UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 10
1200 Sixth Avenue
Seattle, WA 98101

APR 10 2003

Reply To
Attn Of: WCM-127

James Rasmussen, Director
Environmental Management Division
United States Department of Energy
Office of River Protection
P.O. Box 450
Richland, WA 99352

Lee Bostic
Bechtel National, Inc.
River Protection Project
Waste Treatment Plant
3000 George Washington Way
Richland, WA 99352

Dear Mr. Rasmussen and Mr. Bostic:

Please find enclosed a policy paper developed by the U.S. Environmental Protection Agency (EPA) Region 10 in cooperation with your respective organizations concerning destruction of hazardous organic constituents in Hanford tank wastes as part of on-going efforts to develop Resource Conservation and Recovery Act (RCRA) delisting and land disposal restriction (LDR) decision documents. Briefly, this policy document establishes EPA's position that vitrification units, such as those being constructed as part of the Hanford Waste Treatment Plant, are expected to provide effective destruction or removal of organics from vitrified high-level wastes. Further, it outlines the technical basis for EPA's conclusion that in certain circumstances analytical sampling of vitrified glass is not necessary to demonstrate compliance with delisting and LDR treatability variance standards that are expected to be developed to treat and dispose of Hanford high-level wastes in a national geologic repository. While this policy document does not constitute a regulatory decision or rulemaking, EPA believes that it provides important guidance that the Office of River Protection and Bechtel Hanford, Inc., may use as the basis for developing research and testing programs, and for preparation of delisting and LDR treatability variance applications applicable to vitrified Hanford high-level wastes.

Should you have any questions, please feel free to contact Dave Bartus, at (509) 736-5704, or bartus.dave@epa.gov.

Sincerely,

Richard Albright, Director
Office of Waste and Chemicals Management

cc:
Mike Wilson, Ecology
Dave Blumencrantz, BNI
Nick Ceto, HPO
Hugh Davis, EPA Office of Solid Waste, Waste Treatment Branch

Hanford Federal Facility Waste Treatment Plant
High-level Waste Delisting and LDR Compliance White Paper
Organic Constituent Destruction/Removal Performance in Vitrified Glass Wastes
April, 2003

As part of an overall regulatory strategy for managing treated Hanford tank waste destined for national repository or on-site disposal, DOE-ORP has developed two "approach" documents outlining regulatory strategies for delisting and achieving compliance with RCRA Land Disposal Restriction (LDR) requirements (Refer to RPT-W375HV-EN0001 and RPT-W375HV-EN0002, dated November, 2000). These documents, along with follow-up Data Quality Objective (DQO) report[1] supporting research and testing programs currently under way, have examined the question of what data are needed to demonstrate that organics in Hanford tank waste are effectively destroyed or removed from the final vitrified waste form. While the technical and regulatory communities generally regard thermal processes such as the Hanford high-level waste vitrification system to be an effective means of immobilizing radionuclides and certain inorganic hazardous constituents, little specific guidance is available to aid in quantifying the performance of vitrification technologies with respect to hazardous organic constituent treatment efficacy. This paper specifically addresses EPA's perspective on two issues, which include the extent to which organics are destroyed or removed from the vitrified glass (as opposed to off-gases from the vitrification process), and a presumption that analysis for organics in glass treated waste forms is not needed for purposes of demonstrating compliance with delisting and LDR treatment requirements.

In previous guidance ("Vitrification Technologies for Treatment of Hazardous and Radioactive Waste," EPA 625/R-92/002, May, 1992), EPA provided generic guidance on the performance of vitrification technologies. This guidance recognizes that "When accomplished through a thermal process, vitrification <u>may</u> destroy organic contaminants via pyrolysis or combustion." (emphasis added). However, this guidance does not provide specific data or decision criteria for any particular waste stream or constituent, but rather establishes a reasonable presumption that vitrification is acceptable for treatment of mixed organic-containing wastes subject to site/waste stream validation. This paper extends the reasonable presumption established in the 1992 guidance to the conclusion specific to vitrified high-level wastes that the treated borosilicate glass waste form does not contain organics at levels of concern with respect to delisting and LDR treatment requirements.

The 1992 guidance does establish two key concepts that may be used to develop the necessary site/waste stream-specific validation. First, destruction/removal of organics from vitrified glass is a secondary process to immobilization of waste constituents in a glass or ceramic matrix. That is, organic waste constituents in the glass matrix are removed or destroyed during processing through mechanisms distinct from those that result in formation of a glass matrix, and are not incorporated into or immobilized by the final glass matrix. Therefore, the efficacy of vitrification with respect to organics is less dependent on the final waste form characteristics than on conditions during operation of the vitrification process. Second, organic destruction/removal efficiency is dependent on chemical kinetics (pyrolysis and combustion), which in turn are well established through basic chemical principles to be dependent on time and temperature relationships. More specifically, vitrification takes place at a sufficiently high temperature, and with a sufficiently long glass residence time to effectively destroy or remove organics from the vitrified residual[2]. Note: Absent secondary combustion or other air pollution control systems, offgases may contain

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[1] Blumenkranz, D.B., and J.R. Cook, 2003, Data Quality Objectives Process in Support of LDR/Delisting at RPP-WTP, Rev. 2,24590-WTP-RPT-ENV-01-012, Bechtel National, Inc., Richland, WA, March 26, 2003.

[2] Many if not all thermal processes such as the Hanford vitrification melters can create organic constituents as by-products of various chemical reactions that may take place. EPA believes that the analysis presented in this paper regarding the ability of Hanford melters to destroy or remove organics from the vitrified glass waste form apply equally to organics created during vitrification as well as organics present in feed to the melter.

volatilized organics. This policy does not address destruction or removal of organics in the vitrification melter off-gas system or secondary (including liquid) waste management systems – the fate of organics in these non-glass waste streams are addressed separately in other risk assessment, permit or regulatory decision documents as applicable.

EPA is also aware of additional investigations that corroborate the principles outlined in the referenced guidance. The Department of Energy (DOE) has conducted investigations to determine the fate of organic constituents in wastes that are treated by vitrification. DOE spiked wastes prior to their vitrification with high levels of organic compounds possessing a range of boiling points and thermal stability rankings. With the exception of trace laboratory contamination, analyses of the resulting vitrified wastes indicated that organic and cyanide constituents were not present at detectable levels[3].

More recent data generated by the Department of Energy specific to simulated Hanford high-level waste feeds confirms these findings. To obtain these data, the DM1200 melter (a 1/3-scale high-level waste test melter) was run with simulated Hanford waste feed, sub-envelopes A1 and C1. The feed was spiked with large quantities (compared to the expected levels of hazardous organic constituents[4] in Hanford tank wastes scheduled for vitrification) of chlorobenzene, trichloroethylene, naphthalene. The organic spike was introduced into the melter feed stream immediately upstream of the melter feed tube (closed system). Analyses of vitrified test glasses were conducted using SW-846 (including applicable QA/QC procedures) 8260B, 8270C, and 8290 (for dioxins and furans). The resulting data are presented in "Organic Compound Destruction as a Byproduct of Vitrification," Document Number 24590-WTP-RPT-RT-02-005, Rev. 0., 26 December 2002, River Protection Project, Waste Treatment Plant. These results do indicate detections of several volatile organics and certain dioxins/furans in a very small number of treated waste samples (0.5 percent of the total number of sample results). However, most of the spike constituents detected in treated waste samples were also detected at similar levels in blank samples. Further, essentially all detections of spike constituents in treated waste samples were below the laboratory reporting limit. EPA believes, in the context of evaluating vitrified glass, that these detections are indicative of the lower limits of laboratory cleanliness and the exceedingly low detection levels achievable for dioxin and furan analyses rather than the actual presence of organic compounds in vitrified waste forms. Perhaps most importantly, all detections in treated waste samples and blank samples (single-digit part-per-billion level for detected volatiles, and sub-part-per-billion levels for dioxins and furans) were far below a level that EPA believes warrant consideration in either a delisting or an LDR treatment context.

As noted above, destruction of organics is directly related to temperature and time in a treatment unit. Within most if not all joule-heated glass melters such as the Hanford high-level waste vitrification units, neither the temperature nor the residence time or waste in the glass melt is fixed. Temperature, for example, varies somewhat around the nominal operating temperature within volume of the glass melt, as does residence time around the average value. Never the less, EPA believes, several secondary measures of melter operations can be established that can demonstrate sufficient temperature and residence time are provided to insure effective organic destruction and removal.

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[3] Matlack KS, and Pegg IL. 1999. "Determination of the Fate of Hazardous Organics During Vitrification of RPP-WTP LAW and HLW Simulants", VSL-99R3580-2, Revision 0. Vitreous State Laboratory, Catholic University of America, Washington D.C., October 4, 1999.

[4] Organic compounds are a necessary component of melter feeds to control foaming in the melter, reduce nitrates and control NOx emissions, and maintain the proper glass oxidation/reduction state. Typically, a stoichiometric ratio of 0.5 carbon to feed nitrate/nitrite is needed for these purposes. High-level waste melter feed has few if any waste organic constituents, so the necessary reductants are added in the form of sucrose (table sugar). Some low-activity melter feeds contain large quantities of organic constituents (typically non-hazardous organic acids and tri-butyl phosphate), but still require additional sucrose to maintain the required level of organics/reductants. Therefore, Hanford glass melters are not only capable of removing or destroying organics at levels significantly above those represented by the cited test programs, the melters require these higher levels for proper operation and production of "good glass."

In general, EPA believes that vitrification processes that operate with sufficiently high temperature and residence time to completely liquefy all waste and glass former (additive) constituents will destroy or remove organic constituents to levels below detection using commonly-employed analytical techniques, as well as below levels of regulatory concern with respect to risk-based delisting and technology-based LDR standards. Hanford vitrification units will be designed and operated to make "good glass[5]," which is defined as glass in a final physical waste form that passes the Product Consistency Test (PCT) and meets waste acceptance criteria for placement in the proposed high-level waste national repository[6]. Well-designed vitrification units operated in a manner that results in "good glass" ensures effective destruction/removal of organic contaminants from the glass melt, as supported by the following points:

- The design of the Hanford high-level melters is such that glass can exit the melter into treated waste stainless steel canisters only when it is at a sufficiently high temperature and low viscosity to flow through an air-lift device and a gravity-driven pour spout. The physical configuration of the pouring passageways is such that only thoroughly molten glass from the body of the glass melt can exit the melter, insuring that glass that is not thoroughly liquefied or mixed cannot exit the melter. Specifics of the design and operation of the melter pour mechanism may be found in the permit modification request for the Hanford waste treatment plant[7].
- Processing of waste so that it passes the PCT requires that the glass melt be well-mixed and homogeneous. Treated waste that was not well mixed would likely have zones of higher waste loading that exceeded the capacity of the glass matrix to immobilize radionuclide waste constituents, and would fail the aggressive PCT test. Proper mixing of the glass melt is accomplished through a sufficiently-long residence time to allow natural thermal convection and air-assisted mixing devices (bubblers) to thoroughly mix the glass melt prior to discharge into waste canisters.

Although cyanide is generally not considered an organic constituent, it is amenable to thermal treatment, and may be considered equivalent to organics with respect to the physical and chemical mechanisms associated with organic destruction and removal described in this policy.

In conclusion, EPA believes that Hanford high-level waste (including both high level waste and low-activity waste) treated using vitrification as permitted by the Washington State Department of Ecology will destroy or remove the organic and cyanide constituents present in the feed to non-detectable levels in the final glass waste form using generally accepted analytical methodologies. Further, non-detect organic levels in glass waste forms achieved via application of vitrification technology satisfy risk-based delisting levels and technology-based LDR treatment standards (including alternate standards that may be established through the treatability variance process). Finally, EPA believes that sound engineering principles and available research data are sufficient to conclude that application of vitrification producing "good glass" alone without additional verification analytical sampling of the vitrified waste may be used to demonstrate compliance with delisting and LDR treatment requirements. Final regulatory decisions reflecting this policy must, of course, be made according to the applicable administrative requirements of 40 CFR Parts 260 and 268, respectively, and construction and operation of vitrification units managing RCRA-regulated wastes must be conducted pursuant to applicable state- and federally-issued operating permits. EPA is basing these policy conclusions on the design of the Hanford high-level waste melters as of the January, 2003, and as documented in the various referenced documents. EPA reserves the right to re-evaluate these policy conclusions if there are substantial changes to the proposed melter system,

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5 Contract DE-AC27-01RV14136, dated August 31,2000, issued by the United States Department of Energy, Office of River Protection, to Bechtel National, Inc.

6 Other measures of "good glass" may exist in addition to the PCT test with respect to the efficacy of vitrification as a means to destroy or remove organics from a vitrified glass waste form, and vitrification may result in effective destruction or removal of organics from a vitrified glass waste form even if the PCT test is not passed. Evaluation of these circumstances is beyond the scope of this policy paper, and EPA believes that such circumstances are best evaluated on a case-by-case basis.

7 Waste Treatment Plant Dangerous Waste Permit Application, Rev. 0, DOE/RL-2001-64, November 28, 2001.

including, but not limited to changes in the glass waste form composition, design of the melters, or changes in operating conditions.

This policy considers only the destruction/removal performance of vitrification with respect to organic hazardous constituents in vitrified glass waste forms, and does not consider performance of vitrification with respect to hazardous metal constituents. It is not intended to apply to other forms of thermal treatment or waste forms other than borosilicate glass, which has been extensively investigated as a waste form appropriate for long-term immobilization of high-level radioactive wastes. Further, this policy is specific to the Hanford high-level waste melters and associated pretreatment system permitted by the Washington State Department of Ecology[8]. Since immobilization of inorganic constituents (metals in particular) occur through fundamentally distinct physical and chemical mechanisms (specifically, chemical bonding within the glass matrix as opposed to volatilization, pyrolysis and combustion in the melter), performance of vitrification with respect to hazardous waste delisting and LDR requirements may separately consider organic and inorganic constituents. In the case of vitrified Hanford high-level tank wastes, it is expected that the referenced approach documents and associated DQO exercises will establish the necessary demonstration criteria and data needs for inorganic tank waste constituents.

[8] The limitation to Hanford wastes and treatment permitted by the Washington State Department of Ecology principally reflects current research and testing programs specific to Hanford wastes, and current Department of Energy Performance Management Plans which do not call for vitrification of certain other high-level wastes such as calcine at the Idaho National Engineering and Environmental Laboratory. Should the Department of Energy elect to apply borosilicate glass vitrification to other high-level wastes containing organic RCRA hazardous constituents, EPA believes it likely that this policy could be easily extended to include such additional treatment processes and waste streams. Any such extension of this policy to additional waste streams or treatment processes would be accomplished on a case-by-case basis.