Upfront Delisting of F006 Mixed Waste (U)

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DISCLAIMER

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ABSTRACT

The U.S Department of Energy at the Savannah River Site (DOE-SRS) will petition the Environmental Protection Agency (EPA) to "upfront" delist treatment residues generated from the vitrification of approximately 650,000 gallons of a Resource Conservation and Recovery Act regulated mixed (hazardous and radioactive) waste. The upfront petition, based on bench-scale treatability studies and pilot-scale system data, will exclude the vitrified wasteform from hazardous waste management regulations. The EPA encourages the use of the upfront delisting method as it allows applicants prior knowledge of waste specific treatment standards, which when met will render the waste non-hazardous, before generating the final wasteform.

To meet the EPA performance based treatment standards, the waste must be stabilized to control the leaching of hazardous and radioactive constituents from the final wasteform. SRS has contracted a vendor to stabilize the mixed waste in a temporary Vitrification Treatment Facility (VTF). The EPA has declared vitrification as the Best Demonstrated Available Technology for high level radioactive wastes[1] and the DOE Office of Technology Development has taken the position that mixed waste needs to be stabilized to the highest degree possible to ensure that the resulting wasteform meets both current and future regulatory specifications. Treatability studies conducted on a VTF pilot-scale system unit indicates that the mixed waste can be converted into a highly durable glass form, which exceeds the projected EPA performance based criteria. Upfront petitions can be processed by the EPA concurrently during facility construction or permitting activities; therefore, the SRS VTF will be capable of producing wastes which are considered non-hazardous sooner than otherwise expected. At the same time, EPA imposed conditional testing requirements to verify that the delisting levels are achieved by the fully operational VTF, ensures that only non-hazardous wastes are removed from hazardous waste management regulations.

Vitrification of the above waste will result in a volume reduction of approximately 75%. Volume reduction combined with excluding the waste from hazardous waste management regulations through delisting will significantly reduce overall management and disposal costs, resulting in an approximate $2.5 million cost savings.

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INTRODUCTION

Fuel and target assemblies for the Savannah River Site (SRS) nuclear reactors were fabricated in metal finishing and aluminum forming facilities within the 300 M-Area. 300 M-Area manufacturing operations ended in 1992 as a result of the cessation of the cold war. Liquid effluents generated from past 300 M-Area manufacturing operations consisted primarily of metal finishing and aluminum forming process effluents, including nickel electroplating process effluents. These process waste effluents contained rinsewaters, stack acid scrubber effluents, and spent process solutions. Area support facilities (e.g., degreasing activities, laboratory effluents) contributed halogenated organics to the above wastestream to a lesser degree.

Since July 1985, area process wastewaters have been discharged to the M-Area Liquid Effluent Treatment Facility (LETF). The LETF utilizes the Best Available Technology Economically Achievable for the aluminum forming and metal finishing industries. The LETF is composed of three closed-coupled treatment facilities: the Dilute Effluent Treatment Facility (DETF), an Industrial Wastewater Treatment Plant; the Chemical Transfer Facility (CTF); and the Process Waste Interim Treatment/Storage Facility (PWIT/SF). Wastewater treatment sludges generated from both CTF and DETF operations are characterized as a Resource Conservation & Recovery Act (RCRA) listed F006 mixed waste (contains both hazardous and radioactive constituents). Approximately 1.5 million gallons of F006 mixed waste was generated, with 650,000 gallons remaining in the PWIT/SF awaiting stabilization. The remainder of the waste, a supernate which separated from the residual precipitate, was treated in the DETF and released via a National Pollutant Discharge Elimination System permitted outfall.

The above M-Area Plating Line Wastes (MPLW) are subject to the Land Disposal Restrictions (LDR) in 40 CFR §268. The LDRs prohibits any storage of a land disposal prohibited waste except for the purpose of the accumulation of such quantities of hazardous waste as are necessary to facilitate proper recovery, treatment, or disposal. F006 wastes were restricted from land disposal on May 8, 1990. However, due to a national capacity extension for mixed wastes granted by the EPA, disposal and or storage was not prohibited until May 8, 1992. Subsequently, the PWIT/SF waste was added to the Land Disposal Restriction - Federal Facility Compliance Agreement (LDR-FFCA) between EPA and DOE, on March 13, 1991 to allow continued storage until a stabilization/solidification facility became operational.

Stabilization of this waste is not only required for compliance with hazardous waste regulations, but for the M-Area sludges, the LDR-FFCA specifies that the sludges will be treated in a vendor-supplied temporary Vitrification Treatment Facility (VTF). The LDR-FFCA sets strict milestones for completing the vendor stabilization program. SRS has contracted a vendor to stabilize the MPLW in a temporary VTF located in the 300 M-Area immediately adjacent to the PWIT/SF. The resultant treatment residues will be stored in a RCRA permitted container storage facility while awaiting confirmation that analyses are below the EPA imposed regulatory thresholds.

UPFRONT DELISTING OVERVIEW

The EPA recognizes that listed wastes may not be hazardous due to differences in feed stocks or industrial processes. Therefore, 40 CFR §260.20 & §260.22 contains a procedure whereby anyone can petition the EPA to "delist" or exclude such a listed waste from hazardous waste regulations. Originally, the intent was to ease the regulatory burden of the hazardous waste management of listed wastes improperly captured by the broad listing definitions. Since then, delisting has evolved to include those wastes sufficiently treated such that they no longer pose a threat to human health or the environment.

The DOE-SR will request the EPA for an upfront exclusion for certain wastes yet to be generated, as described in the "derived from" rule [40 CFR §261.3(c)(2)(i)] based on: bench-scale treatability studies; pilot-scale system data; the untreated waste characteristics, and detailed facility process descriptions. To be successful, the analyses of the treatment residues from the bench-scale waste treatment process must show that the waste no longer meets the criteria for which it was originally listed; must not exhibit a hazardous waste characteristic; and must not exhibit any other factors including additional 40 CFR §261 Appendix VIII constituents above regulatory threshold levels.

Regulatory threshold levels are calculated by the use of appropriate fate and transport models, for example the EPA's Composite Model for Landfills[2]. The EPA believes that the primary pathway for a contaminant to adversely affect human health is through the ingestion of contaminated groundwater from the leaching of chemicals from land filled waste. Therefore, delisting petitions are evaluated by comparing leachate concentrations for specific contaminants contained within the petitioned waste against health-based levels, usually the Maximum Contaminant Levels for safe drinking water. The maximum allowable leachate concentration for specific contaminants are a function of waste volume, the smaller the volume of petitioned waste the larger the allowable dilution factor. Site-specific disposal conditions are not considered by the EPA in the evaluation of an upfront delisting petition since the generator is not required to dispose of the excluded wastes in a specific facility once the exclusion is granted.

To determine leachate concentrations for upfront delisting petitions, the EPA requires that treatment residues be analyzed by the Toxicity Characteristic Leaching Procedure (TCLP) and the Multiple Extraction Procedure (MEP)[2]. The MEP is a test developed by the EPA to assist in predicting the long-term leachability of stabilized wastes. This procedure consists of the TCLP extraction, followed by nine sequential extractions on the same sample using synthetic acid rain to simulate multiple washings of percolating rainfall in an improperly designed sanitary landfill. It is estimated that these extractions simulate approximately 1,000 years of rainfall. In addition, total concentration analyses of all the 40 CFR §261 Appendix VIII constituents will be conducted to verify their absence.

Once the EPA grants an exclusion based upon the above information, the treatment residues would receive an upfront delisting with imposed verification testing requirements, which must be met through an EPA approved statistical sampling plan when the VTF becomes operational. The full-scale verification testing requirements may involve more then one round of waste characterizations to address any concerns regarding the potential for waste variability.

M-AREA PLATING LINE WASTES

The M-Area Plating Line Wastes (MPLW) are primarily wastewater treatment sludges generated from electroplating operations, since the wastewaters originated from electroplating

processes involving nickel plating of aluminum-clad, depleted-uranium slugs. The majority of the wastestream is considered a listed F006 mixed waste as it is specifically listed as hazardous per RCRA, Title 40 of the Code of Federal Regulations (CFR) §261.3(a)(2)(ii), and also contains a radioactive component consisting of source material (i.e., depleted uranium) as defined by the Atomic Energy Act Title 10 CFR §20.3(a)(15)(i). The primary hazardous constituent of concern is nickel, while the primary radioactive constituent of concern is depleted uranium (i.e., 238U). The sludges also contain significant levels of nitrate.

To a lesser degree, additional wastes generated from the electroplating process (i.e., Watts Type Nickel Bath Plating Line Solution, Spent Plating Bath Sludge, Mark 15 filtercake) as well as treatment residues generated from bench-scale treatability studies will be incorporated with the PWIT/SF F006 sludge prior to vitrification.

The MPLW partially occupies three 500,000 gallon tanks, six 35,000 gallon tanks, and approximately one hundred and eight 55 gallon drums (i.e. Mark 15 filtercake, and Nickel Plating Line Solution). The quantity of MPLW (i.e., 650,000 gallons) combined with tank capacity limitations (i.e., largest tank capacity equivalent to 500,000 gallons) requires homogenization of the MPLW into two macro batches. The homogenization is designed to ensure that each macro batch will approach each other compositionally to the greatest extent possible. Table 1 provides a detailed chemical composition of the homogenized MPLW[3].

Table 1, Molar Mass Balance

Major Compounds	Mole %
$Al(OH)_3$	19.06
$NaNO_3$	23.01
SiO_2	37.35
$Na_6U_7O_{24}$	4.24
Ca-zeolite	3.10
$AlPO_4$	5.10
SUM	91.86

BENCH-SCALE DATA

Vitrification involves the exposure of hazardous materials to molten glass and related process conditions to effect the destruction, removal, and/or permanent immobilization of hazardous constituents. Vitrification is defined as the conversion of such solids into a glass residual from through the application of heat to the point of fusion. This process forms a molten, vitreous mass, and produces a glass-like residual product upon cooling. The residual solid is a solid (super-cooled liquid) containing an amorphous mixture of oxides (primarily silica and alumina) with little or no crystallization present[4].

Vitrification was chosen as the desired stabilization technique for the MPLW due to: destruction of hazardous organic constituents by pyrolytic decomposition and/or oxidation; removal of inorganic constituents in the residual glass product through chemical incorporation and/or

encapsulation; and the chemical composition of the MPLW is amenable for vitrification as it already contains high levels of glass forming compounds (i.e., Si, Al, Na, Ca). The resulting glass residue exhibits excellent structural, weathering, and biotoxicity characteristics making it suitable for long term environmental exposure and is therefore capable of surpassing the EPA TCLP threshold levels. Vitrification will also result in an approximate 75% volume reduction resulting in reduced waste management costs.

Representative samples of the MPLW were submitted for bench-scale studies. Proportional amounts were homogenized thoroughly prior to vitrification. The resultant treatment residues were analyzed by the TCLP for inorganics only (i.e., Ba, Cr, Pb, Ni, U), as organics compounds are completely destroyed at the high temperatures at which vitrification occurs. All of the treatment residues passed the projected upfront delisting petition regulatory threshold levels by a wide margin[5] (Table 2).

Table 2, Regulatory Threshold Levels and Analytical Results

CC	Dry Wt%[5] Sludge	Wt%[5] Glass	MCL[6] mg/l	DAF[2] < 1,000 cu. yd.	Delist Levels (ppm)	TCLP Glass[5] (ppm)
Ba	0.018	0.013	1	100	100	1.85
Cr	0.007	0.005	0.05	100	5	< 0.04
Ni	0.73	0.51	0.1	100	10	0.17
Pb	0.10	0.074	0.015*	100	1.5	< 0.2
U	2.65	1.85	0.02	100	2	0.10

CC - Constituent of Concern
DAF - Dilution Attenuation Factor
MCL - Maximum Contaminant Level

* Action Level, not MCL per 40 CFR 141.80 (c)(1)

CONCLUSION

Bench-scale waste treatment studies using the process of vitrification have been successfully performed. The success of vitrification is attributable to a number of factors including:

- the powerful solvating properties of glass melts and their ability to incorporate a wide range and large amounts of hazardous inorganics and radioactive components;
- the complete destruction of organic compounds at the high temperatures at which vitrification occurs;
- a stable, relatively homogeneous waste form that is highly resistant to aqueous corrosion; and
- relatively high density waste form resulting in an accompanying large volume reduction.

The upfront delisting petition will show that the resultant treatment residue generated from process vitrification will not: meet any criteria for which it was listed; exhibit any hazardous waste characteristics as identified in 40 CFR §261 Subpart C; and will not exhibit any other factors or additional constituents which would render it to be considered hazardous.

REFERENCES

1 EPA (U.S. Environmental Protection Agency), Land Disposal Restrictions for Third Third Scheduled Wastes, Final Rule, 55 Fed. Reg. 22627 (1990).

2. EPA (U.S. Environmental Protection Agency), Manual: Petitions to Delist Hazardous Wastes, EPA/530-R-93-007, Washington, DC (1993).

3. Jantzen, Carol M. Vitrification of M-Area Mixed (Hazardous and Radioactive) F006 Wastes: I. Sludge and Supernate Characterization. USDOE Report WSRC-TR-94-0234, Savannah River Site, Aiken, SC 29808 (1994).

4. Barth, Edwin F. Stabilization and Solidification of Hazardous Wastes. Park Ridge, NJ: Noyes Data Corporation, 1990.

5. Jantzen, Carol M. et. al. Reactive Additive Stabilization Process for Hazardous and Mixed Waste Vitrification. Mixed Waste Proceedings of the Second International Symposium. August 17-20, 1993, Baltimore, Maryland.

6 EPA (Environmental Protection Agency), 40 Code of Federal Regulations 141.11(b).