HLW & FD

EIS PROJECT - AR/PF
Control # DC-80

FAX

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To: Thomas L. Wichmann, Document Manager
US DOE, ID operations office
850 Energy Drive MS-1125
Idaho Falls, ID 83401-1563

From: Melissa Clark Rhodes, Ph.D.

Fax #: 1-208-524-1184

Message:

ATTN: Public Comment: IDAHO HLW + FD EIS

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Melissa Clark Rhodes <mrhodes@blissnet.com> on 04/20/2000 11:08:30 AM

Please respond to mrhodes@blissnet.com

To: cxb@inel.gov
cc:

Subject: Attention Cindy from M. Rhodes re failed fax

Thank you Cindy for your email! I was online and frustrated until late last night because I have put a great deal of effort into my comments, including the reading of the EIS, and discussion with a number of engineers.
Here is part 1 of 2: Melissa Clark Rhodes (307) 734-7665

- hilevel.doc

Melissa Clark Rhodes <mrhodes@blissnet.com> on 04/20/2000 11:15:28 AM

Please respond to mrhodes@blissnet.com

To: cxb@inel.gov
cc:

Subject: Attn Cindy, here is part 2 of my comment

This part is authored by a materials scientist, actually from the INEEL. Since I'd gathered a small group of engineers, and had had discussions, I feel that this hydroceramic solution made alot of sense. It appears to have been one of the alternatives which had been considered early on, and close to the Direct Cement option. Thank you for your trouble. Best regards, Melissa Rhodes PS: I'll be visiting the INEEL again in May. 307-734-7665

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HLW & FD EIS PROJECT
Control # DC-80

To be included in the ROD comments re: INEEL HLW

April 19, 2000

Re: Comments regarding INEEL's management of its high-level waste treatment and disposal problem. These comments are for the Record of Decision.

My name is Melissa Clark Rhodes. My address is Apt. 345 M. Blair Place, Jackson, Wyoming, 83002.

I hold a Ph.D. in Geology, with a specialty in evolutionary theory and physiological ecology of "living fossils'. I have taught university level introductory courses in Geology, Environmental Science, Oceanography, and Geologic Resources and Hazards, as well as Advanced Optical Mineralogy, Igneous and Metamorphic Petrology, Crystallography, and Paleontology.

Since Chemical and Nuclear Engineering are not my areas of expertise, I am speaking here as a concerned citizen.

80-1
IX.A(2)

The DOE has very considerately provided us with information and time, and has included us in their decision–making process. For this, I am grateful, and I appreciate the efforts of INEEL and DOE to make available to us the various options which will most likely be involved in the final decision-making process regarding INEEL's problems with the high level waste treatment and disposal, as well as the level of environmental remediation required after the INEEl has been closed.

Concerns:

I'll begin by elimination of the most undesirable options (in my opinion):

Undesirable:

80-2
III.D.3(1)

Separations technologies:

The main benefit of these protocols seems to be reduction of the volume of waste – different fractions would be sent to the WIPP and the still hypothetical high-level waste repository. I consider any of the separations alternatives to be unacceptable. Dissolving the previously solidified calcine back into liquid form seems wasteful, since it nullifies all the previous calcining performed in order to get the HLW into a more stable granular form. Liquid HLW is a more hazardous and unstable entity, especially when it is sitting on Southeast Idaho's premier aquifer.

The separations technologies all involve a small incinerator, in order to treat the organic solvents, which would be contaminated with radionuclides. Even the slightest whisper of the word "incinerator" in the Jackson area would arouse more public opposition.

Undesirable:

80-3 II.E(8) + 80-13 II.E(2)

Minimum INEEL processing solution:

This option involves a lot of transportation and handling. There are also too many uncertainties regarding Hanford's ability to deal with SBW/mixed TRU waste. The chemistries required for vitrification at Hanford don't match. INEEL's waste is more acidic than has been provided for at the Hanford facility. There is too much risk in transporting the waste back and forth. Transport presents a greater potential for accidents. Additionally, it appears that this option still hasn't been worked out fully. Too many uncertainties exist, and the planning appears to be complex.

Undesirable:

80-4 III.C(5)

The Hot Isostatic Pressed Waste option

Direct Cement Waste option (see postscript)

These alternatives both require the technology necessary to upgrade the calciner to MACT. This could be costly and time-consuming. The INEEL might encounter additional public opposition to the calciner, even after upgrades to MACT. It is a form of incinerator.

Most desirable:

Early Vitrification Option:

80-5 III.D.2.c(1)

This alternative does not require calcination of the remaining liquid SBW and mixed TRU waste. Therefore, it would not require upgrading of the calciner to MACT, and would eliminate public opposition to the operation of the calciner. The liquid mixed TRU/SBW would be converted into a glass acceptable to the WIPP, already in operation.

The mixed HLW Calcine would be vitrified with another variety of glass frit, and safely stored until a HLW repository could be located and confirmed. The vitrification of the HLW would put it in a stable form, so that if the hypothetical HLW repository were not found right away, it would be relatively safe parked right on the reservation.

Newly generated SBW etc. would be directly vitrified, and would skip the calcining step. The newly generated waste, after vitrification, would most likely be accepted at the WIPP, already in existence and operative.

This type of technology has been successfully utilized in European countries. However, this option is extremely expensive.

Remediation:

80-6 IV.A(1)

My first choice would be the "Clean Closure" Alternative. However, upon reviewing the worker mortality rates, I am doubtful as to whether "Clean Closure" is worth the increased site worker mortality rate.

I am undecided as to which choices are the most desirable for closure. The "Nuke Reservation" is right in the middle of a low gradient flood plain, and over Southeast Idaho's premier aquifer, which is already experiencing some contamination. The integrity of the aquifer must not be breached.

80-7 VIII.C(4)

The main problem is the leftover contaminants' location. The contamination is parked squarely in the path of any flood or alteration of flow pattern of the Big Lost River.

80-8 VIII.C(5)

Paleogeography of the Big Lost River clearly shows alterations in its meander patterns. Since the Arco Desert plain has a very low gradient, the river will be susceptible to large variations in its meander patterns, dependent upon short or long-term climatic variations. It will also be especially inclined to flooding, especially during the current short-term(?) climate changes. The contaminants could possibly end up in the middle of a newly formed river meander channel!

80-9 VIII.G(4)

Techniques involving more remote-handling protocols should be strenuously investigated, so that worker safety could be increased. I feel that it is essential for the underground contaminated structures such as the tanks, vaults and piping to be removed.

80-10 IV.A(2)

Respectfully yours,
Melissa Clark Rhodes, Ph.D. Geology

PostScript:

80-11 III.D.2.b(1)

It has been brought to my attention that vitrification may be prohibitively expensive. It could cost more than $1,000,000.00 per cubic meter of glass produced. Thus, as an alternative, a version of Hydroceramic Solidification might be preferable, even though it most likely would involve calcination of remaining liquids.
The hydroceramics as described in the following paper by Darryl D. Siemer, "WHY HYDROCERAMIC SOLIDIFICATION MAKES MORE SENSE THAN VITRIFICATION FOR INEEL HIGH LEVEL WASTE", submitted to the journal "Nuclear Technology", match leachability test results in comparison to glasses, and are cheaper. However, the main problem appears to be volume reduction. It appears to have been one of the alternatives analyzed and rejected by the DOE. Perhaps volume reduction is not as important as a speedy and cost effective solution for the INEEL's HLW. See the following paper:

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WHY HYDROCERAMIC SOLIDIFICATION MAKES MORE SENSE THAN VITRIFICATION FOR *INEEL* HIGH LEVEL WASTE

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(Note: this paper does not necessarily reflect the views of the author's employer nor does it discuss research funded, encouraged, or otherwise "owned" by that employer)

ABSTRACT

"Hydroceramics" (HC) are geopolymeric[1] concretes designed to match the leach test performance of radwaste-type glasses. They are made by autoclaving mixtures of calcined waste, calcined clay, NaOH, plus water. This paper characterizes them and explains why this approach to solidification would be preferable to vitrification for Idaho National Engineering and Environmental Laboratory (INEEL) reprocessing waste.

INTRODUCTION

In 1970, Idaho's political leadership was assured that the "high level" waste (HLW) generated by the Federal Government's fuel reprocessing operation at INEEL (then "NRTS") would be prepared for disposal (made "road ready") in the first "official" HLW repository by 1980[2]. Since that time, billions of taxdollars have been spent on HLW management, no HLW repository has been provided, none of INEEL's reprocessing waste has been prepared for disposal, and today's official deadline for doing so has slipped to 2035 AD[3]. In 1996, a "controversial" National Research Council (NRC) report identified seven management "symptoms" responsible for the Federal Government's inability to deal with its own waste[4]. One of these is that DOE blinders both itself and its contractors to any but predetermined "preferred alternatives" when it addresses technical problems. This paper discusses one such "preferred alternative", vitrification, and explains why a cementitious technology ought to be used instead.

VITRIFICATION'S DRAWBACKS

A paper scheduled for publication in "*NUCLEAR TECHNOLOGY*" documents that the cost of rendering DOE HLW road-ready via vitrification will be well over $1 million (probably $2-4 million) for every cubic meter of glass produced[5]. Because DOE's contractors are unlikely to achieve >100% volumetric loading of its ~60,000 m^3 of high-solids reprocessing waste (~4000 m^3 of INEEL calcines, ~14,000 m^3 of SRS sludge, and 46,000 m^3 of Hanford sludge), the paper goes on to suggest that vitrification constitutes a barrier to progress and that other technologies should be considered. Another controversial NRC report reached the same conclusion over two decades earlier[6].

Let's critique some of the arguments employed by vitrification's champions.

One of these is, "vitrification is better because a glass melter can achieve greater volumetric waste loading than can low temperature solidification technologies". This argument is misleading, irrelevant, and harmful. It is misleading because it presumes both that alternative technologies *must* be implemented without appropriate waste pretreatment and, as I'll demonstrate later, that only a fraction of the waste "counts". Raw reprocessing waste consists primarily of volatile materials such as water, mineral acids, nitrate/nitrite ions and, in some cases, organics which may include "listed wastes", solvents, extractants, and chelating agents. Calcination (or incineration) [7,8] is a straightforward and well-established way to eliminate those fractions while producing inorganic ashes which can be converted to equally low-volume monoliths by other means. While glass melters can be (and sometimes are) used as "devolatilizers", it is much more efficient to do that unit operation with equipment optimized for that purpose.

Today's obsession with volume is irrelevant because the presumption that the ultimate cost of managing

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HLW will be proportional to the geometric size of any waste forms made from it is invalid. First of all, history tells us that the cost of *any* DOE project will be exorbitant whether or not it actually ever produces anything. For example, the cost of making one canister (~1 m^3) of any sort of "rock" will be >90% that of making ten canisters (~10 m^3) of it with the same equipment. As far as the US taxpayer is concerned, a DOE EM project's overall cost (including research, development, design, licensing, administration, construction, personnel training, testing, decontamination, etc., etc.) is virtually independent of the amount of product created or service rendered. Product/services are *incremental* costs.

Second, the total cost of disposing of waste forms produced from DOE HLW will *not* be proportional to their geometric volumes. Why ? 1) Formal analyses have repeatedly concluded that the transport of finished waste forms to a repository will represent a small fraction of total management cost regardless of their volumes[9], 2) today's official hypothetical HLW repository site, Yucca Mountain (YM), is physically large enough (several cubic miles - several tens of billions of cubic meters) to accommodate any type of material(s) that DOE might choose to make from its reprocessing wastes, 3) YM's "size" is defined in units related to the amount of radionuclides to be buried there (the equivalent of that in 70,000 "metric tons of heavy metal"), not geometric volume[10], 4) the drilling/boring equipment required to create space at YM has already been paid for, and, of course, 5) YM will (and has already) cost US taxpayers billions of dollars whether or not any real waste is ever buried there. Again, the cost of using the facility for its intended purpose will add only a relatively small *incremental* cos attributable to mass/volume.

The "volume obsession" is harmful because it diverts attention/resources from rendering waste road-ready to reclassifying it via "volume reduction". This waste is a "big" problem because it is chemically toxic, radioactive, corrosive, heterogeneous, situated in places poorly suited to become permanent geological repository sites, and has been mismanaged/ignored for several decades - not because of its physical size. In practice, the technologies used/proposed to affect volume reduction serve to decease the physical size of "high level" fractions that "must be vitrified" for offsite disposal by increasing those of "low level" fractions to be left on site. These low-level fractions usually contain the bulk of the original waste's toxic/corrosive components and, due to the fact that chemicals are added to affect separation processes, are generally larger (often much larger) in terms of total mass, solids content, and volume than the waste was before it was "volume reduced". Stratagems used/proposed to make the vitrification of the "high" stuff in DOE's reprocessing waste more affordable range from the relatively simple sludge-washing now done at WVDP & SRS to the elaborate "full separation" scheme that has been championed by INEEL management. Another of history's lessons is that the volume reduction of nuclear reprocessing waste is attractive only to those who might be employed designing, building, operating, managing, and/or overseeing the new facilities that would be required to accomplish it – and equally unattractive both to independent reviewers[11] and people who happen to live near the site in question but do not derive their incomes from it[12]. The only volume reduction operation that really makes much sense for this type of waste is "devolatilization".

Another rationale proffered for vitrification consists of a poor analogy; i.e., "because France and Great Britain vitrify high-level reprocessing waste, it must be 'best' for US HLW too". This argument is invalid because about the only characteristic that these wastes share are their labels. European HLW consists of relatively young, first-cycle, PUREX-type raffinates generated by a process that dissolves mechanically-declad commercial reactor fuel rods in nitric acid. The ash generated by the calciners used to prepare European HLW for vitrification typically contains 20-60 wt% fission products. On the other hand, DOE HLW is much older (typically >30 years out-of-reactor) and consists primarily (>99%) of non-radioactive materials derived from fuel cladding plus added solid-forming process reagents. Consequently, DOE HLWs are two orders of magnitude less radioactive and much more heterogeneous than their European namesakes. The *technical* reason why the vitrification of US HLW is prohibitively expensive is that a US glass melter capable of solidifying any given amount of "bad stuff" must be ~100 times larger and able to accommodate a much wider range of feedstocks than its European counterpart ("bad stuff" = the sum of RCRA metals +fission products + TRU).

A more fundamental drawback of glasses for this purpose is that they are "ineluctably metastable"[2]. Glasses are relatively rare in Nature because they are unstable and therefore inevitably decompose to form crystalline minerals/rocks; e.g, the "zeolitized tuff" that comprises much of today's official HLW repository site (the third such location) was originally volcanic glass. Radwaste-type glasses (i.e, glasses

with low percentages of silica and alumina & high percentages of alkalies and boron) are apt to be especially unstable. Furthermore, because both classes of material enhance the corrosion rates of glasses under hypothesized repository conditions[13], some of DOE's radwaste management experts are suggesting that the YM repository must be implemented without concrete for construction or clays/soils for backfill – which, of course, constitutes a serious barrier to actual implementation.

I do not mean to imply that HLW disposal implemented with glass waste forms would necessarily "fail". "Performance assessments", both formal and otherwise, have consistently concluded that if this waste were to be buried at a suitable repository site, the characteristics of the waste forms would have negligible effect upon overall system performance[10, 14-17]. I do mean to say that glass is neither "best" nor necessary.

Let's examine a more constructive paradigm. Perhaps the best analogy to the US's present situation is Great Britain's "historic waste" problem circa 1980[18,19].

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-plus year backlog of "temporarily" stored reprocessing waste previously generated. Unlike the situation in the USA, the British government did not impose a "preferred technology" - only that finished waste forms must satisfy performance-based standards; i.e., be suitable for disposal in any of the possible repositories that it might choose to implement within the next 50 years or so. Five years worth of constructive collaboration by technologists from BNFL and the British government's DOE (Department of Environment) led to a consensus that "inorganic cements" would be used for all radwastes generating less than ~500 watt/m³ worth of radioactive heat; i.e., that the choice of solidification technology would be determined by a measurable and technically relevant characteristic of the waste, not its history or any labels that it may have picked up (e.g., "high-level", "low-level", "mixed", "incidental", "transuranic", etc.). This conclusion is consistent with sound technical and economic reasoning, IAEA guidelines, and the opinions of US technologists willing to risk the probable consequences of taking an unblindered look at this issue[6]. By 1991, BNFL had completed the new reprocessing plant and its cementitious solidification facilities started "hot operation" two years later – those facilities have since rendered most of Sellafield's >15,000 m³ accumulation of historic radwaste (~150 distinguishable streams) road-ready.

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 for US tax dollars. While this situation is galling to some US nuclear professionals, US taxpayers are being relatively well-served 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 produce from US HLW[5] – those taxpayers would be much better served if it were allowed to apply an updated version of the same technology used for British radwaste.

There are two reasons why INEEL would be the logical place for DOE to initiate such a policy change. First, unlike the situation elsewhere, INEEL's decision makers have not yet *officially* committed themselves to implementing any particular HLW management scheme. 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 mixture of water soluble salts and sludge via neutralization. This plus the fact that those calcines generate ~40 watts/m³ of radioactive heat make its HLW well suited for cementitious solidification.

THE HYDROCERAMIC ALTERNATIVE

There are three reasons why conventional "grouts" (including those employed by BNFL) don't perform as well as do glasses on radwaste-type leach tests. The first is that grouting is applied to the intrinsically soluble fraction of waste (liquids and uncalcined salts) while vitrification is reserved for "volume reduced" fractions from which readily soluble materials have already been leached. While the pH buffering provided by conventional calcium silicate-based cements renders them capable of immobilizing the intrinsically

insoluble constituents of radwastes (this "easy stuff" consists of multivalent cations - all TRU elements[20], the majority of fission product elements, and most RCRA metals[21]), such cements do not chemically fix the alkali-salts that constitute the bulk of the waste so-treated. (From a material scientist's point of view, it would be better to consign salts to the glass melter and sludges to the concrete mixer.] Second, the protocols imposed by radwaste 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 with low geometric surface areas relative to their volumes (in other words, large ones) and equally easy/cheap to then enhance their post-emplacement durability via in-situ grouting (grout "backfill" would destabilize glass waste forms). Third, because concretes are intrinsically porous, the actual surface area exposed to the leachant during these tests is much greater than is the case with equal-sized chunks of glass.

Hydroceramic concretes[22,23] eliminate this performance gap because their binder phases consist of minerals (sodalites, cancrinites, zeolites, etc.) capable of chemically fixing salts as well as the "easy stuff". Individual salt molecules are trapped within aluminosilicate "cages" which form around them during the curing process. Manufacture implements the cancrinite-making chemistry of Hanford's "Clay Reaction Process"[24] via Oak Ridge National Laboratory's almost equally venerable "Fixed Under Elevated Temperature and Pressure" (FUETAP) autoclaved-concrete technology[25]. Raw HC-type "grout" consists of a dough-like mix of water, calcined waste, calcined clay ("metakaolin") and NaOH plus smaller amounts of powdered vermiculite and/or illitic clay (which 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, fluoride, and silicate in the formulation is adjusted to approximate sodalite; 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.

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 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/m² 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 evince individual-constituent ANS/ANSI-16.1 leach indices much higher than the usual "waste acceptance criteria" (6.0) for radwaste grouts and have similar physical strengths (>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, "ANEW cer"[26]. 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). This test exposes a monolith 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 material's components found in the leachate are then used to derive normalized leach rates in units of gram/m²/day.

Figure 1: Comparison of HCs with glasses on the MCC-1 Test

Table I lists detailed results of an ANS/ANSI 16.1 leach test of the same specimen. This protocol measures the mobility [i.e. bulk diffusion constants, D, in units of cm²/s: "leach index" = $-(\Sigma \log_{10} D)/n)$] of individual components of a monolith immersed in water under conditions that discourage saturation effects (the leach water is periodically changed). Note both that 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 grouts (10^{-6} cm²/sec) and that those of "easy" (Zr, Sr) components were