Improving the Integral Fast Reactor's Proposed Salt Waste Management System

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IMPROVING THE INTEGRAL FAST REACTOR'S PROPOSED SALT WASTE MANAGEMENT SYSTEM

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An often cited weakness of the Integral Fast Reactor (IFR) concept is that the chloride salt–based radioactive waste generated by its electrorefiner (ER) cannot be vitrified. Although that assertion is literally true, it is also misleading because it would be quite simple to recycle that waste's chloride and vitrify its cationic components (mostly alkali metals and fission products). Producing this alternative to Argonne National Laboratory's ceramic waste form would entail vitrification of a mixture of orthophosphoric acid, ferric oxide, and powdered ER salt with a melter able to efficiently disengage gas bubbles, e.g., a Stir Melter. The HCl evolved by this process would be absorbed by an aqueous lithium/potassium hydroxide scrub solution, which would then be dried and recycled as fresh ER electrolyte. Because radioiodide would otherwise accumulate in the ER salt, the caustic scrub solution would occasionally be contacted with cuprous or silver chloride before recycle. This scenario's primary advantages would be much lower cost and approximately fivefold greater effective waste loading. This paper describes the experimental work supporting these contentions.

I. INTRODUCTION

Nearly four decades ago Alvin Weinberg and H. E. Goeller published a seminal essay[1] that points out why a nuclear renaissance capable of dealing with the world's energy-related problems would have to be implemented with breeder-type reactors; i.e., because ^{235}U comprises only ~0.2% of the world's potential nuclear fuel supply and is both expensive[2] and politically problematic to obtain, it is too costly to represent a truly sustainable fuel source for everyone.[a,b] Since the United States decided to focus exclusively on the plutonium-breeding, liquid metal–cooled, fast reactor[3] of Argonne National Laboratory (ANL), today's Integral Fast Reactor (IFR[c]) concept[4–8] represents the only genuinely sustainable nuclear fuel cycle (Fig. 1) that could be implemented "quickly."[d] Unfortunately, it possesses drawbacks in perception,[e] waste,[9] and cost that have rendered sustainable nuclear power a tough sell to both electrical utility CEOs and the public at large.

One of the current IFR scenario's drawbacks (Fig. 2) is that the salt waste generated by its electrorefiner (ER) is to be converted to ceramic waste form (CWF) for disposal.[10] Salt-seeking fission products (FP) plus the sodium that serves as a heat transfer agent in liquid metal–

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[a] Witness the current brouhaha about Iran's uranium enrichment facility.
[b] According to the "Red Book" on uranium availability, there is thought to be ~16 million tonnes of natural uranium available at a "reasonable" price. Since mankind would need ~10 000 GW(electric) of nuclear generating capacity to become totally "green" and since once-through reactors consume about 200 tonnes of raw uranium/GW(electric)-yr, 16 million tonnes corresponds to an 8-yr fuel supply (see DOE Web site: http://www.ne.doe.gov/neac/Meetings/June92009/ANTT_Final_report_209_meeting.pdf).

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[c] In this paper, IFR refers to a sodium-cooled fast-spectrum nuclear reactor close coupled to an on-site pyroprocessing-based fuel recycling system, not to a particular ANL program.
[d] U.S. decision makers decided to quit funding Oak Ridge National Laboratory's MSBR research in 1976. Its ^{233}U-from-^{232}Th fissile production cycle generates very little plutonium.
[e] "Perception" because an LMFBR-based fuel cycle would require/generate a huge fissile inventory, most of which would consist of plutonium.
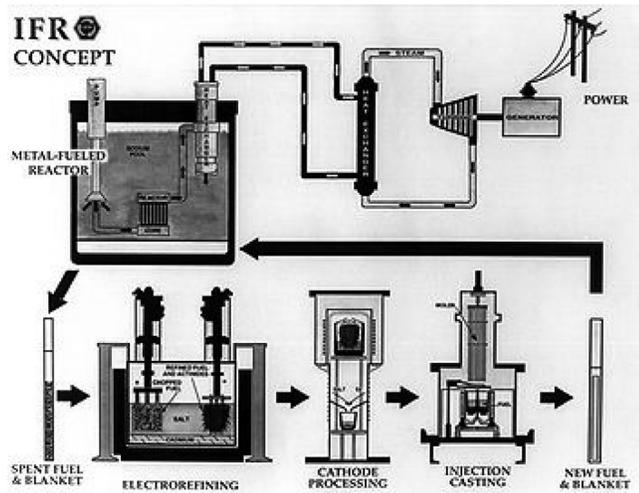
Fig. 1. Modern LMFBR/IFR concept.

cooled fast breeder reactor (LMFBR) fuel pins accumulate in the molten LiCl/KCl electrolyte until one of the following limits is reached[6]: (a) the heat load from FP exceeds the hot cell's cooling capability, (b) sodium/FP buildup increases the electrolyte's melting point beyond an operating limit, and/or (c) its plutonium inventory reaches a criticality limit. The resulting salt waste (Table I) is what goes into the CWF. (Table II provides details regarding some of the acronyms used in this paper.)

Note that ER salt waste consists primarily of the chloride salts of Li, K, and Na (total 82 wt%), not FP

TABLE I

Chemical Composition of a Representative
Waste Salt Generated by the Processing
of EBR-II "Driver Fuel"*

Element	Amount in Salt (wt%)	Element	Amount in Salt (wt%)
Na	4.42	La	0.43
Li	5.26	Ce	0.81
K	20.2	Pr	0.41
Cl	58.5	Nd	1.40
Sr	0.33	Sm	0.27
Y	0.20	Eu	0.017
Cs	1.21	Np	0.055
Pm	0.017	U	4.17
Ba	0.51	Pu	1.65
Rb	0.15	Sum =	100

*After Ref. 8. This table differs from the one in Ref. 8 in that it consists of a list of elements, not salts. It is obviously incomplete (e.g., no iodide) and probably includes a higher concentration of plutonium than a "real" IFR fuel cycle could afford to discard. Another such list is Table 11.1 of Ref. 6.

(total 5.75 wt%). Since CWF can accommodate only 10 to 13 wt% ER salt,[8] the owner/operators of an IFR-based nuclear power plant would have to produce a great deal of it. How much? Let us assume that

1. the LMFBR generates 1 GW(electric) with a thermal-to-electrical efficiency of ~40%, figures consistent with the generation of ~1 tonne total FP per year

2. cesium comprises 11 wt% of that FP (Ref. 11)

3. ER salt contains 1.21 wt% cesium (Table I).

Consequently,

CWF/GW(electric)-yr = (0.11)/(0.10 to 0.13)/0.0121

= 70 to 91 tonnes .

In other words, an IFR-based nuclear fuel cycle utilizing CWF would generate 15 to 19 times more high-level waste (HLW) form/GW(electric)-yr than do today's once-through reactors coupled to a modern Purex-based reprocessing facility.[f] By volume, this disparity is even greater because CWF is considerably less dense (~2 g/cm^3) than is glass (2.6 to 3.0 g/cm^3).

Furthermore, the CWF process is intrinsically more difficult/expensive than vitrification because it is discontinuous and requires more unit operations:

1. One part (by mass) powdered waste salt is added to approximately seven parts finely ground Zeolite 4A and transferred to a heated V mixer.

2. That salt is then occluded by the zeolite via vigorous mixing for ~20 h at 500°C.

3. The product is cooled and mixed with about one-third as much powdered glass.

At this point, there would be two options: either[4,8]

4. The zeolite/salt/glass mixture is *carefully*[g] transferred to a stainless steel, accordion-style, hot isostatic press (HIP) can.

5. The HIP can is connected to a vacuum pump and heated to ~500°C to bake out any water vapor adsorbed during the mixing/transfer steps.

6. Its fill tube is pinched and welded shut.

7. It is transferred to a HIP that converts its powdered contents to CWF and collapses the can around it. This operation involves gradual heating to 900°C under ~135 MPa (~20 000 psi) external gas pressure, a 1-h hold at that temperature, and an even more gradual cooldown.

[f] See the World Nuclear Association Web site: http://www.world-nuclear.org/education/wast.htm.
[g] "Carefully" because powder demixing would seriously degrade the leach resistance of the finished product.
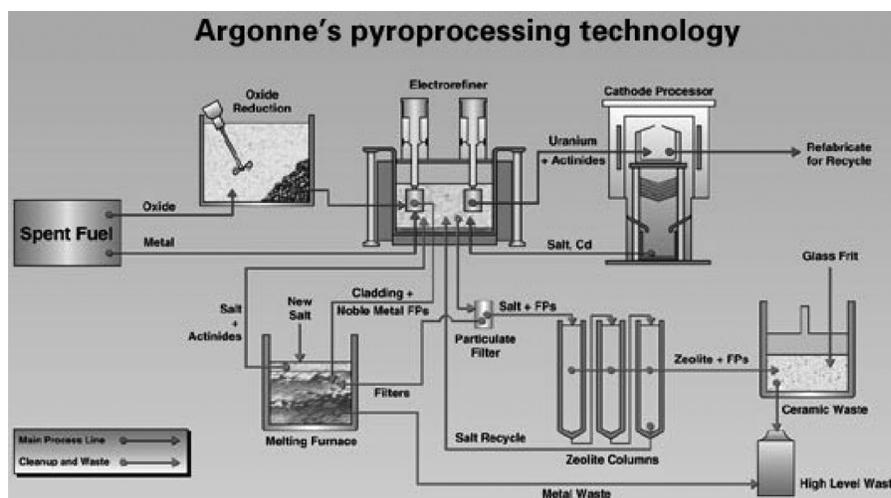
Fig. 2. ANL electrometallurgical nuclear fuel reprocessing system.[4]

or[8,9]

4′. The zeolite/salt/glass mixture is *carefully* transferred to a stainless steel glass canister similar to those currently utilized by Europe's reprocessing facilities.

5′. That canister is put into an atmospheric pressure sintering furnace that converts its contents to CWF by means of a 300-h thermal cycle.

The product of the safer/less expensive ambient pressure sintering option is relatively porous (bulk density $\sim$2.0 g/cm^3 versus $\sim$2.3 g/cm^3) but purportedly exhibits its equivalent leach characteristics (durability).[8] However, *any* way of making CWF would be so expensive to implement that saddling the IFR concept (and therefore the United States' current "sustainable" nuclear power option) with it constitutes a mistake.

II. THE IRON PHOSPHATE (Fe-P) GLASS ALTERNATIVE

Turning around situations like this requires a critical examination of *all* assumptions inherent to the current paradigm (for CWF) in order to identify/challenge/change those that render it unnecessarily inefficient.

In this case, the "wrong" assumption is that an ER salt waste form must immobilize chloride. That assumption is unnecessary because chloride is neither toxic nor radioactive nor difficult to separate. It is also crippling because none of the durable natural minerals that materials scientists set out to emulate can accommodate more than a few weight percent chloride. Since sodalite $[Na_8(AlSiO_4)_6Cl_2]$ represents the best of a poor lot in this respect (7.2 wt% chloride), ANL's materials scientists set out to produce an artificial sodalite and therefore ended up with CWF.

The vitrification alternative described herein would (a) be much less expensive, simpler, and safer to implement, (b) greatly reduce the amount of HLW form required or generated per GW(electric)-yr, and (c) recycle the process's primary chemical component (chloride).

Its implementation would entail the continuous feeding of powdered ER salt, ferric oxide, and concentrated phosphoric acid to a glass melter capable of efficiently disengaging gas bubbles, e.g., a Stir Melter. This melter[12,13] would simultaneously effect the near-quantitative evolution of chloride as gaseous HCl and the conversion of everything else to Fe-P glass,[14,15] which would overflow into stainless steel glass canisters. HCl would be scrubbed from melter off-gas with an aqueous solution of lithium and potassium hydroxides that would then be dried and recycled as fresh ER electrolyte.

To the author (a chemist), the most compelling arguments for why this scheme *should* work[h] are that (a) phosphoric acid boildowns have been used to accomplish halide separations for decades,[16] (b) the U.S. Department of Energy (DOE) has funded numerous demonstrations of the fact that Fe-P glasses could immobilize the solid residuum (alkali metal phosphates) generated by that separation,[14,15] and (c) thermodynamic calculations[17] support it.

Figure 3 depicts equilibrium compositions (major chlorine-containing components only; the software (HSC) that produced this figure considered 110 species) generated by the reaction of 1 kmole of sodium chloride with 1.1 kmole of H_3PO_4 and 0.2 kmole of ferric oxide from 0°C to 1000°C at atmospheric pressure. Note that

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[h]The "reduction to practice" described in this rewrite was undertaken because these arguments were insufficiently compelling to the reviewers (nuclear engineers, perhaps) of the original version of this paper.

TABLE II

Details Regarding Some of the Acronyms Used in the Text

ANL	Argonne National Laboratory. Designed the world's first LMFBR, EBR-I, built at Idaho's National Reactor Testing Station (NRTS, now INL) in 1951.
CWF	Ceramic waste form. The glass-bonded synthetic sodalite that represents ANL's solution to the IFR salt waste treatment problem; also called glass-bonded zeolite (GBZ) or glass-bonded sodalite (GBS).
DOE	U.S. Department of Energy. The agency responsible for managing the United States' "legacy" radioactive wastes, developing repositories, and addressing the technical issues associated with promoting/developing a "nuclear renaissance."
DWPF	Defense Waste Processing Facility. The cold-capped, unstirred, joule-heated, HLW melter installed at DOE's Savannah River Site during the early 1990s.
Fe-P	Iron phosphate glass. The alternative to borosilicate glass developed by D. E. Day et al. at the University of Missouri–Rolla [currently Missouri University of Science and Technology (MST)]. Its advantages as compared with borosilicate glasses include higher waste loading, easier fabrication, and superior leach resistance.
FP	Fission product(s). The radioactive "ash" that initially (for a few hundred years) constitutes the most radiotoxic and heat-generating material in spent reactor fuel. After that time, plutonium and minor actinides dominate.
GW(electric)	Gigawatt electrical power. GW(thermal) times the thermal-to-electrical conversion factor ($\sim$30% for an LWR, 40% for an LMFBR, and 45% for an MSBR): 1 GW(electric)$\cdot$yr $\approx$ 0.030 quadrillion BTU (quad).
HIP	Hot isostatic pressing. The waste form-making technology that best emulates igneous rock formation. Well-mixed powdered ingredients are put into a collapsible can that is first heated to distill off any volatiles, then sealed, and finally subjected to elevated temperature and isostatic pressure in a high-pressure containment vessel.
INL	Idaho National Laboratory. The current acronym/name for that DOE site; previous acronyms include INEEL, INEL, and NRTS.
LMFBR	Liquid metal–cooled fast breeder (of ^{239}Pu from ^{238}U) reactor; also known as IFR or SFR.
LWR	Light water reactor. The enriched uranium–fueled, H_2O-cooled/moderated, high-pressure reactor patented by Alvin Weinberg and subsequently adopted first by Admiral Hyman Rickover and then by most of the world.
MSBR	Molten-salt breeder reactor; also called liquid fluoride thorium reactor, or LFTR. Weinberg's/Wigner's/Oak Ridge National Laboratory's alternative to the LMFBR. The fissile burned in its core is ^{233}U bred from ^{232}Th that is either mixed with the fuel salt (one-salt reactor) or in a separate blanket salt tank surrounding the core (two-salt reactor). In any case, the molten salt stream(s) serve double duty as heat exchange fluids. Since it/they are continuously processed, an MSBR operates at steady state, achieves extremely high burnup, and requires a much smaller fissile inventory/GW(electric) than does an LMFBR. It also generates much less transuranic waste.
PCT	Product consistency test. The relatively rapid (7-day) leach test developed to monitor the durability of the HLW glass produced by the DWPF (Ref. 18).
Purex	Plutonium-uranium extraction. A reprocessing technology involving the liquid extraction of uranium and plutonium from aqueous acid–dissolved spent nuclear fuel with a solution of tributyl phosphate in an organic solvent.
SRS	Savannah River Site. DOE's plutonium production/reprocessing facility in Aiken, South Carolina; also know as Savannah River National Laboratory (SRNL) or Savannah River Project (SRP).

by the time a feed mixture initially at room temperature reached $\sim$300°C, most of its chloride would have volatilized as HCl. HCl evolution/removal would be enhanced by the simultaneous evolution of water vapor generated from that in concentrated orthophosphoric acid (typically 15 wt% H_2O) and the subsequent thermal condensation of orthophosphates to meta/pyrophosphates. HSC also indicates that virtually all

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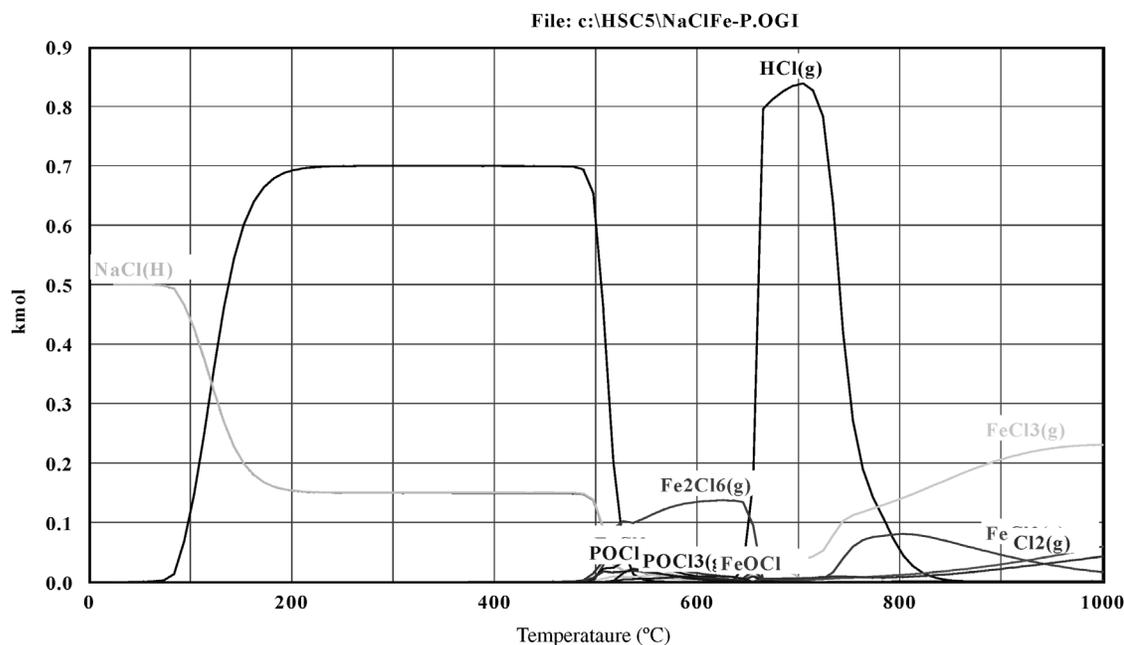
Fig. 3. HSC5 prediction (chlorine-containing species only): 1 kmole NaCl, 1.1 kmole $H_3PO_4 \cdot 5H_2O$, and 0.2 kmole Fe_2O_3.

chloride, bromide, and iodide salts would behave in basically the same fashion.

The primary questions addressed by this study were

1. Do D. E. Day's Fe-P formulation guidelines[15] apply to K and Li too? (His group's research for DOE involved only high-*sodium* radioactive wastes.)

2. What is the potential waste loading [or how much waste form would be generated per GW(electric)-yr]?

3. How leach resistant would the Fe-P glass product be?

4. How should its manufacture be implemented?

III. EXPERIMENTAL

Since the work required for this "proof of principle" was guided solely by curiosity, scientific principles, and observations (not by a predetermined protocol, schedule, budget, and/or scope[i]), it was accomplished within 2 months by the author at a total cost of about $400.

III.A. Chemicals/Supplies

Most of the chemicals used were "technical-grade" materials purchased from organizations that market via

the Internet, e.g., Seattle Pottery Supply, DudaDiesel, eBay, and Amazon. The reasons for this are that such chemicals are pure enough for the intended purpose and far less expensive (usually more than an order of magnitude less) than those sold by scientific supply purveyors. The digital balances (two), pH meter, Nitex screen material, and crucibles came from the same sources. A nearby phosphate plant (Simplot's facility in Pocatello, Idaho) donated samples of the sorts of phosphoric acid (three different grades) that would probably be used in a real process.

III.B. Leach/Durability Testing

The leach resistance of the product glasses was determined by a streamlined version of the product consistency test[18] (PCT). The PCT was chosen because it is reproducible and simple to perform and because it measures a characteristic (gross matrix dissolution) that is relevant for glassy materials.[j] Furthermore, in practice, *any* candidate HLW form's performance on the PCT relative to that of DOE's benchmark, Environmental Assessment (EA) glass,[19] has come to define whether or not it is "satisfactory."

The version of the PCT developed/used for this study generates the same solutions (leachates) produced by the "official" protocol because it exposes same-sized (75 to 150 μm) glass particles to the same amount of water

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[i]For example, the application of Fe-P glass to INL's already calcined radioactive wastes—an "obvious" application that would probably save millions of tax dollars—was never investigated because DOE did not choose to issue a "request for proposals" identifying that particular waste.

[j]The PCT is apt to generate grossly misleading results when applied to intrinsically heterogeneous and/or porous materials such as "steam reformer" calcines.[19]

(10× as much) for the same time (7 days) at the same temperature (90°C). It also measures the same glass characteristic (gross matrix dissolution). However, for practical reasons it differs in that

1. The water used to rinse off the dust clinging to freshly ground/screened PCT sample particles is characterized before being discarded.

2. Rinsed-off sample particles are not dried before being washed into the leach vessel with/by the distilled water leachant.

3. The leach vessels are small HDPE (Nalgene) bottles, not Teflon or stainless steel "bombs."

4. The atmosphere surrounding these bottles is water saturated, not dry (they are put into a loosely capped canning jar containing liquid water).

5. Leachates are primarily characterized via conductivity measurements, not chemical analysis.

6. They are characterized several times, not just once after the entire 7-day exposure period.

The amount of colloidal dust washed off the ground/screened sample particles is determined by spinning down the rinsates in tared centrifuge tubes, pouring off the liquid, drying the tubes, and reweighing. Dust generally represents 1% to 3% of total sample mass. Before the clarified rinsates are discarded, their electrical conductivities, pH, and chloride concentrations are measured. A high conductivity or chloride concentration or an unusual pH (<6 or $>8.5^k$) suggests that the specimen may perform poorly on the PCT.

III.C. Equipment

Figures 4 and 5 depict the glass kiln (melter) constructed for this project. It is made of (a) high alumina furnace cement, (b) asbestos fiber yarn to reinforce components fabricated from that cement (Figs. 4A, lid; 4B, top ring; and 4C, heating tube), (c) 20-gauge Kanthal heating wire, (d) expanded vermiculite granules that serve as insulation between the heating tube and the steel "shell" (Fig. 4D), (e) a type K thermocouple potted to the outside center of the heating tube, (f) a 1-gal steel paint can shell, (g) a light dimmer power controller, (h) a small fan to cool the dimmer, and, finally, (i) a wooden box to support the kiln and contain its dimmer/fan power supply. The digital voltmeter that measures the thermocouple's voltage is not depicted. [Temperature (°C) $\approx 20 +$ volts/0.000041.]

The uniform-temperature "melting zone" (Fig. 5A) situated at the center of the kiln's heating tube is ~8 cm

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^{k}The reason for this is that water dissolution of a "good" Fe-P glass generates a dilute phosphate buffer solution with a pH ~ 7.
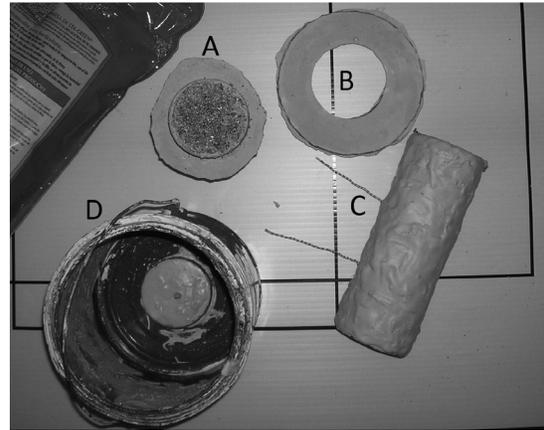
Fig. 4. Kiln components.
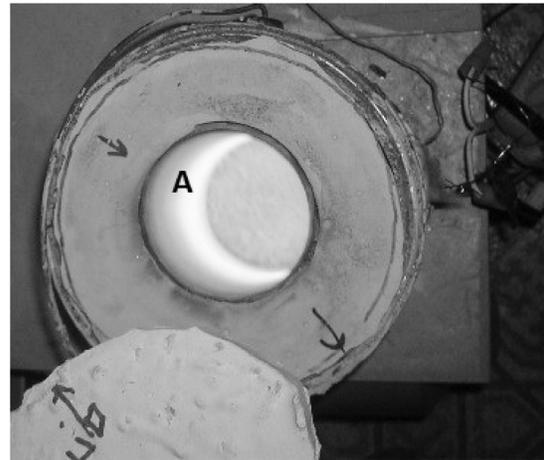
Fig. 5. Top view of hot kiln.

high and 7 cm wide. Porcelain crucibles containing waste simulant/phosphoric acid/Fe_2O_3 feed mixtures were placed onto a bed of expanded vermiculite granules situated at the bottom of this zone. This kiln can reach 1100°C within 20 min and hold that temperature indefinitely.

A centrifuge (Fig. 6) was built because accurate characterization of the product glass's leach resistance requires a determination of the amount of dust occluded by the sample particles so tested. It is made from (a) a three-speed fan, (b) two plastic snap-top vials, (c) faux wood flooring material, and (d) miscellaneous screws/glue. A 10-lb barbell plate situated at the bottom of the box upon which the motor is mounted enhances stability.

The screens (Fig. 7) utilized to isolate the 75- to 150-μm sample particles specified by the PCT protocol are made of Nitex nylon screening material, 2-in. PVC pipe fittings, and silicone glue. A mortar/pestle consisting of a 2-in. steel pipe cap (its internal threads were

Fig. 6. Centrifuge.

Fig. 8. Mortar, crucible, and glass sample.

Fig. 7. Sample screens.
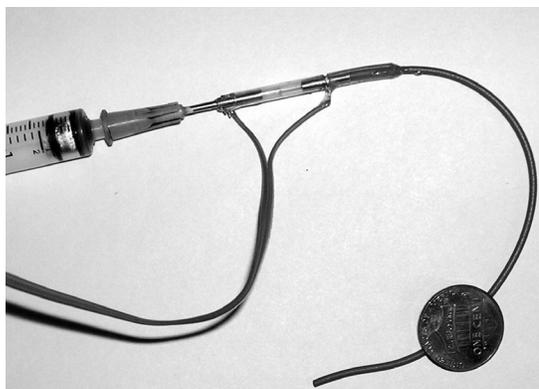
Fig. 9. Conductivity cell.

ground out to facilitate cleaning) and a 16-oz hammer head was used to crush/grind glass samples. Figure 8 depicts the mortar along with the first glass specimen generated by this project—it had been poured directly from the crucible into the mortar.

Leachates were primarily characterized via electrical conductivity because it is an easily implemented and accurate measure of total salt in aqueous solutions. The gadget built to make that measurement consists of a two-operation amplifier circuit (ac current-to-voltage amplifier followed by a peak-detecting amplifier/rectifier)[1] and a conductivity cell (Fig. 9) consisting of two sections of 16-gauge syringe needle tubing connected with fine

bore plastic tubing. Sample/reference solutions are drawn into/expressed from the cell's $\sim$10-μl active volume (between the ends of the needle sections) with a plastic syringe.

The amount of chloride in leachates containing measurable ($>$5 ppm) amounts of it was determined via turbidimetry.[m] Instrumentally, turbidimetry is identical to colorimetry/spectrophotometry in that the analytical response is equivalent to $\log_{10}$ of the ratio of light passing through a transparent "blank" solution divided by that getting through a solution that attenuates it—in this case because light is scattered by AgCl particles generated by adding phosphoric acid and $AgNO_3$ to a solution containing chloride. This determination was made with a

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[1]Contact the author for circuit diagrams.

[m]Leachates are so analyzed if a drop of silver nitrate solution added to an aliquot generates "cloudiness."
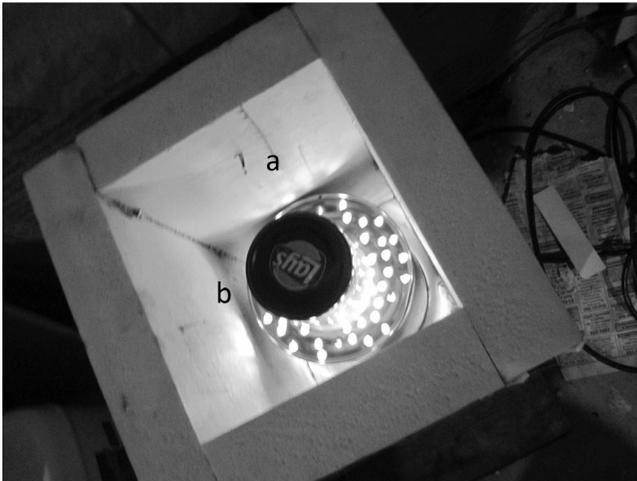
Fig. 10. Top view of PCT oven.

Fig. 11. Boildown apparatus.

Fig. 12. Venturi scrubber.

rewired HACH Soil Test Laboratory (colorimeter) purchased at a thrift store (different light source—white LED instead of tungsten light bulb; different light detector—phototransistor instead of silicon photocell; and homemade analog signal processing circuitry). This instrument shares the same homemade ±6-V power supply utilized by the conductivity meter.

An accurately thermostated oven was built to provide the $90°C \pm 2°C$ environment specified by the PCT protocol (Fig. 10; its lid was removed for this picture). It consists of a box made of 2-in.-thick high-density polystyrene insulation board ("blueboard") that is heated with a 60-W incandescent light bulb situated at its bottom. The light bulb is covered with a perforated steel coffee can upon which the canning jar (b in Fig. 10) containing the leach vessels is perched. Its power supply consists of a forward-biased silicon diode temperature sensor and a 200-V, 6-A, "sensitive gate" silicon-controlled rectifier that is switched on/off around the setpoint ($90°C$) by a operational amplifier–based comparator. This circuit's error band is $<2°C$.

III.D. Glass Preparation

Most of the specimens were prepared as follows:

1. The ER salt simulant (some combination of LiCl, NaCl, and/or KCl), ferric oxide, and orthophosphoric acid are weighed into a tared 15-cm^3 porcelain crucible.

2. The crucible is placed on an electrical heating element (kitchen stove burner, Fig. 11) and gradually heated to drive off most of the HCl/water.

3. It is then placed into the preheated (generally $\sim1050°C$) kiln and its contents cooked for a total of 30 min; after its contents have liquefied, it is picked up and swirled once during that time to enhance mixing.

4. Most of the resulting molten glass is poured into the steel mortar and the crucible is set aside to cool.

The purpose served by the stovetop boildown is to enable preparation of sufficient glass (at least 2 g) to do the leach test—so much gas is evolved that sufficient feed mix to produce that much glass would immediately boil up and out of a 15-cm^3 crucible placed directly into a preheated kiln. The majority of the HCl generated by this boildown is sucked into the tin-can "hood" (see Fig. 11[n]), absorbed by the tap water utilized by its "venturi scrubber" (Fig. 12), and flushed into a septic tank.

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[n] The thermocouple-equipped sand bath depicted in this picture was used only during preliminary studies.
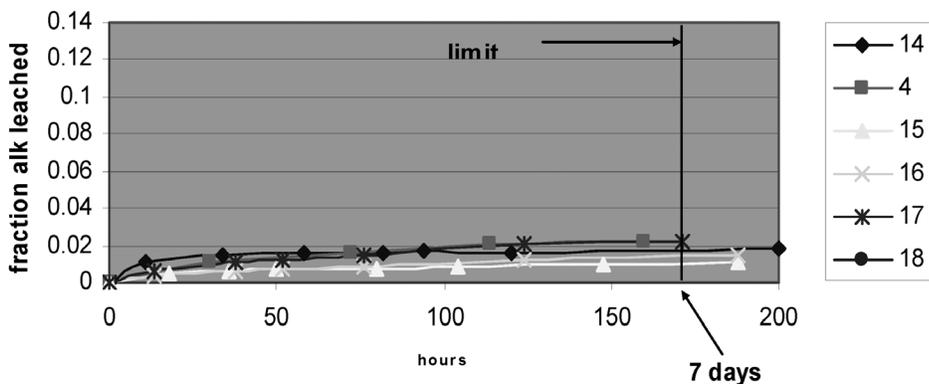
Fig. 13. PCT leach results.

IV. RESULTS

To be deemed "satisfactory," the fraction of a candidate U.S. HLW glass's bulk matrix constituents dissolving under PCT leach conditions must be less than that leached from DOE's benchmark EA borosilicate glass.[18] Since alkali metals (generally mostly sodium) constitute the most readily leached cationic components of most radioactive waste–type glasses, that judgment is generally based on the fraction of its alkalis solubilized.

EA glass is formulated so that its alkalis (sodium and lithium) dissolve at a concentration-adjusted rate of ~ 1 g/day·m^{-2} during the 7-day PCT. Its relatively poor durability is due to the fact that it has been deliberately overloaded with alkali [total = 8.3 milliequivalents/g (meq/g)]. In practice, a 7-day PCT dissolves $\sim 12.9\%$ of its alkali metals, which in turn generates a leachate containing ~ 0.11 equivalents/ℓ of salt.

The predominant species in PCT leachates generated from a properly made Fe-P glass will be its alkali metal ions balanced by an equivalent amount of mono and di-hydrogen phosphate ions. Since most of the FP in real ER salts form intrinsically insoluble phosphates that wouldn't "leach" if the bulk matrix glass totally dissolved, doing a scoping project such as this with waste simulants containing FP surrogates constitutes overkill. It is also the reason why a pH 7 phosphate buffer solution served as the conductivity meter's calibration solution.[o,p]

Figure 13 plots the fraction of the total alkali in several "good" Fe-P glasses dissolving under PCT conditions as a function of time. Please note that all of them

were much more leach resistant (better) than EA glass. Note too that it would not be necessary to leach them for 7 days to arrive at that conclusion.

Table III gives more information about these specimens. They differ in four respects: (a) alkali waste loading (meq/g), (b) iron/phosphorous (atomic) ratio, (c) alkali/phosphorous (atomic) ratio, and (d) relative proportions of the salts (LiCl, NaCl, and KCl) comprising the waste simulant. The "spent ER" salt was a 1:2.5:3.0 (by mass) mix of NaCl, LiCl, and KCl (the proportions suggested by Table 11.1 of the "CWF Handbook"[6]). The "virgin ER" salt consisted of a 5:6 (by mass) mix of LiCl and KCl.

These glasses are "good" because they were formulated correctly, i.e., not overloaded with alkali and containing sufficient iron with respect to phosphorous to chemically bind the alkalis into a water-insoluble matrix. Two things learned during the first week of this project are that potassium (a much bigger atom) is "tougher" to immobilize than either lithium or sodium and that the solution to that problem is to add more iron oxide (Fe/P ~ 0.8) than is in most of the formulations developed for DOE's high-sodium radioactive wastes.[17,18]

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[o] Since the intrinsic mobility of different hydrated alkali metal cations varies somewhat, a concentration estimate based on a conductivity measurement of a solution that may contain several of them possesses an "error band" of roughly $\pm 15\%$. This error is "important" only if the absolute value so suggested is close to a limit/standard (e.g., 12.9% alkali dissolution).

[p] Acid/base titration of the leachates verified that their predominant anions are $H_2PO_4^-$ and $HPO_4^=$.

TABLE III

Compositions and Chemical Durabilities
of Several Representative Glasses

Specimen Number	Total Alkali (meq/g)	Waste Surrogate	Fe/P	Total Alkali/P	Fraction Dissolved via 7-day PCT
4	6.811	NaCl only	0.4	0.905	0.022
14	5.682	Spent ER	0.8	0.905	0.017
15	6.118	Virgin ER	0.8	0.957	0.010
16	6.88	Virgin ER	0.8	1.147	0.014
17	7.562	Virgin ER	0.8	1.264	0.022
18	8.00	Virgin ER	0.8	1.47	0.034

TABLE IV

Reaction Kinetics Experiment

Reaction Time (min)	Fraction of Total Alkali Dissolved via 7-day PCT	Fraction as Chloride Salt	Fraction of Total Alkali in Sample Powder Rinsate	Chloride in Rinsate?
5	0.052	69	0.104	Yes!
10	0.019	29	0.029	Yes
20	0.015	8	0.001	No

Specimens 15 through 18 differed only with respect to waste loading. The feed mixture going into the highest-loaded/worst-performing (but nevertheless "satisfactory") of them (specimen 18) consisted of 1.4 g of KCl, 1.00 g of LiCl, 3.37 g of phosphoric acid, and 1.90 g of ferric oxide. Its mass was 5.30 g, which corresponds to an alkali waste loading of 8.00 meq/g, similar to that of EA glass. Its leach test performance was three and one-half times superior to that of EA glass, which suggests that waste loading could be pushed even higher.

The kinetics of this process was investigated by putting aliquots of a single, partially dechlorinated (on the stovetop) batch of a 7.56-meq alkali/g virgin ER salt/Fe_2O_3/H_3PO_4 feed mix into three different crucibles and placing them in the preheated 1050°C furnace for 5, 10, or 20 min (Table IV). The resulting glasses were PCT leach tested and the fraction of total alkali present as chloride salts in the leachates was measured. The fraction of the total alkali in sample powder rinsates was also determined.

The results of this experiment suggest that (a) chloride volatilization/removal is not instantaneous; (b) longer reaction times tend to improve the durability (leach resistance) of the glass; (c) this improvement is largely due to the fact that longer reaction times drive out more chloride; (d) most of the readily leached chloride exists

as a separate salt phase (see rinsate results), and, most important, (e) a 20-min kiln/melter residence time should be sufficient to produce a good-quality waste form.

Because the pure phosphoric acid purchased from scientific supply companies typically costs two to three orders of magnitude more than "raw" acids,[q] four otherwise identical[r] virgin ER salt/Fe_2O_3/H_3PO_4 glasses were made with different acids: reagent-grade, plus Simplot's "Merchant" (least pure), "Deflo" (somewhat purer, especially with respect to fluoride), and "Super" (most concentrated) acids. The PCT results (Fig. 14) suggest that less expensive acid would be perfectly satisfactory for this purpose.

V. CONCLUSIONS

What does all this mean?

First, it would be quite simple to produce Fe-P waste forms that would satisfy DOE's durability criterion. Every formulation containing up to 50% by mass ER waste stimulant (~8 meq alkali/g) with appropriate amounts of phosphoric acid and iron oxide (Table III) easily surpassed the performance of DOE's benchmark HLW glass.[s] In other words, this process is not "fussy."

Another advantage of Fe-P relative to CWF is that it is intrinsically much more homogeneous. A rarely mentioned property of CWF is that it is often inhomogeneous,[10] which means it may contain tiny inclusions of salts ($^{137}CsCl$?) that will readily dissolve if/when they encounter water. The PCT protocol does not "notice" this

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[q]For example, $120/half liter versus about $600/ton.

[r]Since the exact concentrations of Simplot's fertilizer-grade acids were unknown, the proportion of phosphate in these specimens is probably somewhat different.

[s]References 15 and 16 describe other formal leach/durability tests to which Fe-P glasses have been subjected: The bottom line is that glass that performs well on the PCT performs well on all tests.
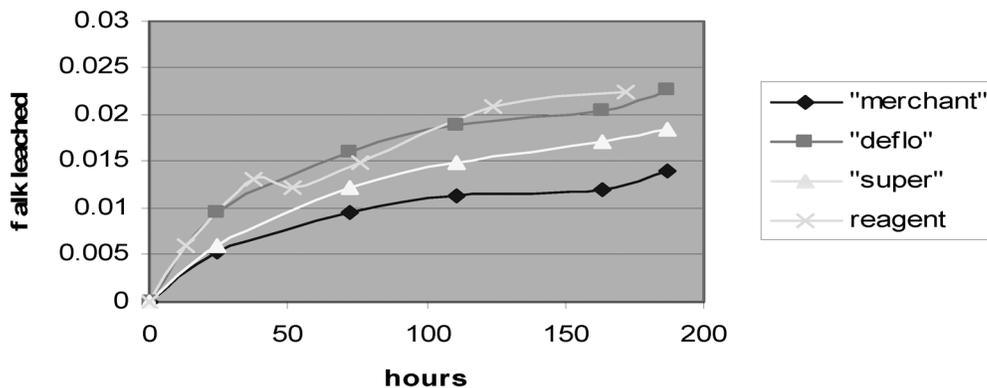
Fig. 14. Durability of glasses made with different "grades" of phosphoric acid.

characteristic unless the rinsates generated by its sample powder rinsing step are analyzed and the results duly reported along with sufficient background information to enable quantitative evaluation.[t] Glasses are intrinsically more homogeneous ("simpler") because they are frozen liquids whose constituents have been much more intimately mixed.

Next, let us compare the amount of Fe-P waste form that would be made from 1 GW(electric)-yr of ER salt waste to the 70 to 91 tonnes generated by the CWF process. Since most of the chloride in ER salt is associated with its alkali metals and 58.5 wt% chloride (Table I) corresponds to 16.4 meq/g (0.585/35.46), the effective ER salt waste loading of an 8 meq/g alkali Fe-P glass (e.g., specimen 18) would be ~50 wt% (8/16.4). Since 1 GW(electric)-yr of IFR power would generate ~0.11 tonne of FP cesium and ER salt waste is 1.21 wt% Cs (Table I), the amount of Fe-P glass generated per year would be ~18 tonnes [0.11/0.0121/(8/16.4)]. This is four to five times less than the amount of CWF required to treat the same waste.

Furthermore, since this process is also intrinsically simpler than is making CWF, it should be much less expensive to implement. For example, when fed with a 40% solids aqueous slurry, the 6-in. Stir Melter™ utilized to demonstrate the vitrification of Rocky Flats ash[12] produced 2.5 kg/h of borosilicate glass.[u] Since the manufacture of Fe-P from ER salt would be "easier" than making that glass (less gas evolution plus a lower viscosity/melting temperature glass product), that tiny/less expensive melter should be able to keep up with a 1 GW(electric)-yr IFR's salt waste production rate (18 000/365/24 = 2.05 kg/h). If one assumes that this process would be implemented during 8-h work shifts 5 days/week, rather than 24/7, a 12-in. Stir Melter could surely do the job.

A 6-in. Stir Melter possesses a working volume of about 3.5 ℓ. Since the density of Fe-P glass is ~2.9 g/cm^3, the production of 2.05 kg/h corresponds to an in-melter residence time of ~5 h (3.5·2.9/2.05)[v]—much longer than is necessary to produce "good" glass (anything over ~20 min, see Table IV).

The phosphoric acid required to convert 1 GW(electric)-yr of ER salt waste to Fe-P glass should cost about $7000. The iron oxide should cost much less.

Since the authors of technical papers must scrupulously avoid "commercialism," I must point out the reasons why this process should be implemented with a Stir Melter rather than with one of the melters generally invoked by DOE's radioactive waste management experts. Basically, it boils down to the fact that the former are much faster, much easier to use, and capable of process-

ing a much wider range of feed streams.[w] The reason for this is that both mass and heat transfer rates are greatly enhanced by the mixing impeller, which also serves as one of its heating electrodes.[x] This is why the relatively small (~1 m^3) Stir Melter purchased to make the glass used to full-scale test the new/improved pour spout of DOE's much bigger (~2.5 m^3) DWPF could produce that glass three times faster than it actually had to.[13] In this particular case, when the proposed feed stream is introduced into a melter, it will immediately form a viscous fudgelike liquid that evolves a great deal of gas (HCl and steam). If this foamy "fudge" is not actively stirred to disengage that gas,[y] it will boil over unless the feed (process) rate is very low.

An efficient glass melter could be small/affordable enough to be considered expendable, which, in turn, would simplify IFR plant maintenance and thereby reduce the cost of its electricity.

What would be needed to clean up this system's off-gas? The manufacture of 2.05 kg/h of Fe-P would generate 0.59 kg/h of HCl—about 0.26 gram-mole or 5.9 ℓ/min of gas (standard temperature and pressure). A reasonable way to deal with it would be to run the off-gas through a small quencher/scrubber that utilizes a 2/3 by mole aqueous solution of potassium and lithium hydroxides. This would simultaneously remove/collect virtually all of the contaminants evolved by this process (both gaseous and particulate) and enable recycle of the chloride back to the ER as fresh electrolyte (the scrub solution would be dried first).

Since real ER waste salt would contain traces of radioiodide, which would behave much like chloride, it would occasionally have to be removed from the scrub solution before recycle. An affordable, simple way to do this would be to stir a slight stoichiometric excess of cuprous chloride (or silver chloride) into a slightly acidified (with HCl) batch of scrub solution (1 day's worth perhaps), mix until iodide has displaced chloride from that salt, and then filter off (centrifuge perhaps) the solids [now primarily cuprous (or silver) iodide[z]] before drying

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[t]Such information is rarely included in readily accessible ANL reports.

[u]This figure (2.5 kg/h) is probably conservative (low) because the area-normalized production rate of the 3-ft melter described in Ref. 13 was three times greater.

[v]The mean residence time of feed material in DWPF is ~70 h.

[w]For example, a Stir Melter could also readily produce a deliberately inhomogeneous "glass ceramic" product. Doing this with an unstirred melter is apt to be both problematic and potentially dangerous.

[x]The other electrode is the wall of the melter itself; both should be made of INCONEL® alloy 693 (Ref. 15). (INCONEL is a registered trademark of the Special Metals Corporation group of companies.)

[y]The "cold crucible" melters currently being touted as a solution to DOE's inefficient melter-related (i.e., cost) problems are not much, if any, better at disengaging gasses than are its existing melters.

[z]Cuprous iodide is a promising candidate waste form material because it is inexpensive, insoluble in water ($K_{sp} = 10^{-11.96}$) and could be readily consolidated to a theoretically dense "ceramic" by low-temperature HIPing in copper cans. The resulting tiny waste forms [the volume of CuI so generated

the scrub salt for recycle. The equipment (scrubber, salt drier, filter, and/or centrifuge) required to implement these operations would not have to be either large or expensive.

As the paper was going through review, this process was successfully demonstrated with surrogates of several of the fluoride salt–based waste streams[20] apt to be generated by the even more sustainable MSBR-based nuclear fuel cycle.

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REFERENCES

1. H. E. GOELLER and A. M. WEINBERG, "The Age of Substitutability," *Science*, **191**, *4228*, 683 (Feb. 20, 1976) (OSTI 5045860).

2. "Famous Moments in FoE History: Exposing the Uranium Cartel in 1876," W. Lichacz, *Chain Reaction*, edition #100 (Aug. 2007); http://www.foe.org.au/anti-nuclear/issues/oz/u/cartel (current as of March 6, 2012).

3. A. WEINBERG, *The First Nuclear Era—The Life and Times of a Technological Fixer*, Chap. 6, AIP Press (1994).

4. "Electrometallurgical Techniques for DOE Spent Fuel Treatment: Final Report," U.S. National Research Council (2000).

5. C. SOLBRIG et al., "Pyroprocessing Progress at Idaho National Laboratory," *Proc. Advanced Nuclear Fuel Cycles and Systems GLOBAL 2007*, Boise, Idaho, September 9–13, 2007, American Nuclear Society, LINL/CON-07-12983, OSTI ID 927638; see also "Nuclear Reprocessing," Wikipedia Web site: http://en.wikipedia.org/wiki/Nuclear_fuel_reprocessing (current as of May 5, 2011).

6. "Ceramic Waste Form (CWF) Handbook," ANL-NT-119, L. MORSS, compiler, Argonne National Laboratory (1999).

7. "Method of Preparing Sodalite from Chloride Salt Occluded Zeolite," U.S. Patent 5,613,240 (1997); http://www.patsnap.com/patents/view/US5613240.html (current as of May 5, 2011).

would be ~1.4 ℓ/GW(electric)-yr] would last virtually "forever" at the bottom of an oil exploration–type borehole.

8. S. PRIEBE, "The Ceramic Waste Form Process at Idaho National Laboratory," IT3 '07 Conf., Phoenix, Arizona, May 14–18, 2007, INL/CON-07-12580; www.inl.gov/technical publications/Documents/3792214.pdf (current as of May 5, 2011).

9. J. MAHAFFEY, *Atomic Awakening*, pp. 304–305, Pegasus Books, New York (2009).

10. "Assessment of Partitioning Processes for Separation and Transmutation of Actinides," IAEA TECDOC 1648, Sec. 9.5.3:10, International Atomic Energy Agency (Mar. 2010); see also "Nuclear Reprocessing," Wikipedia Web site: http://en.wikipedia.org/wiki/Nuclear_fuel_reprocessing (current as of May 5, 2011).

11. M. BENEDICT, T. H. PIGFORD, and H. W. LEVY, *Nuclear Chemical Engineering*, 2nd ed., Table 8.8, McGraw-Hill (1980).

12. C. MARRA, "Vitrification of Simulated Radioactive Rocky Flats Plutonium Containing Ash Residue with a Stir Melter System," WSRC-MS-96-0442, Westinghouse Savannah River Company (1996).

13. D. F. BICKFORD et al., "Functional Test of Pour Spout Insert and Knife Edge," TTP SRI-6-WT-31, Milestone XXX, Milestone C.I-2 Report, WSRC TR 99 DO232, Rev. 0, Westinghouse Savannah River Company (1999).

14. R. LEERSON, "Fe Phosphate Glass for the Vitrification of INEEL SBW and Hanford LAW," MS Thesis, University of Missouri–Rolla (2002).

15. D. E. DAY and C.-W. KIM, "Reaction of INCONEL 690 and 693 in Iron Phosphate Melts: Alternative Glasses for Waste Vitrification," DE-FG02-04ER63831, Project 0010255, University of Missouri–Rolla (Aug. 2005).

16. J. BRADY and G. HUMISTON, *General Chemistry: Principles and Structure*, 3rd ed., p. 639, John Wiley and Sons (1982); see also "Phosphoric Acid," Wikipedia Web site: http://en.wikipedia.org/wiki/Phosphoric_acid (current as of May 5, 2011).

17. "HSC Chemistry: Chemical Reaction and Equilibrium Thermodynamics," Version 5, Chempute Software (2001).

18. C. M. JANTZEN, N. E. BIBLER, and C. E. BEAM, "Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material," WSRC-TR-92-346, OSTI ID 6876372, Westinghouse Savannah River Company (1992).

19. D. D. SIEMER, "Steam Reformation of Sodium Bearing Waste: Pros & Cons," *Ceramic Trans*., **168**, 81 (2005).

20. W. R. GRIMES, "Molten Salt Reactor Chemistry," *Nucl. Applic. Technol*., **8**, 137 (Feb. 1970).