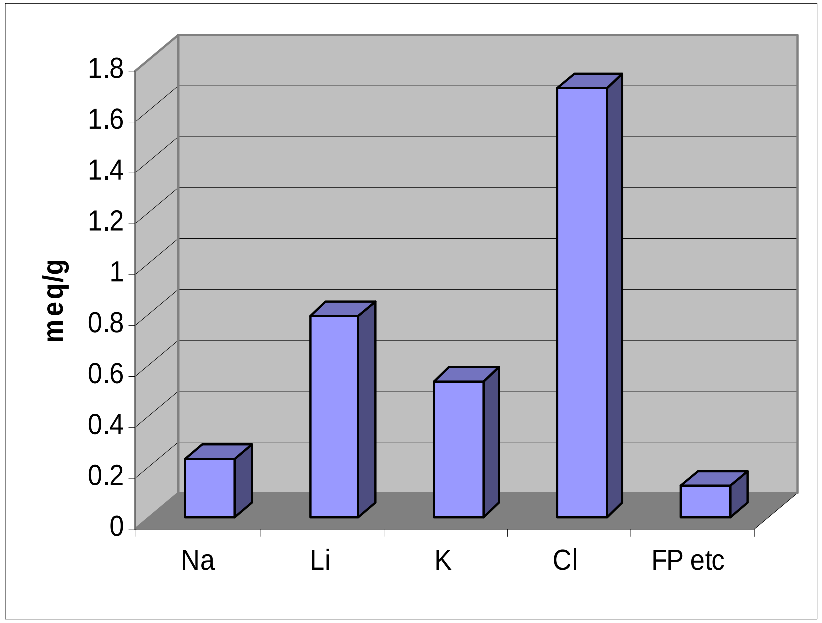
What’s wrong with the “CWF”?

- Today’s IFR implementation paradigm assumes that the electrorefiner’s salt-waste form must immobilize chloride
- This assumption has driven development of today’s “Ceramic Waste Form” (CWF) – a multiphasic artificial sodalite
- CWF is intrinsically difficult to produce and its low waste loading (under 1% FP) translates to high fabrication, transport, and disposal costs

cost is also hindering a US nuclear renaissance

*electrorefiner waste salt**





- **CWF contains about 8 wt% salt**
- **ER salt contains about 8 wt% FP**
- **Radwaste loading = 0.08*0.08 ≈ 0.0064**

Translates to ~ 53 tonnes of CWF/GW$_e$-year

***L. Morss et. al., “Ceramic Waste Form (CWF) Handbook“,ANL-NT-119, 1999**

The iron phosphate (Fe-P) glass alternative

- Chloride is neither toxic nor radioactive – why discard it?
- Alkali chlorides comprise >90% of ER salt waste
- It’s simple to remove/recycle chloride from salts
- One way is to heat them with orthophosphoric acid - chloride boils off as HCl which would be easy to “scrub” & recycle as fresh ER electrolyte
- Professor Day and his students (MST) have repeatedly demonstrated that Fe-P glass constitutes an excellent waste form for high alkali (sodium) radwastes
- Vitrification via Fe-P should be <u>much</u> cheaper than CWF

The goal of this project is to put these pieces together

ANECDOTAL GUIDELINES

”normalized release of Al, K, Na, and P from Fe-P is about 10 times less than B, Li, Na, and Si release from EA borosilicate glass”

“Na_2O and K_2O behave similarly in a glass”

“intermediate metal cations, such as Al^{+3}, Fe^{+3}, Cr^{+3}, and Zr^{+4}, are believed to form O–Me–O–P bonds in these glasses that connect isolated $P_2O_7^{-4}$ (pyro) or PO_4^{-3} (ortho) groups at high waste loadings so as to provide a high resistance to crystallization”

“… good chemical durability when Fe (or Fe+Al)/P is between 0.4 and 0.8”

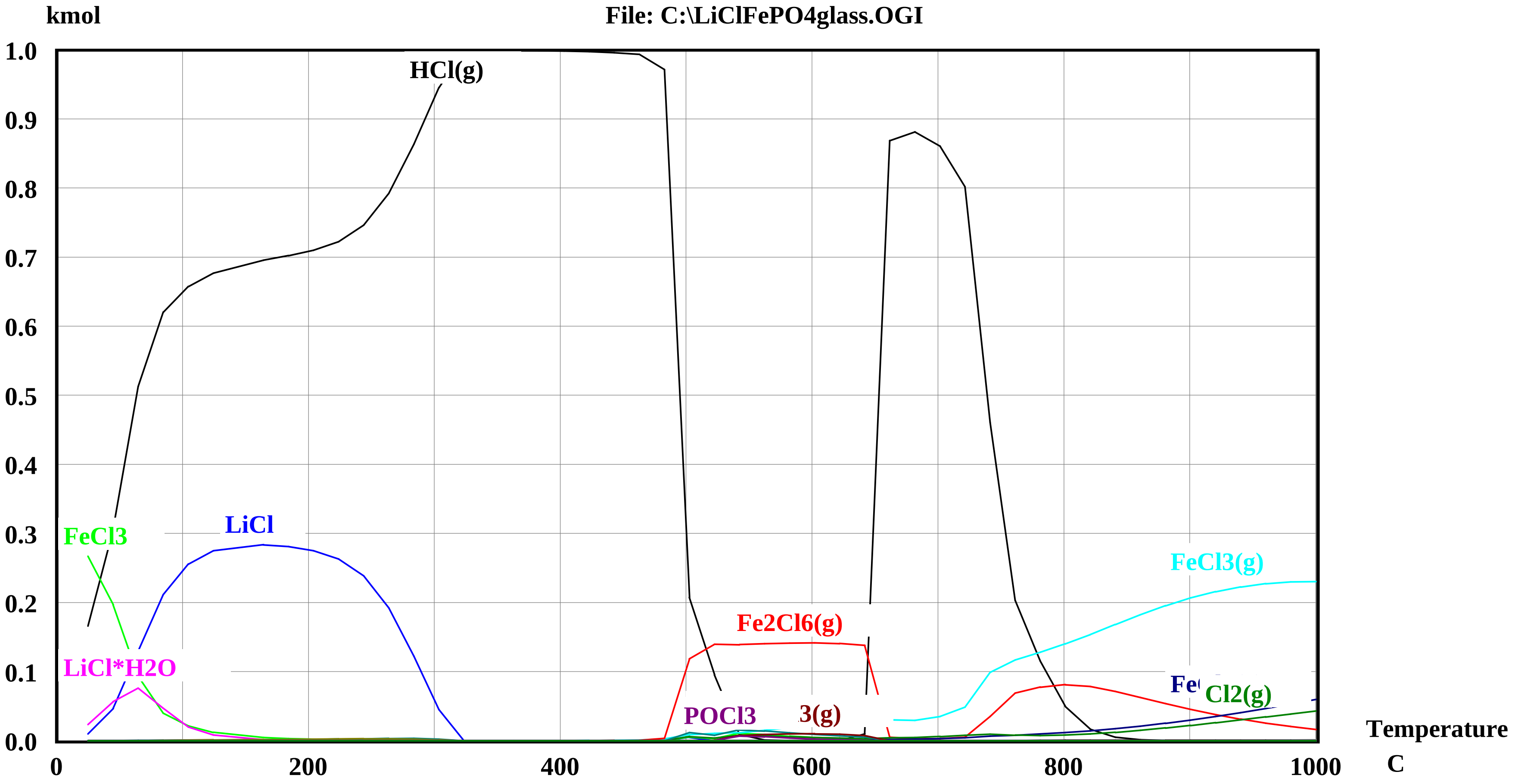
….when the O/P (or O/(P+Si) ratio is between 3.4 and 3.8”

…when Na_2O content < 23wt%

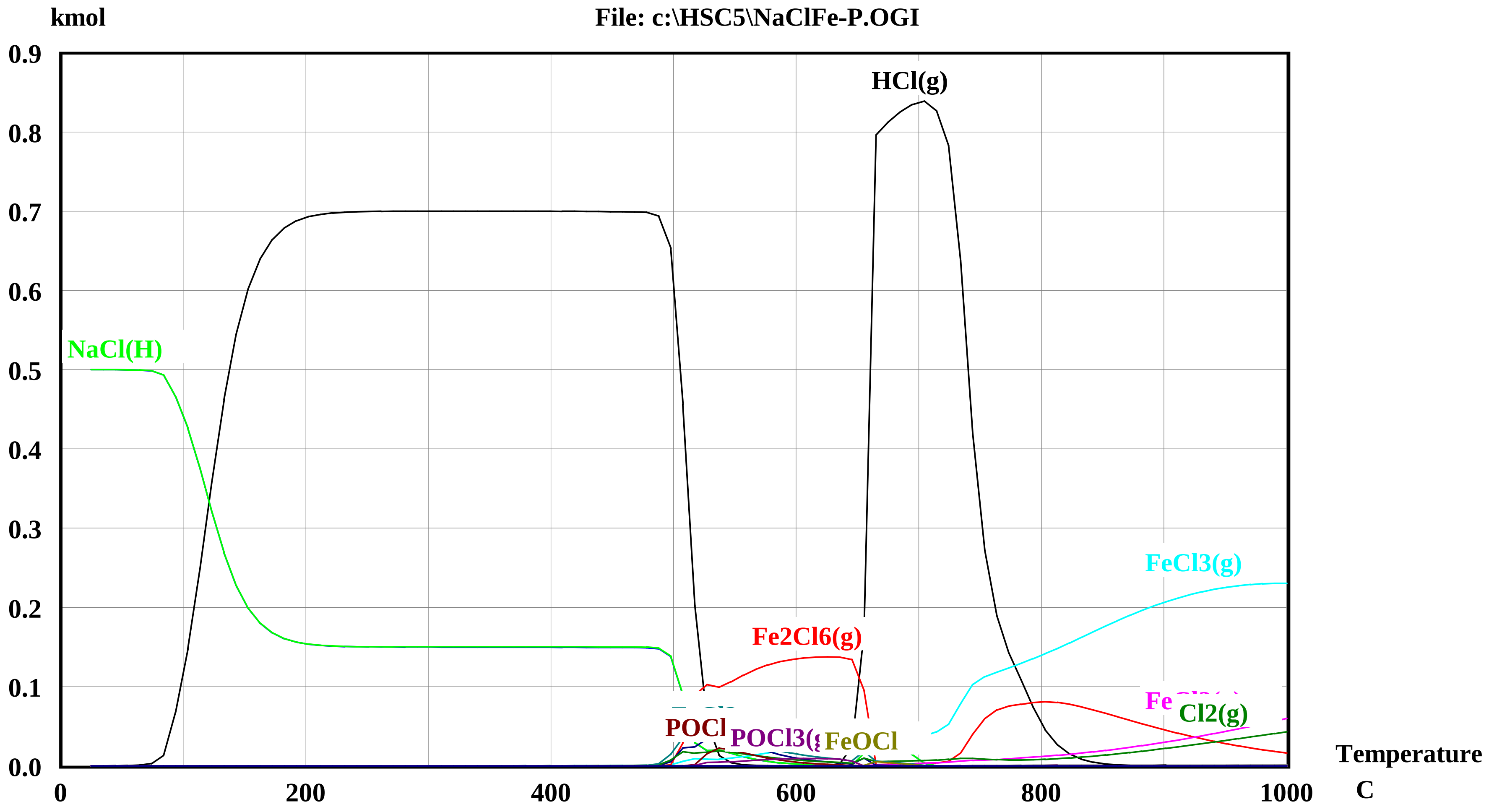
…when $P/Na \geq 1$

Huang et al., Journal of Nuclear Materials, 327(2004) 46-57

R. Leerssen, “Fe Phosphate Glass for the Vitrification of INEEL SBW and Hanford LAW”, MS Thesis, UMR (now MST), 2002



HSC 5 prediction: 1 kmole LiCl, 1.1 K mole $H_3PO_4.5H_2O$, and 0.2 kmole Fe_2O_3 @ at various temperatures (please note that in a real system, chloride would totally volatilize as HCl)



HSC 5 prediction: 1 kmole NaCl, 1.1 kmole $H_3PO_4.5H_2O$, and 0.2 kmole Fe_2O_3 @ at various temperatures (please note that in a real system, chloride would totally volatilize as HCl)

1st step: “Dechlorination”

Heating chloride salts with orthophosphoric acid generates <u>two</u> gasses

- **HCl via displacement: the solid product is a biphosphate salt mixture**
- **H_2O vapor via thermal decomposition of biphosphates: the solid product is a polyphosphate salt mixture**

QUESTIONS

- Do MST/UMR’s formulation guidelines apply to K & Li too? (its research for DOE involved only high *sodium* radwastes)
- How much chloride ends up in the glass?
- Waste loading?
- Is a separate “dechlorinator” necessary? (or “can the melter do everything”?)

“HOBBY” 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 ~$335)
- Fun!

Sand bath
& TC probe

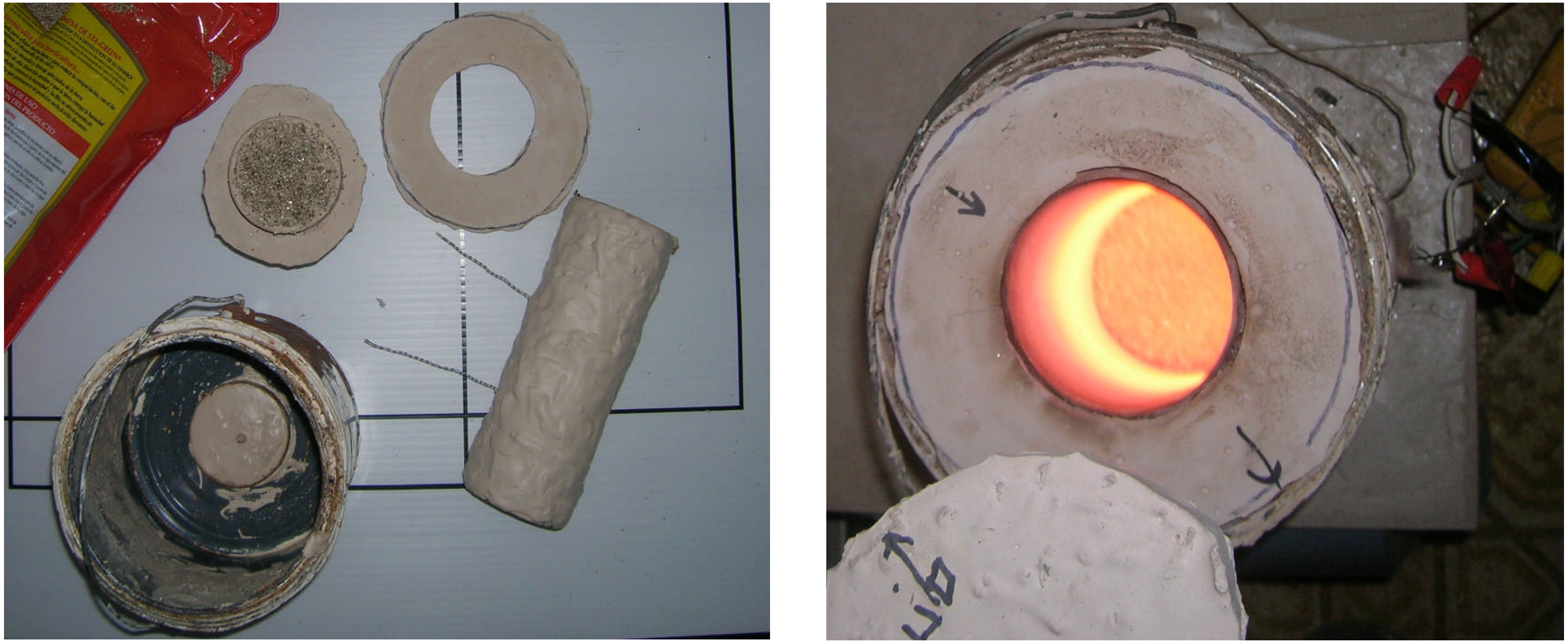
crucible

“hood”

To sink aspirator

To “hood”

BOIL-DOWN (aka “dechlorination”)



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

Steel mortar (made from 2” pipe cap)

glass

15 cc porcelain crucible

First pour!

CHARACTERIZATION

- APPEARANCE (clear or crystallized?)
- MASS (consistent with dechlorination?)
- PCT LEACH TEST
  1. Crush & isolate 75-150µ fraction
  2. Rinse off dust
  3. Add 10x as much distilled water
  4. Seal vial & “cook” at 90ºC for 7 days
  5. Cool, spin down particulates & measure the solution’s pH, conductivity, and Cl^-/PO_4^{-3} conc’s

How does “mass” characterize this process?

- The cations in a glass must be accompanied by an equivalent amount of anions
- The equivalent weight of chloride (35.46) is much greater than that of oxygen (8)
- Consequently, a glass consisting of AlkCl salt(s) dissolved in a Fe_2O_3-P_2O_5 matrix will weigh much more than one consisting of Alk_2O dissolved in a Fe_2O_3-P_2O_5 matrix (both masses are readily calculated)

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

CENTRIFUGE: 3 speed fan, faux wood flooring, plastic snap vials, barbell plate, screws, etc.

SIDE

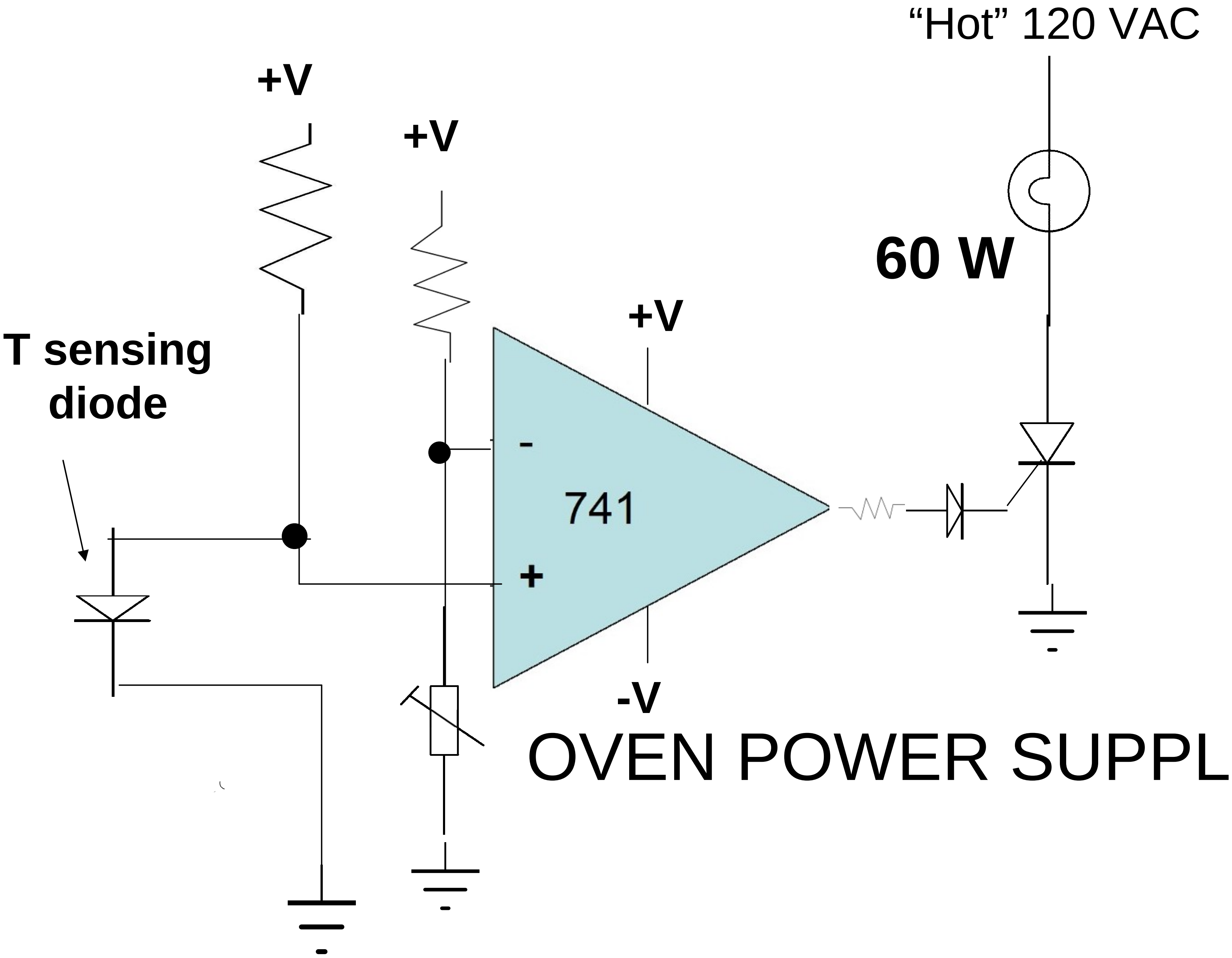
T sensor

TOP

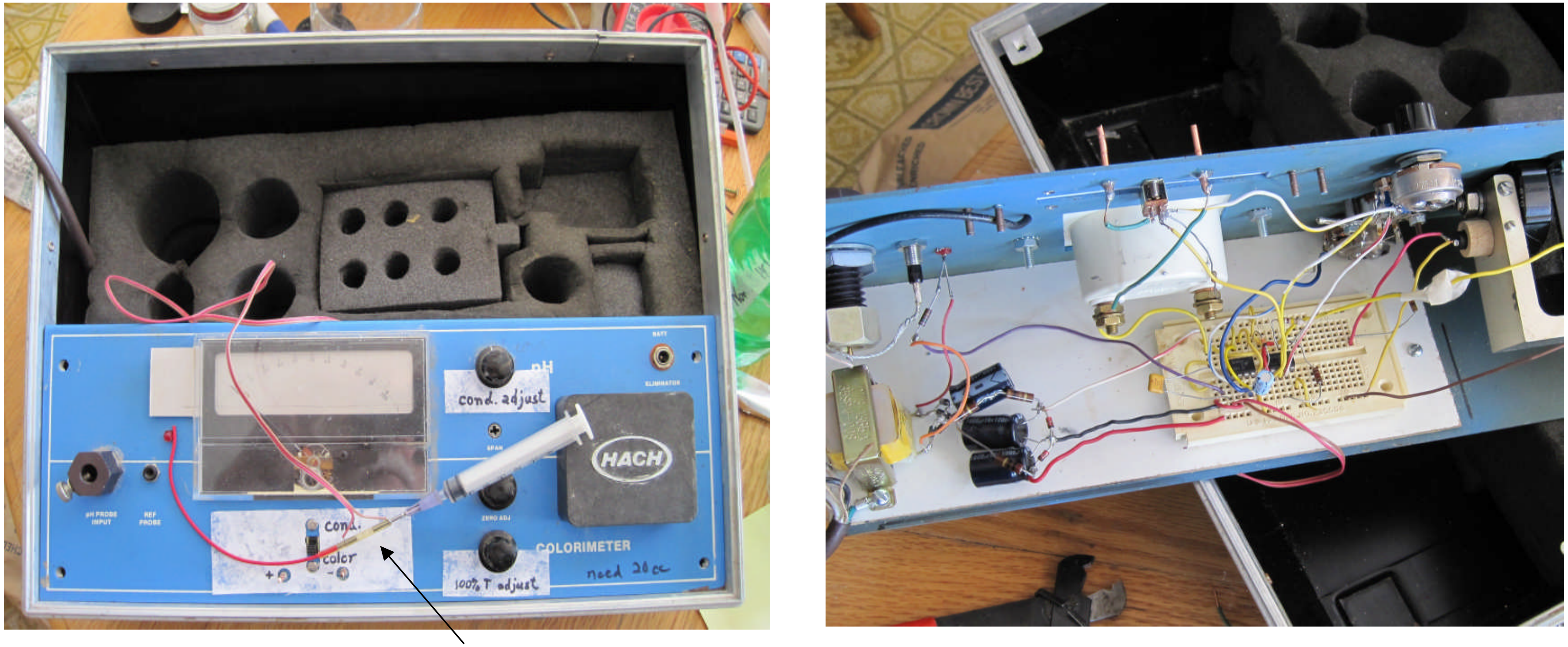
Jar with water &
sample vials

Light bulb-in-can
heater

PCT OVEN (90ºC)



OVEN POWER SUPPLY

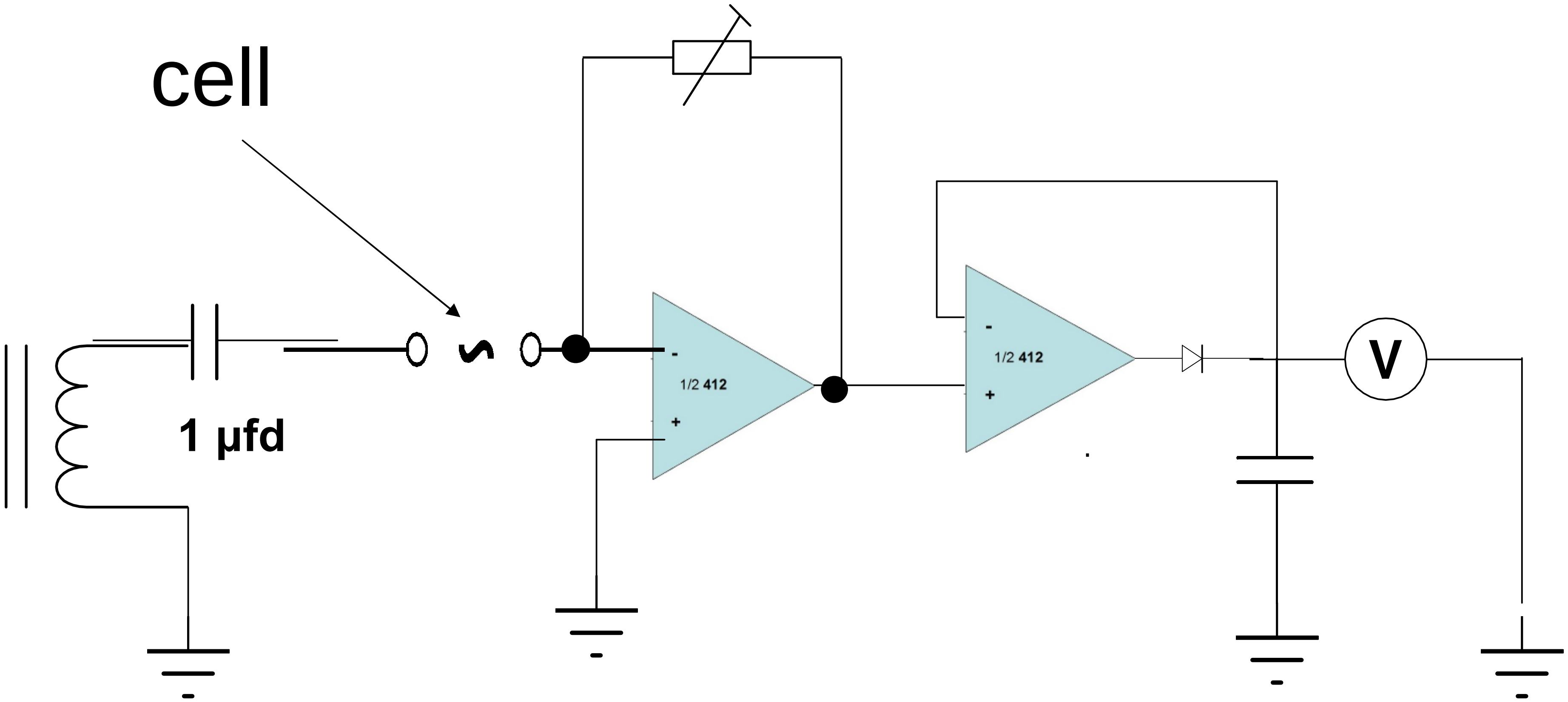


Conductivity cell

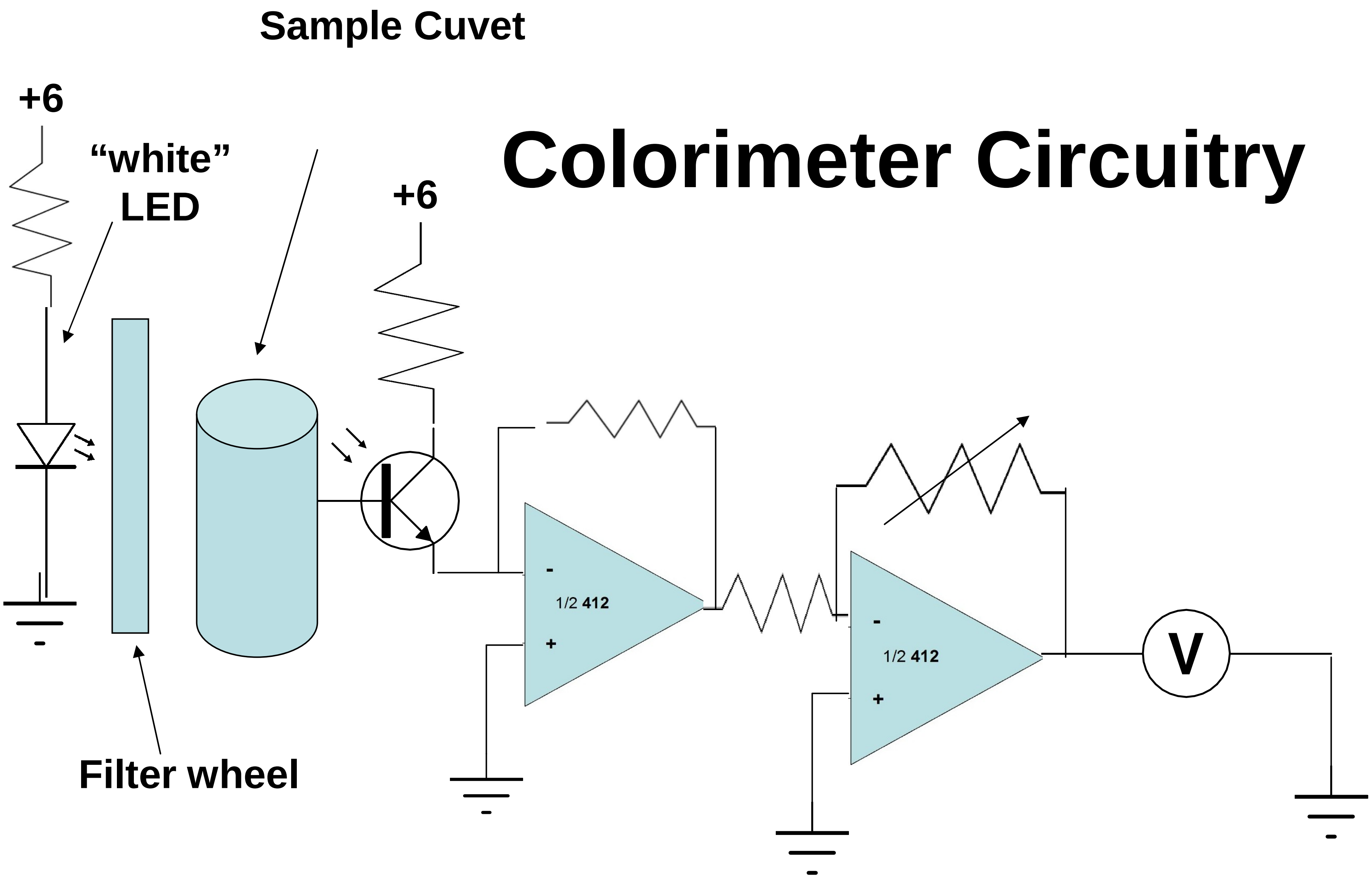
Colorimeter/Conductivity Meter

(rewired 70’s era HACH analyzer)

Conductivity Meter



Colorimeter Circuitry



CHARACTERIZATION cont.

- Key question: is the glass more or less water-soluble than EA glass via PCT?
- The corrosion of radwaste glasses via PCT produces aqueous salt solutions – primarily salts of their alkali metals
- Solution conductivity is an excellent measure of an aqueous solution’s total salt content
- pH 7 sodium bi/mono phosphate standard
- Fraction of alk salt as Cl^- in final PCT leachates determined via turbidimetry (small)

Unconventional PCT

What's the same?

- Particle size (75-150 micron or ~200 cm^2/g)
- Water/solids ratio (10:1)
- Temperature ($90^{+/-}2$ºC)

What's different?

- Rinsed sample particles are not dried before leach
- Leachate characterization via conductivity/pH, not chemical analysis
- HDPE (Nalgene™), not SS or Teflon "bomb", leach vessel
- Water vapor-saturated, not dry, "oven" (canning jar)
- Time – leachates periodically characterized, not just once after 7 days

PCT details

1. **Smash/grind glass with mortar/hammer**
2. **Dump onto seriesed 150-75 μ screens – tap & shake**
3. **Dump >150 μ chunks back into mortar**
4. **Repeat 1-3 at until entire sample passes 150 μ screen**
5. **Dump 75-150 μ fraction (typ 1.5 g) into tared 50 cc centrifuge tube**
6. **Squirt in DI water & let the particles settle about 45 sec**
7. **Remove the water/colloidal dust "rinsate" with eye dropper**
8. **Repeat 6 &7 collecting the rinsates in another centrifuge tube**
9. **Wash glass particles into tared PCT bottle with 10x as much water**
10. **Put bottle into PCT oven, note the time**
11. **Spin down the dust in rinsates, measure conductivity of solution, pour off liquid, dry tube+dust, & reweigh to determine dust (typ. 1-3%)**
12. **Periodically remove ~0.2 g of PCT leachate, dilute with water & measure conductivity**

Typical Fe-P Glass PCT Leachate

Element*	ppm	Meq/l
Al (anion)	39.3	1.44
Na (cation)	138	5.57
P (anion)	73	2.43
Si (anion)	22.5	0.8
. Huang et al., Fe-P HANFORD LLW glass *OTHER COMPONENTS INSOLUBLE		

Na=1.193(Al+P+Si)   or Na-(Al+P+Si)=0.90

Get ion balance when 37% of the P is divalent ($HPO_4^=$)

Since pK_2 H_3PO_4 =7.2, this solution's pH is pretty close to 7.2

EA glass

- DOE’s HLW benchmark (& not very durable)
- Exhaustively characterized
- Designed to dissolve at a rate of ~1g/day/m^2 via conc.-normalized 7 day PCT

In practice, this means that about 12.8% of its alkali metals end up as cations (salts) in a 7 day PCT leachate

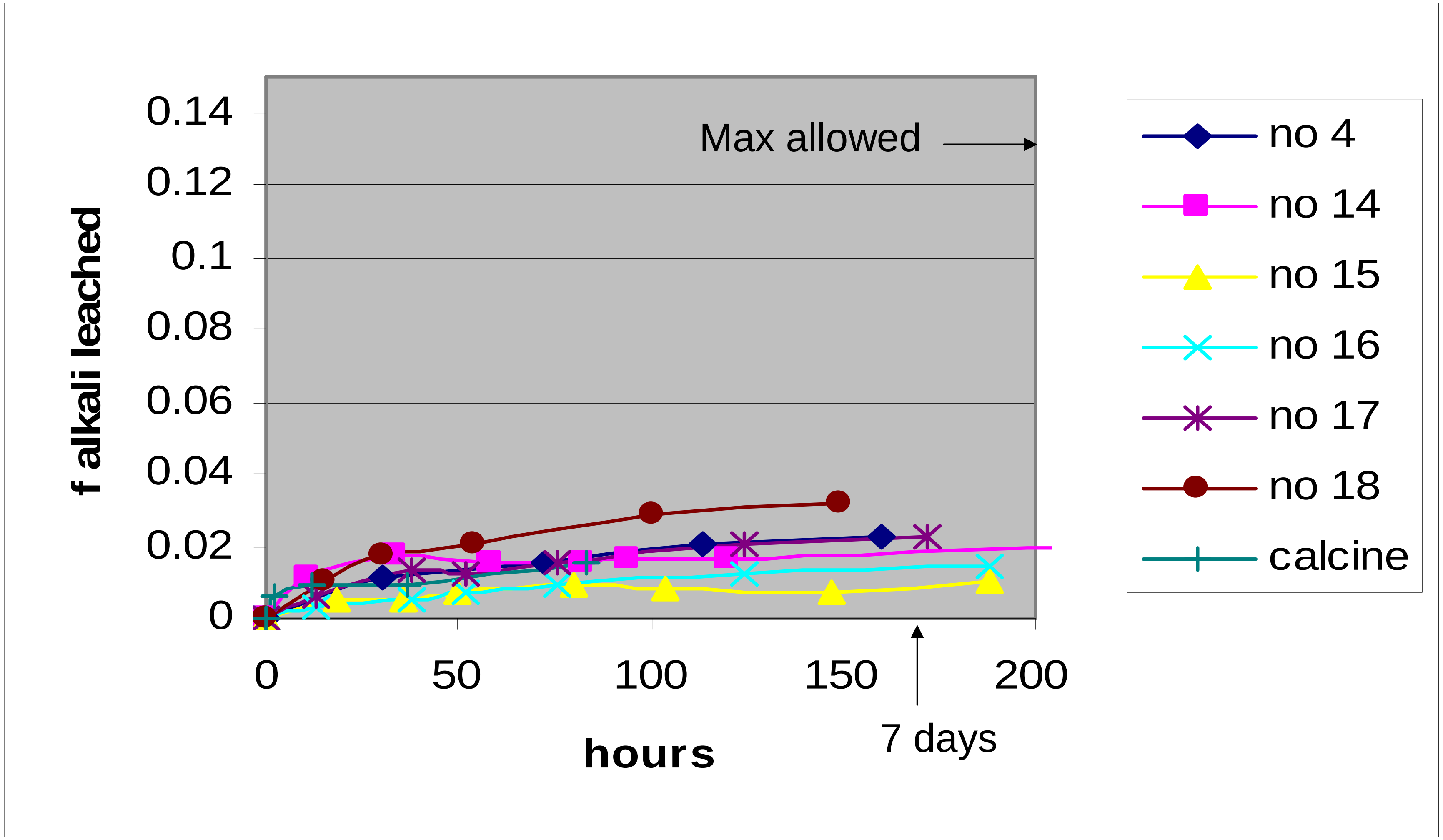
That solution’s salt content is ~ 0.11 equivalent/liter.

EA Glass continued*

	wt % in glass	ppm in leachates	% diss.
Na	16.8	~1700	13.6
Li	4.3	~200	8.3

~12.8% of its alkalis (8.33 mM/g)
dissolve via 7 day PCT

***Janzen et. al., "Characterization of the DWPF Environmental Assessment (EA) Glass", WSRC-TR-92, 1993.**



Typical Fe-P PCT leach curves

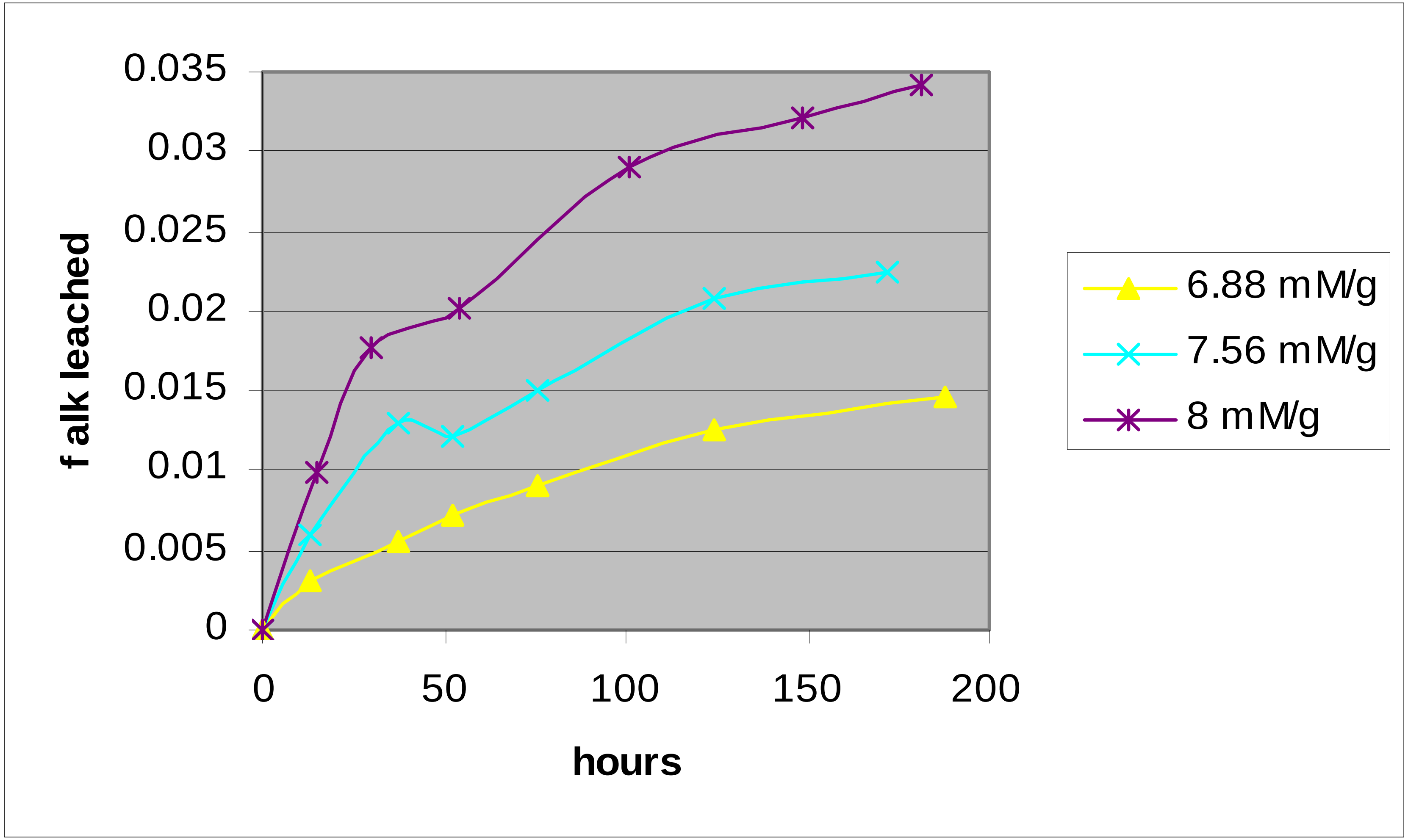
ER salt specimens PCT results *

#	Σalk meq/g	what?	Fe/P	Σalk/P	f_{alk} lost. 7 day PCT
4	6.811	Na only	0.4	0.905	0.022
14	5.682	spent ER**	0.8	0.905	0.018
15	6.118	virgin ER***	0.8	0.957	0.009
16	6.88	virgin ER	0.8	1.147	0.013
17	7.562	virgin ER	0.8	1.264	0.022
18	8	virgin ER	0.8	1.47	0.035

***all melted for one-half hour at ~1050ºC (stirred once at about 15 minutes)**

**** CWF Handbook's waste salt Na/K/Li ratio**

***** KCl/LiCl mass ratio = 1.33:1**



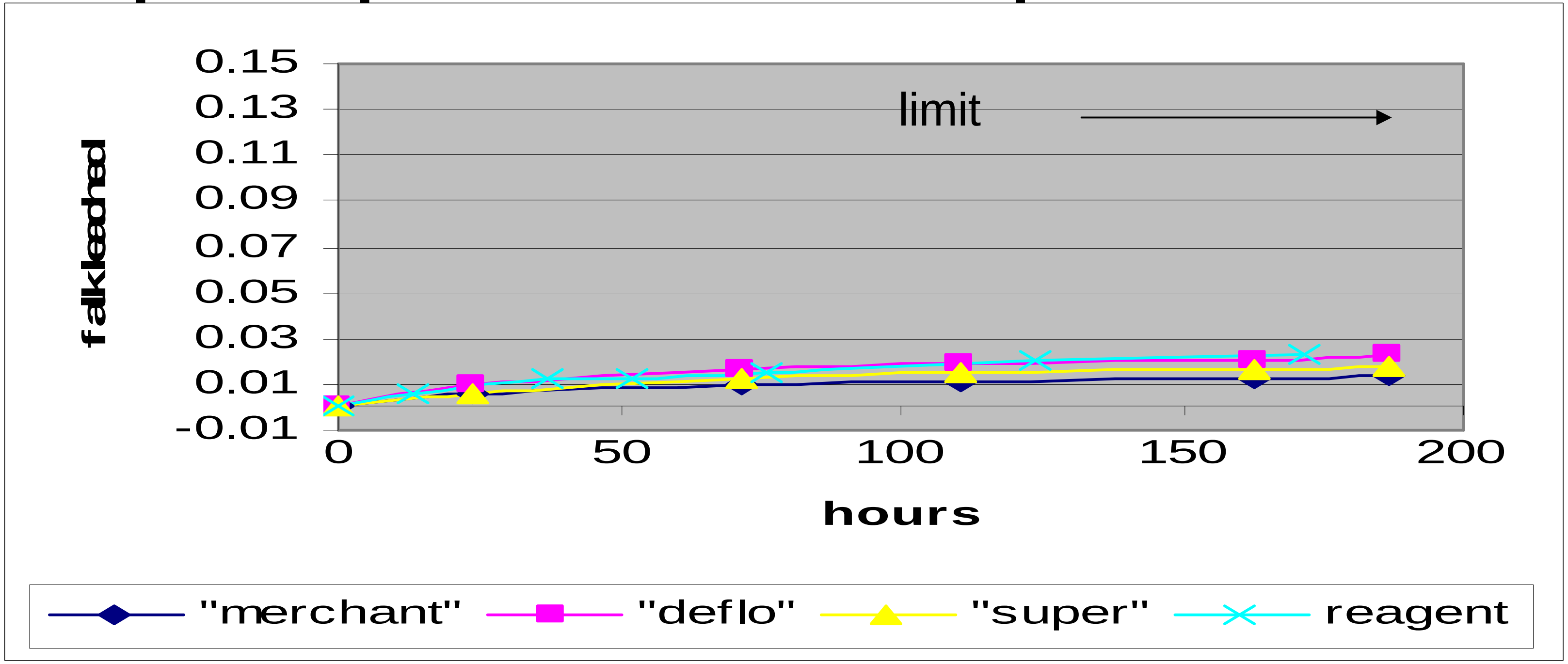
Leach resistance vs Waste (Σalkali) Loading

Melt Kinetics? Aliquots of a single partially dechlorinated 7.56 mM/g feed mix melted for 5, 10, and 20 minutes in 1050º C furnace. PCT samples prepared and f_{alk} in both PCT rinsates & 7 day PCTs measured

MELT TIME	$f_{alk\ loss}$ 7 day PCT	% alk in PCT as chloride	f_{alk} in rinsate	AgCl ppt?
5	0.052	69	0.104	Y!
10	0.19	29	0.0295	Y
20	0.015	8	0.0011	N

Conclusions: 1) virtually all chlorine volatilizes within 20 minutes, 2) up until then most of the residual is within a separate phase, not "in" the glass

Is “reagent grade” (expensive) phosphoric acid required?



PCT results of high-loaded ER salt waste Fe-P specimens made with all three of SIMPLOT’s “ag grade” phosphoric acids plus reagent grade acid

The Answer is “No”

WHY “STIR MELTER™”

- **OUR MELTER SHOULD ALSO BE A GOOD “DECHLORINATOR”**

    (i.e., ABLE TO DISENGAGE GAS BUBBLES EFFICIENTLY

- **IT SHOULD ALSO BE AS SMALL/CHEAP AS POSSIBLE**
- **IT SHOULD ALSO BE ABLE TO HANDLE “CHUNKS”, CRYSTALS, etc.**

ref. C. Marra et. al., “Vitrification...with a Stir Melter System”, WSRC-MS-96-42 (1996) (see OSTI)

- **A 6” (square) Stir Melter vitrified 6.25 kg/hr of a 33 moles volatiles/kg feed slurry to produce 2.5 kg/hr of BSG glass**
- **An ER salt Fe-P feed mixture would contain ~ 27 moles volatiles/kg**
- **Since Fe-P glass is easier to melt than BSG (lower mp & viscosity) and the feed would contain less volatiles, productivity would be greater – probably over 4 kg glass/hr**
- **Consequently, a “6 incher” should be able to keep up with a 1GW$_e$ IFR (i.e., make 9900 kg of glass/year)**

recycle

- Scrub offgas with aqueous solution of potassium/lithium hydroxides (converts the HCl to a ”virgin” ER salt solution)
- Remove any co-volatilized phosphate & dust by adding $FeCl_3$ followed by centrifugation ($FePO_X$ ppt. + dust recycled to the melter)
- Dry the Li/K chloride solution & recycle to ER
- Periodically remove radioiodide via adsorption onto cuprous or silver chloride before dry/recycle

Waste Loading

Fe-P assumptions

- 100% of the Cs ends up in ER salt
- 1 GW_e-year generates about 78 kg of Cs
- Spent ER salt is 1.82% Cs*
- ER salt waste loading (@6.6 mM/g) of Fe-P glass is 43 wt% (as chlorides, this work)

therefore

- Glass generated/GW_e-year =78/0.43/0.078 = 9.9 tonnes (vs ~53 tonnes of CWF)

***L. Morss et. al., “Ceramic Waste Form (CWF) Handbook" (ANL-NT-119), 1999**

ANSWERS

- Do MST/UMR’s formulation guidelines apply to K & Li too? (its research for DOE involved only high *sodium* radwastes)

  Ans. *“yes”*

- How much chloride ends up in the glass?

  Ans. *“Very little”*

- Waste loading?

  Ans. *“over 5 times greater than CWF”*

- Would a separate “dechlorinator” be necessary?

  Ans. “*Probably no*”

LESSONS/CONCLUSIONS

- It works! ER salt waste is readily vitrified & chloride would be simple to recycle
- Potassium is “tougher” to vitrify than is Na & Li – however additional iron ($Fe/P \approx 0.8$) fixes the problem
- PCT performance is much better than EA glass
- The glass is easy to melt (low mp & viscosity)
- “Ag” grade phosphoric acid works fine too
- With the right sort of melter it would not be necessary to have a separate “dechlorinator”
- Renders the IFR concept more attractive

And, most importantly

Don’t assume that our “experts” haven’t been wearing blinders