which, of course, constitutes another hurdle to be overcome by the engineers responsible for implementing it. I do not mean to imply that HLW disposal via glass waste forms would necessarily "fail" (if the repository is properly sited, the waste form itself will have negligible effect upon overall system performance[9, 13,14]), only that glass is neither "best" nor necessary.

Let's look at a more constructive approach to rendering this sort of waste road-ready. Perhaps the best analogy to the US's present situation is Great Britain's "historic waste" problem circa 1980[15,16].

In 1982, the British government directed its prime nuclear contractor, British Nuclear Fuels, Limited (BNFL), to design an up-to-date commercial fuel recycling facility at Sellafield (aka Windscale). It mandated that the new facility must not only be able to immediately process all newly-generated reprocessing wastes to disposable waste forms, but also to similarly deal with a 30+ year backlog of "temporarily" stored reprocessing waste generated previously. Unlike the situation in the USA, the British government did not impose a "preferred technology" - only that the waste forms must satisfy performance-based standards; i.e., be suitable for disposal in any of the possible repository systems that it might choose to implement within the next 50 years or so. Five years worth of collaborative effort by technologists from BNFL and the British Government's Department of Environment led to a consensus that "inorganic cements" would be appropriate for all radwaste streams which generate less than ~500 watt/m^3 worth of radioactive heat; i.e., the choice of solidification technology would be determined by a measurable and technically relevant characteristic of the waste - its history and any arbitrary labels that may have been applied to it (e.g., "high-level", "low-level", "mixed", "incidental", "transuranic", etc.) didn't matter. This conclusion is consistent with sound technical and economic reasoning, IAEA guidelines, and the opinions of US technologists willing to assume the professional risks inherent in taking an unblindered look at the issue[5]. By 1991, BNFL had completed the new reprocessing plant and its cementitious solidification facilities started "hot" operation two years later - it has since rendered most of Sellafield's >15,000 m^3 accumulation of historic radwaste (~150 distinguishable "streams") road-ready in the form of 500-liter stainless steel canisters filled with concrete "encapsulated" wastes.

Since then BNFL has become a prominent player in the US radwaste technology marketplace - in effect leveraging its success at home to compete with US-owned firms (many of whose employees work at DOE sites) for US tax dollars. While this situation is rather galling to some US nuclear professionals (e.g., this writer), US taxpayers are relatively well-served by it because, unlike the situation with many of USDOE's contractors, BNFL generally accomplishes what it promises to do on time and on budget. Of course, this does not mean that it is in the *best* interests of US taxpayers for USDOE to promise BNFL several million dollars for every glass "log" it might be able to produce from US HLW[4] – those taxpayers would be much better served if USDOE would instead permit it to use an updated version of the same technology applied to similarly radioactive British reprocessing radwastes.

There are two reasons why INEEL is the logical place for DOE to initiate this change of policy. First, unlike the situation elsewhere, INEEL's decision makers have not yet officially committed themselves to any particular HLW management scenario. Second, INEEL's fuel reprocessing facility, the "Idaho Chemical Processing Plant" (ICPP, recently reacronymed "INTEC") calcined >90% of its raw liquid waste rather than converting it to a mix of water soluble salts and sludge via neutralization with NaOH. This plus the fact that those calcines generate only ~40 watts/m^3 of total radioactive heat make its waste intrinsically well suited for cementitious solidification.

THE HYDROCERAMIC ALTERNATIVE

There are three reasons why conventional "grouts" (including those employed by BNFL) usually don't perform as well as do glasses on radwaste leach tests. The first is that grouting is usually applied to the intrinsically soluble fraction of the waste (raw uncalcined salts) while glass-making is reserved for a "volume reduced" fraction from which readily soluble material has already been leached. While the pH buffering provided by conventional calcium silicate-based concretes makes them able to do an excellent job of immobilizing the intrinsically insoluble components of US radwastes (this "easy stuff" includes all multivalent cations - all TRU elements[17], the majority of fission products, and most RCRA metals[18]), they do not chemically fix the alkali metal (e.g., sodium and ^{137}Cs) salts that constitute the majority of the waste so-treated. (From a material science point of view, it would make more sense to consign the salts to the

glass melter and the sludges to the concrete mixer.] Second, the protocols imposed by those leach tests (small scale, short term, etc.) obviate the key advantages of cementitious solidification, i.e., that it would be relatively easy/cheap to make waste forms possessing low geometric surface areas relative to their volumes (in other words, large ones) and equally easy/cheap to then enhance their post-emplacement durability at the repository via in-situ grouting ("backfilling") with a chemically compatible grout ("grout" would destabilize glasses). Third, because concretes are intrinsically porous, the actual surface area exposed to the leachant is much greater than is the case with equal-sized chunks of glass.

Hydroceramic concrete[19,20] eliminates this "performance gap" because it consists of minerals (sodalites, cancrinites, zeolites, etc.) capable of chemically fixing both salts and "easy stuff". The process implements the chemistry of Hanford's circa-1970 "Clay Reaction Process"[21] via Oak Ridge National Laboratory's almost equally venerable "Fixed Under Elevated Temperature and Pressure" (FUETAP) autoclaved-concrete making technology[22]. HC "grout" consists primarily of calcined kaolinic clay ("metakaolin) and NaOH plus smaller amounts of powdered vermiculite (to enhance Cs fixation) and sodium sulfide (which serves both as a redox buffer and a precipitant for RCRA metals). The relative amounts of alkali metals, aluminum, silicon and all anions other than hydroxide, aluminate, and silicate in it are adjusted to approximate a "sodalite" composition; i.e., ratios of $(Na+K+Cs)_a:Al_b:Si_c:X_d$ are $b \geq a$, $c \geq a$, & $d<0.25a$. The physical characteristics (appearance, strength, porosity, density, etc., etc.) of the finished concretes are similar to those of conventional calcium silicate-based concretes.

The decision to confound disposal of its own waste with that produced by the commercial nuclear power industry constitutes another reason why the US Federal Government has failed to honor its promises to Idaho. Due to DOD insistence that DOE's civilian waste management responsibilities not interfere with its own interests at NTS[1, pp 251-252], the Federal government chose to "withdraw" another ~600 km^2 of land from Nevada for today's official HLW repository modeling exercise (YM). This plus the assumption that *all* commercially-produced HLW is to be sent there engenders enough litigation to indefinitely block implementation of that repository – which means that linking these problems causes total paralysis. The most reasonable place for the Federal Government to site a repository dedicated to cold-war defense-type waste is at its cold-war defense-type test range, the Nevada Test Site (NTS). The NTS makes good sense because, a) it's already "federal land" ,b) it receives less precipitation than do other DOE sites, c) it possesses the USA's deepest water table, d) it has already been the object of more than thirty years worth of immediately relevant hydrogelological research[13,14], e) it's already been irredeemably "crapped up" by ~950 nuclear "events", and, finally, f) a little-publicized real example of a practical (cheap) repository for this sort of waste has already been implemented and (then) exhaustively tested[23]. However, it is *not* necessary to wait for a repository siting decision to begin rendering INEEL waste road-ready (the UK didn't) - regardless of exactly where that waste might eventually end up, it is reasonable to assume that HC-type concrete would be at least as durable as glass due to the fact that its mineralogical similarity to natural soil minerals provides less thermodynamic driving force for alteration.

LEACH TESTS

In order to have a reasonable chance of breaking vitrification's lock on US HLW solidification, an alternative must not only be simpler, cheaper, and safer to implement, it must also produce products that satisfy performance criteria that have been established for glasses. Consequently, "good" HC concretes ought to possess the following characteristics: 1) gross matrix solubility less than that of DOE's HLW QC benchmark, "Environmental Assessment" (EA) glass as measured by the 7-day "Product Consistency Test"; 2) normalized 28-day MCC-1 leach test performance <1 g/day/m^2 for the toxic & radioactive materials in INEEL calcines; 3) satisfy "universal treatment standard" (UTS) criteria for RCRA metals via TCLP; and , 4) accommodate waste loadings ≥ 25%. In addition, they should also evince individual-constituent ANS/ANSI-16.1 leach indices much higher than the usual "waste acceptance criteria" (6.0) for radwaste grouts and possess similar physical strength (>500 psi compressive).

Figure 1 compares 28-day MCC-1 leach test performance of a typical HC with those of several radwaste-type glasses and a hot-isostatically-pressed ceramic material, "ANLW cer"[25]. This test exposes a monolithic specimen of known composition and geometric surface area to a relatively large volume (to discourage saturation) of 90°C distilled water for one month. The fractions of the specimen's components

found in the leachate are then used to calculate normalized leach rates in units of gram/m^2/day. (The data in figure 1 were not normalized with respect to time – to do so, divide by 28.) The HC contained 42 wt % of a representative INEEL "zirconia-type" pilot-plant calcine, a calcined clay pozzolan produced by the ASHGROVE Cement Co. ("Troy clay"), powdered raw vermiculite, a small amount of sodium sulfide, plus household lye (sodium hydroxide).

Figure 1: Comparison of HCs with glasses on the PCT

Table I lists detailed results of an ANS/ANSI 16.1 leach test of the same specimen. This protocol measures the mobility (bulk diffusion constant, D in units of cm^2/s: the "leach index" = $-(\Sigma \log_{10} D)/n)$] of individual components of a monolithic specimen immersed in water under conditions that discourage saturation (the leach water is periodically changed). The most readily-soluble bulk constituents of US radwaste (sodium and nitrate) evinced diffusivities ~four orders of magnitude lower (better) than the usual waste acceptance criterion for radwaste grouts (10^{-6} cm^2/sec) - those of the "easy" components were several orders of magnitude lower yet. The shift in nitrate diffusivity between the first and later leach intervals indicates that ~90% of it had been "microencapsulated" in sodalite/cancrinite crystalites – the remainder leached as fast as it would from a conventional grout.

Table I: ANS/ANSI 16.1 Leach Test Performance

Today's most popular HLW leach test is the "product consistency test" (PCT)[26]. By exposing a finely powdered specimen to a relatively small amount (10 x as much) of hot (90°C) water for one week, this test generates an estimate of its gross solubility under conditions apt to cause saturation. Compared to the older ANS/ANSI 16.1 and MCC-1 protocols, it is relatively simple and quick to do. Table II compares several "representative" radwaste-type glasses[27] with some HCs with respect to their most readily-leached common component (sodium). For "easy" components such as ^{90}Sr, HC's outperform the glasses by a greater margin.

Table II: Comparison of HCs with glasses on the PCT test

Most of the attention now being paid to INEEL's reprocessing wastes is focused upon the <10% which had not yet been calcined by the time (1991) ICPP/INTEC lost its original mission – and which still hasn't been. The reason for this is that because it contains a relatively high proportion of thermally-stable Na/K nitrate salts, "sodium bearing waste" (SBW) cannot be efficiently processed in the existing calciner unless a reducing agent (e.g., sugar) is mixed with it[6,7] - a option considered **not** be a "preferred alternative" (BNFL's new Sellafield facility routinely "sugar calcines" its SBW). Table III gives the results of a TCLP (EPA Method 1311, SWP 846) leach test applied to an HC made with a sugar-calcined SBW simulant that had been doped with unrealistically high levels of several RCRA metals. The simulant was calcined as follows: After 38 grams of sucrose per mole of nitrate had been dissolved in the liquid, it was then slowly added to a stainless steel beaker situated on a maximum-temperature hotplate. Then that beaker was placed into a muffle furnace preheated to NWCF's normal operating temperature (500°C) to burn out the residual elemental carbon. The HC formulation consisted of 30 wt % of this calcine, ~1% sodium sulfide, a small amount of household lye to provide some "free" hydroxide (the sodium in the calcine itself was present as a ~1:2 mix of sodium aluminate plus sodium carbonate), plus sufficient water to make a "stiff" (modeling clay-like) dough. This was rolled into a ball, wrapped with tin (not aluminum!) foil, and than autoclaved for two hours at ~200°C. Table III lists regulatory limits along with the concentrations of "characteristic" metals in both the original calcine and the TCLP leachate.

TABLE III: TCLP Results: Sugar-calcined "sodium bearing waste" specimen

HYDROCERAMICs vs GEOPOLYMERIC CONCRETES

Hydroceramics are "geopolymeric"[28] concretes designed to minimize solubility of the "aggregate". In order to achieve the quick-set characteristics needed for construction work, commercial geopolymeric cements are usually activated with alkali polysilicate(s), not alkali hydroxide(s) and often contain substantial proportions of CSH-forming components (e.g., granulated blast furnace slag) as well. Table 4 compares PCT leach results seen with three concretes (same formulation, different curing conditions) activated with sodium silicate and another activated with hydroxide alone. The waste simulant represented the soluble fraction of a caustic-neutralized liquid reprocessing waste present in one of the tanks at DOE's SRS site [~11.5 M sodium hydroxide, 1.5 M sodium nitrate, 1.13 M sodium nitrate, 0.4 M sodium aluminate, 0.2 M sodium carbonate, plus a trace of cesium chloride.] A 10:1 mix of "Troy clay" plus powdered vermiculite was used for all of them. 1.1 grams of a 37% NaOH was added to the "hydroceramic" formulation (10 grams of the clay mix plus 5 grams of the simulant). The "geopolymeric" formulation (11 grams of the clay mix plus 5.06 grams of the waste simulant) was activated with 2.5 grams of liquid sodium silicate ("water glass", ~38% solids, SiO_2:Na_2O wt. ratio of 3.22:1). While the physical characteristics of all of the concretes appeared to be similar, the leach results indicate that polysilicate did not reform the substrate clay into salt-fixing minerals as effectively as did hydroxide alone. Because of their excellent durability and compatibility with HCs, the best use for a conventional geopolymeric cement in this context would be as a construction and/or backfill material.

TABLE IV: PCT leachability of geopolymeric vs hydroceramic concretes

OTHER CONSIDERATIONS

The developers of the FUETAP process addressed the "radiolytic pressurization issue" by demonstrating that only the uncombined water in concrete serves as a source of radiolytic gases[22]. Consequently, the HC process would bake out porewater before the canister is sealed. (Sellafield's cementitious solidification facilities sidestep this issue by venting canisters through filters.) Due to stakeholder insistence that DOE-ID consider HLW management scenarios which would render all of it road-ready (not just a "volume-reduced" fraction), several engineering-feasibility "paper" studies of the HC process have been comissioned[29,30]. However, because no programmatic funding was allocated for laboratory or pilot plant studies, its primary technical liability is that only a limited amount of research and no scale-up work has been done. While its scientific basis is established and there is good reason to believe that it could be implemented in a straightforward fashion, there are a number of questions that/ need to be answered before a full-scale facility is designed. [For example, "would a few month's worth of curing at the ambient-pressure boiling point of water at INEEL (zero gauge pressure) make concretes comparable to those produced within two hours by a 200 psi autoclave?" If the answer to this is "yes", the process would be safer/simpler/cheaper to implement.]

CONCLUSIONS

The leach test results indicate both that the chemical durability of HCs is equivalent to that of vitrified materials and that the leaching of individual constituents from them is not determined by congruent matrix dissolution. Single-phase materials such as "WV-39-2" glass tend to release everything at the same rate – HCs do not. Like many natural rocks, HC concretes are assemblages of physically interlocked crystalline minerals possessing different intrinsic solubilities. Due to the rapid, batch-nature of the process used to make them, both their porosities (~15-25 %) and total (BET) surface areas (~15 m^2/g) are more like those of conventional concretes than natural rocks or glasses. HCs behave like glasses on leach tests because their lower intrinsic solubility compensates for their greater surface areas. Because conventional grouts tend to saturate their cation fixation sites with calcium ions (portland cement is ~65 wt% CaO), HC's generally outperform them with respect to the degree of immobilization of the polyvalent cation "easy stuff" (e.g., ^{90}Sr) too. This may also explain why the MCC-1 leachrate of Cs from HCs is about two orders of magnitude lower than it was from the original FUETAP concretes[22].

The "hydroceramic alternative" makes especially good sense at INEEL for the following reasons:

1) INEEL has not yet officially committed to vitrification.
2) Because INEEL calcines do not contain excessive concentrations of soluble salts, it would be possible to satisfy the "sodalite formulation" rule-of-thumb with high (>25%) waste loadings.
3) Since two of the three elements making up HC binder phases (Na & Al) are high-percentage constituents of INEEL calcines, there is no need to separate them (or anything else) prior to solidification. This means that everything would be prepared for offsite disposal – the wish of INEEL's stakeholders. {A primary goal of the "volume reduction" activities practiced at WVDP and SRS is to transfer those elements to "low level" fractions.}
4) Simple changes to the existing calcination facility would permit it to efficiently calcine the remaining liquid reprocessing waste[5,6] – either by itself or (preferably) after it's been slurry-mixed with existing calcines[30]. The latter scenario would consolidate all INEEL reprocessing wastes into a homogeneous feedstream suitable for HC solidification.
5) It would also provide a good way to deal with many of INEEL's other wastes. For example, INEEL must find a way to dispose of ~1000 metric tons of radioactive NaOH generated by reacting metallic sodium reactor coolant with water. Since this just happens to be the same amount of "activator" that would be required to turn ICPP/INTEC's calcines into HC concrete, coprocessing these wastes would solve two problems. If the changes to the existing calcination facility alluded to above were to be implemented, virtually any sort of liquid or particulate waste (e.g., contaminated soils) could be readily converted to HCs.
6) It is probable that a formal proposal to properly implement an HC-type solidification process would satisfy INEEL's stakeholders[31].
7) Finally, if a future generation deems it to be both politically expedient and affordable, HC concrete monoliths could be hot-isostatically-pressed into "vitrified" monoliths without removing them from their original canisters[32-34].

The National Research Council raised the same questions about INEEL's HLW management paradigm that have been addressed by this paper[35]. From a "pro nuke's" point of view, the most compelling reason to challenge that paradigm is that its cost provides the Federal Government with another excuse to perpetuate its tradition of waffleing on waste disposal. Because radionuclides have finite lifetimes and defense-type reprocessing wastes will never pose an *immediate* hazard to the public-at-large, it will **always** be possible to make a case for more "temporary delay". The viability of the US nuclear power industry requires tangible proof that its government's "nuclear establishment" can deal with its own waste.

ACKNOWLEDGMENT

Without the technical input of my colleagues at Pennsylvania State University's Materials Research Laboratory, Professors Barry Scheetz, Michael Grutzeck, and Della Roy, the "hydroceramic alternative" could not have been developed. Without the vision provided by that institution's founder, Professor Rustum Roy, the need for it would not have been realized.

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