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HOT ISOSTATIC PRESS (HIP) VITRIFICATION OF RADWASTE CONCRETES

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ABSTRACT

Properly formulated and properly "canned" radwaste concretes can be readily hot-isostatically-pressed (HIPed) into materials that exhibit performance equivalent to typical radwaste-type glasses. The HIPing conditions (temperature/pressure) required to turn a concrete waste form into a "vitrified" waste form are quite mild and therefore consistent with both safety and high productivity. This paper describes the process and its products with reference to its potential application to Idaho Chemical Processing Plant (ICPP) reprocessing wastes.

INTRODUCTION

Two of the reasons for the US Federal government's inability to dispose of its reprocessing radwaste are that:

1) the radwaste classification system it uses suggests that because of its origin (reprocessing), the bulk of the ICPP's radwaste is "HLW" and must therefore be shoehorned into the most current version of DOE's "official" spent fuel/HLW repository...this in spite of the fact that that repository is generally accepted to be a chimera and that more appropriate alternatives are available[1-4].

2) again, because of its origin, today's radwaste management paradigm suggests that DOE's reprocessing waste must be prepared for disposal (i.e., "vitrified") in the same manner as is the HLW that BNFL/COGEMA make doing commercial fuel reprocessing...in spite of the fact that US defense-type HLW is hundreds of times less radioactive, hundreds of times more voluminous, and much more heterogeneous.

These assumptions cause DOE-Complex systems analysts to assign inordinate weight to "volume minimization" and "separations" - which turns them into potent cost-drivers. Unfortunately, today, cost-drivers simply perpetuate paralysis. Issac Winograd has characterized the phenomenon as a "transscientific problem"[5].

Great Britain has adopted a more constructive paradigm[6]. When the Thatcher government gave BNFL the go-ahead in 1982 to design that nation's latest commercial fuel reprocessing facility (THORP), it mandated that the new facility would not only have to process all *new* waste completely through to road-ready waste forms (no more "interim" storage of raw waste), but that it would also have to work off the UK's backlog of "historic" reprocessing waste...more than 140 distinguishable streams of intermediate-level radwaste having a total volume (at that time) of ~20,000 m^3. Five years worth of collaborative effort by BNFL technologists and UK governmental agencies eventually led to an agreement that all radwastes emitting less than ~500 watt/m^3 worth of radiative heat would be solidified with inorganic cements...irrespective of their origins. That conclusion was consistent with IAEA guidelines & the research effort supporting it engendered more than 700 technical reports. It is also consistent with the opinions of many US scientists[7-9].

DOE and EPA have agreed that if the ICPP's calcined radwaste were to be mixed with fritting agents and then HIPed to form a glass-ceramic, it would be "vitrified"[10]. Both because the HIP cans used for previous waste form development work at ICPP[11] bear a striking resemblance to the canisters that BNFL uses for its hydrocramic waste forms (except for size), and because the compositions of some cementitious binders are similar to those of some of the HIP frits used previously, we decided to see if "staged" solidification might be technically viable; i.e., waste would first be solidified in the same manner that the UK uses for similarly-radioactive waste and then, if the political drivers for doing so persist, those waste forms could be "vitrified" later.

EXPERIMENTAL

About 90% of the ICPP's historic reprocessing waste has already been converted to a dry granular powder by calcination in two fluidized bed reactors - the second of which is still operative. These calcines are typical US defense-type reprocessing wastes in that they are moderately radioactive (typically ~40 watt/m^3), slightly toxic (some of them contain enough readily-leachable Cr^{VI}, Hg, and/or Cd to fail a TCLP test), TRansUranic (~3000 nCi/g total TRU), chemically heterogeneous, and very large in volume. They are atypical in that they are readily retrievable (95% of them anyway), contain only modest amounts of soluble sodium salts, and no tangible committment to any particular solidification process has yet been made.

In order for any remoted waste solidification process to be run efficiently, its feed must be both compatible with that process and reasonably consistent. Because it would probably be possible to use the existing calcination facility to simultaneously denitrate and homogenize all existing ICPP radwaste (including LLW) into such a feedstream in under three years [by slurrying existing calcines with the remaining liquid wastes, adding sugar, and then (re)calcining them], we decided to devote a good deal of attention to waste simulants consistent with this "preferred scenario".

Cementitious "Intermediate" Waste Form

Cementitious solidification was complicated by the fact that we not only wanted to make a "intermediate" hydroceramic product capable of satisfying the usual waste form performance criteria but one which could then be easily converted to an equally competent "vitrified" product. Another factor is that ICPP calcines contain both set accelerators (e.g., soluble aluminates) and set retarders (e.g., borates). [Accelerators are more apt to cause trouble during scale-up.] The process used to generate lab-scale samples for this study is based on the FUETAP process developed for Savannah River Project HLW over a decade ago[9]. Calcined waste is mixed with a combination of cementitious agents, a minimum of mix water is added, and the resulting "stiff" grout then transferred to a stainless steel can...a can designed so that it could subsequently serve as a HIP can. After the grout has set at ambient temperature, the can is transferred to an autoclave and its contents cured with saturated steam (typically for 2 hours @ 200 psi).

A few month's worth of scoping experiments indicated that a mixture of blast furnace slag cement, some form of reactive silica powder (rice hull ash, silica fume, INEL soil, and 5 μ Minusil® have all been successfully used), plus vermiculite (the raw material does a better job than does the expanded of retaining Cs) "activated" with a solution of sodium hydroxide (~1 M NaOH) would solidify any reasonable mixture of calcined ICPP wastes. This combination discourages flash set, buffers the redox state of the hydroceramic product at an appropriate

level, and provides the fritting elements necessary to make a durable glass phase when the concrete is HIPed.

The composition and leach-test performance of a typical hydroceramic ("concrete") product is described in Table I. [A small amount of FeS was added to the cementitious mix to bolster its redox buffering capacity.] The waste simulant was a mixture of non-radioactive pilot plant calcines and sugar slurried together with a surrogate liquid waste (~38 grams of sucrose per mole of nitrate) and then pan-calcined together...it represented "average" ICPP radwaste. The concrete's waste loading was 36% and its compressive strength was 4600 psi.

TABLE I: TYPICAL HYDROCERAMIC MATERIAL

Element & Assumed Speciation	Wt % in that form	TCLP Results mg/l	ANSI 16.1 Leach Index (need >6.0)	normalized 28 day MCC-1 $g/m^2/day$
Al_2O_3	11.8	-	11.8	0.59
B_2O_3	1.1	-	-	-
CdO	0.70	<0.01(limit=1)	-	-
CaO	14.1	-	(all Ca) 13.6	(all Ca) 0.17
CaF_2	8.9	-		
Cs_2O	0.18	-	11.7	0.94
Cr_2O_3	0.28	<0.02(limit=5)		0.39
Fe_2O_3	0.24	-	-	-
K_2O	0.60	-	8.4	45
MgO	3.0	-	-	-
Na_2O	5.0	-	8.6	48
SiO_2	11.2	-	11.9	0.62
ZrO_2	5.0	-	-	-
PbO	0.03	<0.03(limit=5)	-	-
FeS	0.52	-	-	-
H_2O	22.2	-	-	-
NiO	0.5	0.07	-	-
SrO	0.34	-	13.5	0.29

The preparation of ~80-such samples has convinced us that it will be possible to convert any reasonable combination of calcined ICPP radwastes into cementitious waste forms that...

- possess an ANSI 16-1 leach index in excess of 6.0 for all components (NRC LLW requirement)

- will pass the EPA TCLP test protocol

- exhibit a <1 g/d/m^2 normalized, 28-day, 90°C, MCC-1 leach rate for all radionuclides actually present in such waste

- are physically strong...possess a compressive strength well in excess of 500 psi

- are inherently good at retaining essentially all polyvalent cations (e.g., TRU) and cesium - and relatively poor at retaining some common harmless univalent anions and cations

"Vitrification" of Concrete

The HIPing of a properly-canned concrete waste form is quite simple: First, vent the can, place it into a furnace and heat it to ~800°C to drive out volatiles (with simulants made to model the "preferred scenario", essentially nothing but water vapor is evolved during this satge.) Next, while pulling a rough vacuum on the vent tube, pinch it off, and then weld it shut. Transfer the can to the HIP chamber, pump in inert gas (usually argon) to the desired pressure (typically 30 to 125 MPa), and heat to the desired "soak" temperature (typically 850 - 1050 °C). After the "soak" time has elapsed (typically 1 to 6 hours), remove the can and let it cool.

Properly-formulated (what this means will be explained later) HIPed radwaste-concretes have the following characteristics:

- because they exhibit very little porosity and contain no water, they are typically about 60% more dense than the hydroceramic products from which they were made

- their compressive strengths are very high...on the order of 250 - 750 MPa

- they consist of a mix of crystalline mineral phases "glued" together with a durable glass phase

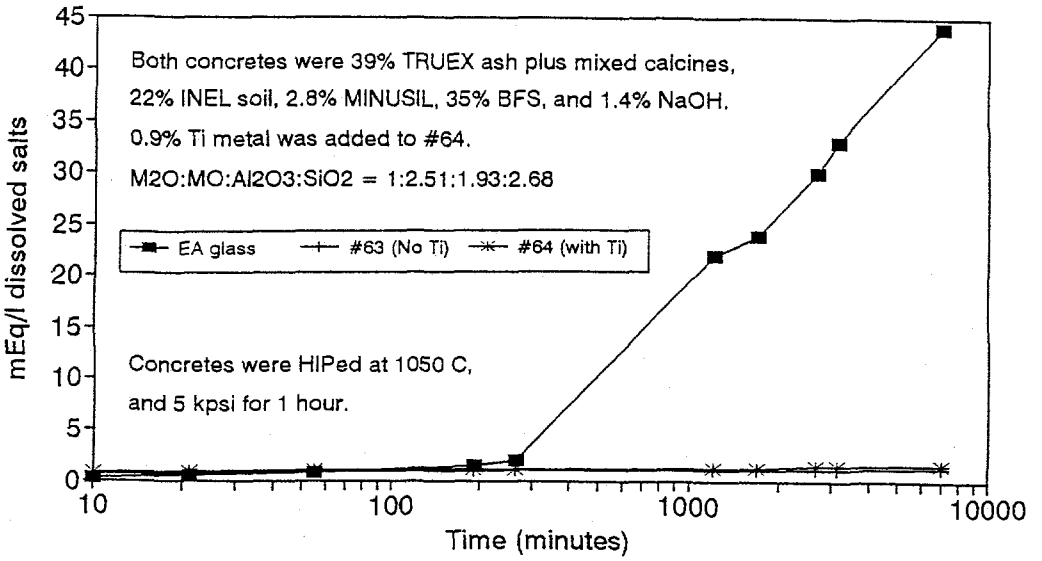
- good performance on the leach tests used to characterize "vitrified" waste forms

In this context, a "properly formulated" concrete is one that, 1) does not contain excessive amounts of nitrate, chloride, or sulfate and 2), with the exception of components that do not react under the HIPing conditions used (primarily fluorite and zirconia[12]), its gross composition approximates that of natural assemblages of feldspathic minerals (rocks). For example, there should be at least as many moles of (Al+Fe) as of (K+Na), and twice as many moles of Si as of (Na+K). Such concretes invariably form durable glass phases. In practice, satisfying these criteria with reasonable mixes of ICPP wastes simply boils down to making sure that enough silica has been added.

Figures 1-3 are examples of comparisons of the performance of HIPed concretes with that of EA glass on a simplified version of the PCT test[13]. These sorts of comparisons are especially relevant because their product's performance relative to that of EA glass on the PCT leach test

has been specified as a key process-control criterion for operators of the DOE Complex's glass melters (i.e., DWPF, WVNS, & HWVPF)[14]. In the experiment described by Figure 1, the two glass-ceramics were identical except that a small amount of titanium metal powder had been added to one of the original grouts (Ti° has been shown to be beneficial in conventional HIPing). It had no effect...both specimens out-performed EA glass to a similar degree.

FIGURE 1: Does titanium metal improve PCT performance of HIPed concrete?



The experiment described by Figure 2 addressed the question, "is it really necessary that all of the nitrate be removed from the waste before solidification"? The answer appears to be "no" (at least in terms of what the PCT test measures) - while residual nitrate in the concrete obviously affected the redox state of the final HIPed product (its color was yellow instead of black), PCT leach performance did not appear to be different - and, again, both specimens performed much better than did the EA glass.

FIGURE 2: PCT Results...HIPed Concretes made from totally denitrated vs "normal" calcines

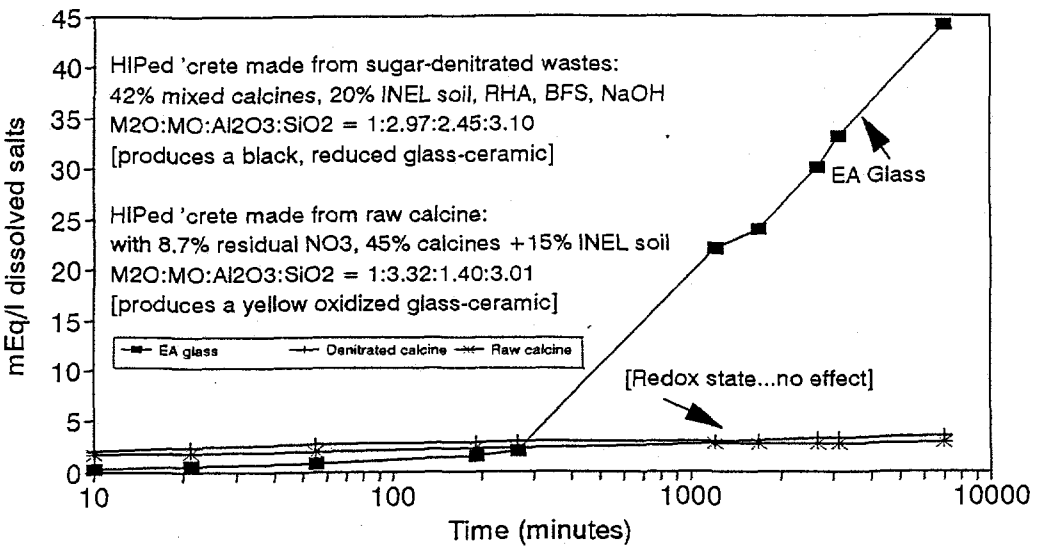
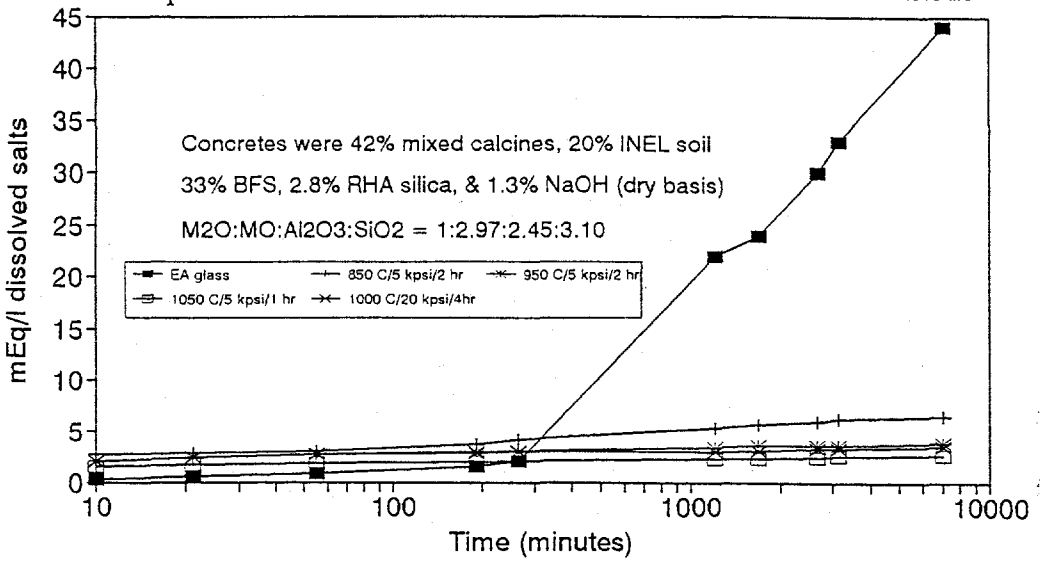


Figure 3 shows what happens when a concrete is HIPed under a wide range of conditions.

FIGURE 3: PCT performance of a concrete HIPed under different conditions



The performance of HIPed concretes on other leach tests has been discussed previously[15].

The HIPing of radwaste concretes seems to require less rigorous conditions (lower temperatures & pressures) than does conventional dry-powder radwaste HIPing. This is probably due to the fact that the molecular-scale mixing occuring during the grout mixing/curing process tends to influence the product's subsequent vitrification for the same reason as would sol-gel processing. The propensity of the easily leachable components in calcine particles (e.g., cesium) to diffuse out and into the "frit" matrix during the cementitious mixing & curing stages means that it is not necessary to grind calcined wastes to a fine powder in order to produce good waste forms.

The cost of a HIPing facility able to process ~35,000 55-gallon canisters of hydroceramic rock (all existing ICPP radwaste) within five years has recently been estimated at $10-$12 million[16].

CONCLUSION

"Staging" of solidification would allow DOE Contractors to make tangible progress while US decision-makers take time to reconsider whether or not vitrification really makes sense for huge volumes of moderate radioactivity, no-intrinsic-value radwaste. In any reasonably-sited repository, both the original hydroceramic materials and any glass-ceramic waste form products made from them would satisfy the disposal requirements of 40 CFR 191.

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