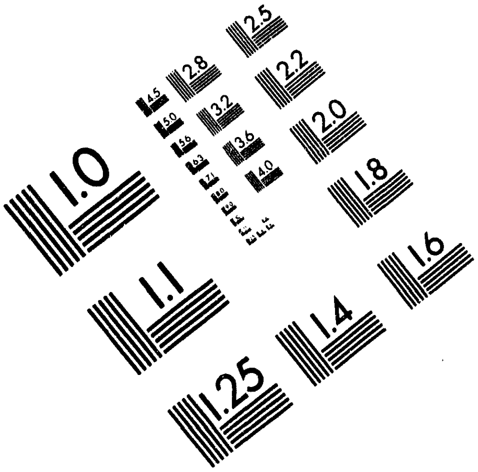

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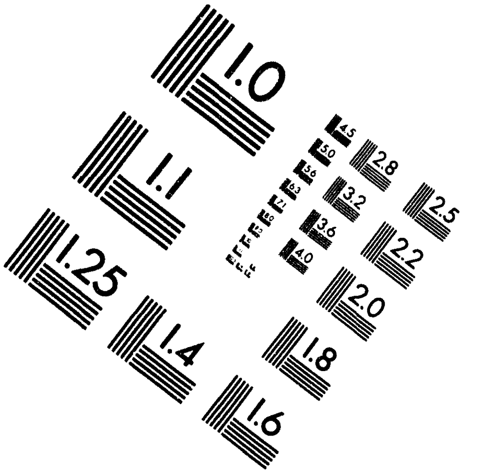

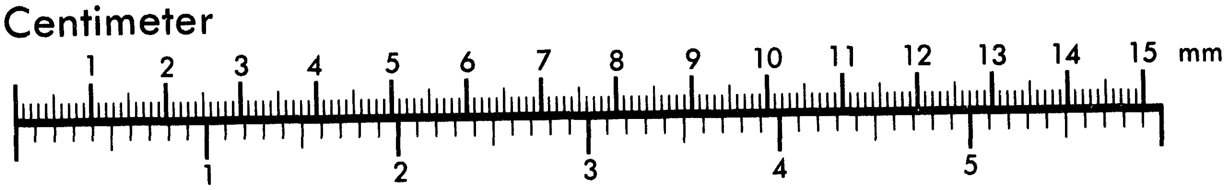

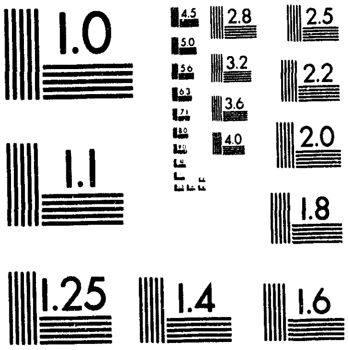

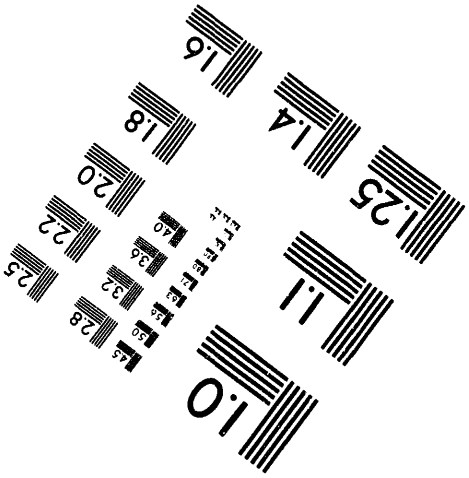

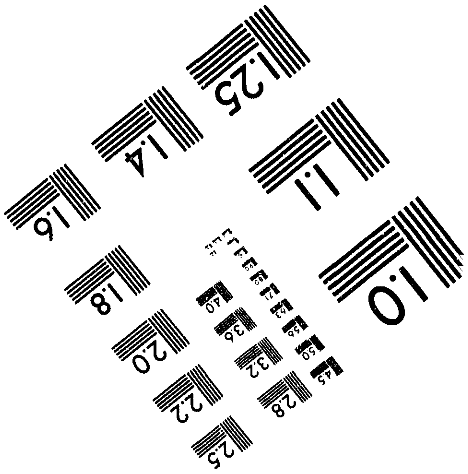

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VITRIFICATION OF F006 PLATING WASTE SLUDGE BY REACTIVE ADDITIVE STABILIZATION PROCESS (RASP)*

by

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American Electroplaters & Surface Finishers (AESF) SUR/FIN '94 Technical Conference
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* Patent pending

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VITRIFICATION OF F006 PLATING WASTE SLUDGE BY REACTIVE ADDITIVE STABILIZATION PROCESS (RASP)

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ABSTRACT

Solidification into glass of nickel-on-uranium plating wastewater treatment plant sludge (F006 Mixed Waste) has been demonstrated at the Savannah River Site (SRS). Vitrification using high surface area additives, the Reactive Additive Stabilization Process (RASP), greatly enhanced the solubility and retention of heavy metals in glass. The bench-scale tests using RASP achieved 75 wt% waste loading in both soda-lime-silica and borosilicate glasses. The RASP has been independently verified by a commercial waste management company, and a contract awarded to vitrify the approximately 500,000 gallons of stored waste sludge. The waste volume reduction of 89% will greatly reduce the disposal costs, and delisting of the glass waste is anticipated. This will be the world's first commercial-scale vitrification system used for environmental cleanup of Mixed Waste. Its stabilization and volume reduction abilities are expected to set standards for the future of the waste management industry.

VITRIFICATION OF F006 PLATING WASTE SLUDGE BY REACTIVE ADDITIVE STABILIZATION PROCESS (RASP)[1]

by

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INTRODUCTION

Fuel and target assemblies for the nuclear reactors of the Savannah River Site (SRS) were fabricated in 300-M Area metal finishing and aluminum forming operations. With the end of the cold war, these components for production of nuclear weapons materials for the U.S. Department of Energy are no longer being fabricated. However, 500,000 to 600,000 gallons of nickel plating line sludge, which is a F-006 mixed (hazardous and radioactive) waste, will remain in RCRA permitted interim storage tanks after the supernatant from those tanks has been processed by the wastewater treatment facility. Technologies have been developed by the SRS to convert the sludge to a solid stabilized waste form for permanent disposal.

The M Area Liquid Effluent Treatment Facility (LETF) is an end-of-pipe industrial wastewater treatment facility, that uses precipitation and filtration which is the EPA Best Available Technology economically achievable for Metal Finishing and Aluminum Form Industries. The physical and heavy metal characteristics of the sludge are similar to the F-006 waste sludge generated from wastewater treatment in commercial industry, except it also contains uranium and more than the normal concentration of nickel. There was no market to justify recovery of radioactive nickel from the Watts plating bath. Achieving the Environmental Protection Agency (EPA) Land Disposal Restrictions (LDR) for nickel concentration by the Toxic Characteristic Leaching Procedure (TCLP) has been difficult during commercial F-006 waste stabilization, but the technologies developed by the SRS reliably achieve the LDR standard and greatly reduce the volume of waste for final disposal.

Vitrification was one of those alternative technologies, and full scale demonstration of this Reactive Additive Stabilization Process (RASP) at SRS is scheduled in 1995 and 1996. Vitrification into simple glass compositions was achieved by tailoring the glass composition to take advantage of the common glass constituents of silicon, aluminum, sodium, and calcium that are already in the waste. Stabilization of the heavy metals in the glass is achieved by use of reactive additives such as diatomaceous earth, perlite, rice husk ash, and/or precipitated silica These filter aids are also already in the waste. The process and product models developed for high level radioactive waste glass were utilized to develop glass formulations which optimize processability (viz. viscosity) and product durability.[2] Vitrification produces durable waste forms at volume reduction of 50% compared to commercial cement stabilization of this F-006 sludge and a volume reduction of 10% compared to the Filtration & Stabilization (FIST) process alternative.[3] An 89% total reduction and delisting of the final waste form in M-Area is anticipated.

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[1] Patent pending.

[2] C. M. Jantzen, "Relationship of Glass Composition to Glass Viscosity, Resistivity, Liquidus Temperature, and Durability: First Principles Process-Product Models for Vitrification of Nuclear Waste," CeramicTransactions, V. 23, American Ceramic Society, Westerville, OH, 37-51 (1991).

[3] H. L. Martin, J. B. Pickett and C. A. Langton, "Radioactive and Hazardous Waste Sludge Treatment and Stabilization by Filtration," J. Advances In Filtration and Separation Technology, V.6, American Filtration Society, Chicago, IL, 195-199 (1992)

DISCUSSION

Experimental

The nickel plating line waste glasses were made of the actual nickel plating line sludge and the spent perlite filter aid from supernatant wastewater treatment by adding reagent grade chemicals. Waste loadings varied from 90 to 70 wt%. Other mixed wastes were also tested to demonstrate the RASP. All glasses were melted at a temperatures of 1150°C in high purity Al_2O_3 crucibles for 4 hours. Small amounts of glass, ~100 gram batches, were made to optimize the best compositions for further testing.

Each vitrified sample was submitted for x-ray diffraction (XRD) analysis so that the homogeneity of the resulting glass could be determined. For glasses which were not homogeneous, the crystalline phases were identified by XRD. If analysis by XRD was inconclusive, elemental scans by x-ray fluorescence (XRF) were substituted.

A modified EPA Toxic Characteristic Leaching Procedure (TCLP) was performed at the Savannah River Technology Center on representative homogeneous glasses.

Nickel Plating Waste Sludge

M-Area nickel plating line waste sludge plus the spent filter aid from the associated supernatant treatment are examples of RASP stabilization. Representative samples of the RCRA F006 sludge in each of the M-area tanks, including the tank with the spent filter aid, was analyzed. The X-ray diffraction analysis of the sludge dried at 90°, 300°, and 600°C allowed the chemical phases to be identified and a molar mass balance calculation to be performed (Table 1). The aluminum is present primarily as $Al(OH)_3$, while the Na is present as $NaNO_3$. Using the current and projected tank volume inventories a calculated composite waste composition based on a dry calcine basis was determined (Table 1).

Table 1. M-Area Calculated Composite Sludge Composition.*

Oxide	Wt%	Oxide	Wt%	Speculation	Wt% **
Al_2O_3	17.47	TiO_2	0.04	$Al(OH)_3$	23.18
CaO	0.48	K_2O	1.48	$NaNO_3$	17.88
Fe_2O_3	0.88	P_2O_5	3.22	SiO_2	43.44
MgO	0.20	BaO	0.02	$Na_6U_7O_{24}$	3.48
MnO	0.28	PbO	0.11	Ca-zeolite	3.15
Na_2O	10.83	MoO_3	0.01	$AlPO_4$	4.32
NiO	0.93	ZnO	0.59	SUM	95.44
SiO_2	43.58	CuO	0.03		
Cr_2O_3	0.01	SO_4	0.03		
B_2O_3	0.03	NO_3	13.05		
UO_2	3.00	SUMS	96.28		

* Current inventory plus additional filter aid projected from continued supernatant treatment.
** Species identified by x-ray diffraction analysis.

Vitrification

The high SiO_2, Al_2O_3 and Na_2O content of the M-Area waste indicated that stabilization in either sodium borosilicate or SLS glass was feasible. The addition of only one additive, B_2O_3, borax ($Na_2O \cdot 2B_2O_3 \cdot 10H_2O$), or $Na_2O \cdot B_2O_3$ enabled the waste mixture to be made into a borosilicate glass (Figure 1, Table 2) while the addition of only $CaCO_3$ or a mixture of $CaCO_3$ and Na_2CO_3 allowed solidification into SLS glass (Figure 2, Table 2). The use of only one additive simplifies processability of the waste as only two components need to be adjusted in order to optimize processability and waste loading (Figure 1).

Vitrification was achieved in both borosilicate and SLS glass at waste loadings varying between 70 to 90 wt% waste (Table 2). Higher waste loadings were achieved at higher melt temperatures. Homogeneous glasses formed at temperatures between 115C° and 1300°C at waste loadings of 70 to 80 wt%. The borosilicate system is a well known glass forming system used to make commercial pyrex and vycor glasses which are very stable but are phase separated. Many types of high-level radioactive wastes are being solidified in borosilicate glasses which are in the known glass forming region of the Na_2O-B_2O_3-SiO_2 system, but away from the known region of phase

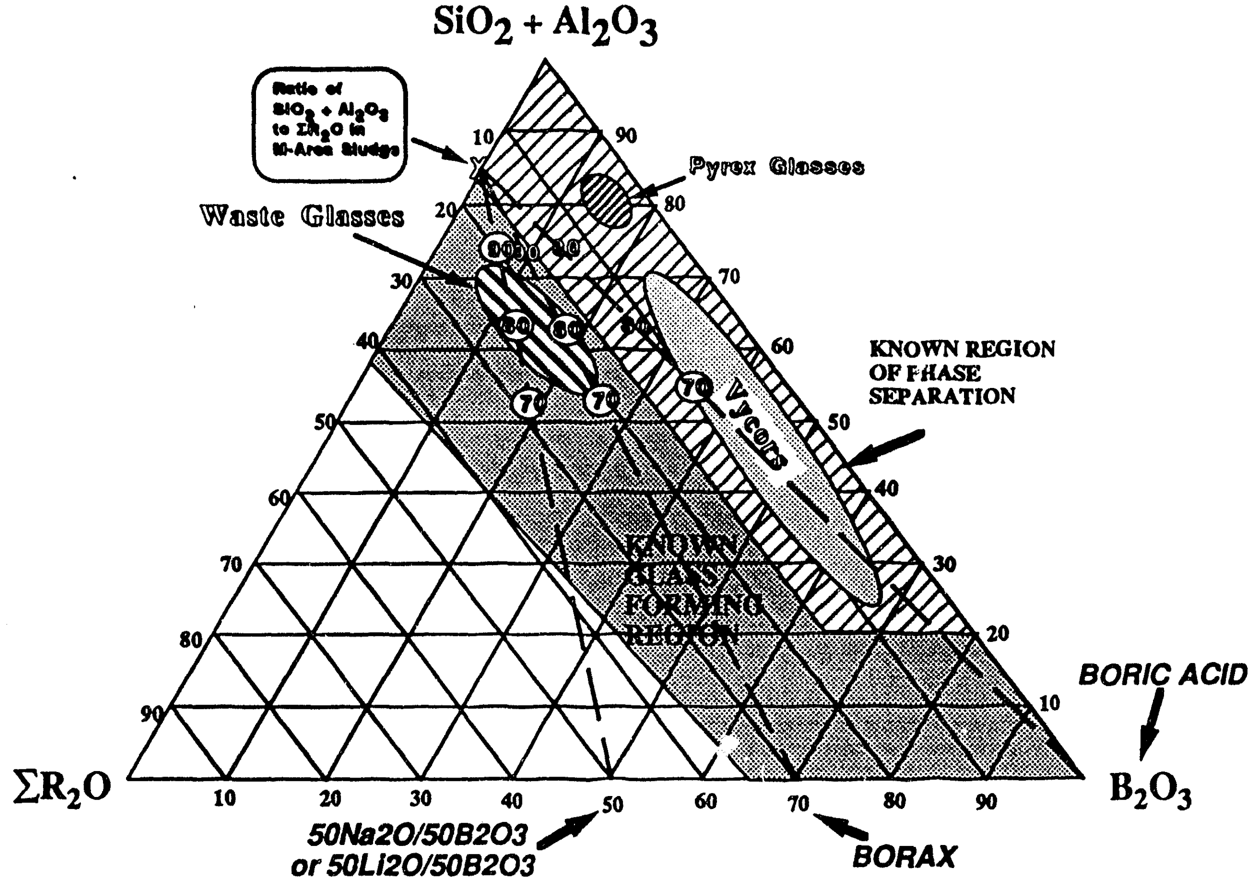

Figure 1. Ternary phase diagram for the system Na_2O-B_2O_3-SiO_2 with the glasses formulated for M-Area sludges superimposed (wt%). The "X" indicates the ratio of SiO_2 + Al_2O_3 to the alkali oxides (R_2O) in the M-Area sludge and filter aid. The stippled area indicates the known glass forming region in the Na_2O-B_2O_3-SiO_2 system. The cross hatched area indicates the known region of phase separation and includes the commercial pyrex and vycor glasses. Glasses in the region of phase separation tend to be less durable than glasses in the other region of the Na_2O-B_2O_3-SiO_2 system.

separation.[4] Phase separation is undesirable for waste stabilization because phase separated glasses tend to be less durable than homogeneous glasses.[5]

Table 2. Glass Formulations and Additives for M-Area Sludge with Spent Filter Aid

Glass	Waste Wt%*	Temp. (°C)	Type of Additive	Type of Glass	Results
M-1	90	>1300	Borax	Borosilicate	Poorly Melted
M-2	85	>1300	Borax	Borosilicate	Poorly Melted
M-3	90	>1300	H_3BO_3	Borosilicate	Poorly Melted
M-4	90	>1300	$CaCO_3$	SLS	Poorly melted
M-5	80	>1250	$H_3BO_3 + Na_2CO_3$	Borosilicate	Poorly melted
M-6	70	1150	Borax + Na_2CO_3	Borosilicate	Homogeneous Glass
M-7	80	>1150	$CaCO_3 + Na_2CO_3$	SLS	Poorly melted
M-8	70	1150	Borax	Borosilicate	Homogeneous Glass
M-9	70	1150	$CaCO_3 + Na_2CO_3$	SLS	Homogeneous Glass

M-area waste glass formulations are being optimized in the region of the borosilicate system-where the high-level radioactive waste glasses are known to form stable homogeneous glasses. The process models developed for high level borosilicate waste glasses can be utilized to calculate the glass viscosity and durability as a function of temperature.

The SLS glass forming system is a well known system used to make window glass and it has been extensively studied by glass chemists since 1925.[6,7,8,9] Soda-silica glass is known to readily incorporate heavy metals.[10] SLS glass formulations have been used for In-Situ Vitrification (ISV) to solidify contaminated soils.[11,12] And, a barium analog (soda-baria-silica)

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[4] C. M. Jantzen, "Systems Approach to Nuclear Waste Glass Development," J. Non-Crystalline Solids, V.84, 215-225 (1986)

[5] C. M. Jantzen and R. F. Schumacher, "Glass Phase Separation; Implications for Waste Glass Durability Modeling," Ceramic Transactions, American Ceramic Society, Westerville, OH (in press)

[6] G. W. Morey and N. L. Bowen, "The Ternary system Sodium Metasilicate-Calcium MetasilicateSilica," J. Soc. Glass Technology, V.9, 226-264 (1925).

[7] G.W. Morey, "The Devitrification of Soda-Lime-Silica Glasses," J. Am. Ceram. Soc., V.13[10], 683-713 (1930).

[8] E.R. Segnit, "Further Data on the System Na_2O-CaO-SiO_2," Am. J. Sci., V.251[8], 586-601 (1953).

[9] A.E. Holland and E.R. Segnit, "The Ternary System Na_2O-ZnO-SiO_2." Australian J. Chemistry, V.19[6], 905-913 (1966).

[10] R.L. Lehman, "Lead-Ion Stability in Soda Lime Lead Silicate Glasses," Am. Ceramic Soc. Abstracts from 92nd Annual Meeting, Dallas, TX (1990).

[11] G.F. Piepel and J.W. Shade, "In-Situ Vitrification and the Effects of Soil Additives: A Mixture Experiment Case Study," J. Am. Ceram. Soc., (in press).

glass has been used at Fernald to solidify residues from uranium ore processing that contain large amounts of uranium, radium, and lead.[13] For Fernald waste solidification the barium rich glass was chosen due to the high barium content of the waste. SLS glasses have also been successfully fabricated from reactive sodium metal contaminated during efforts to develop sodium-cooled fast breeder nuclear reactors.[14] For the M-Area wastes, Figure 2 demonstrates that the use of reactive silica, in this case the spent filter aid already a part of the waste, extends the known glass forming region in the SLS system.

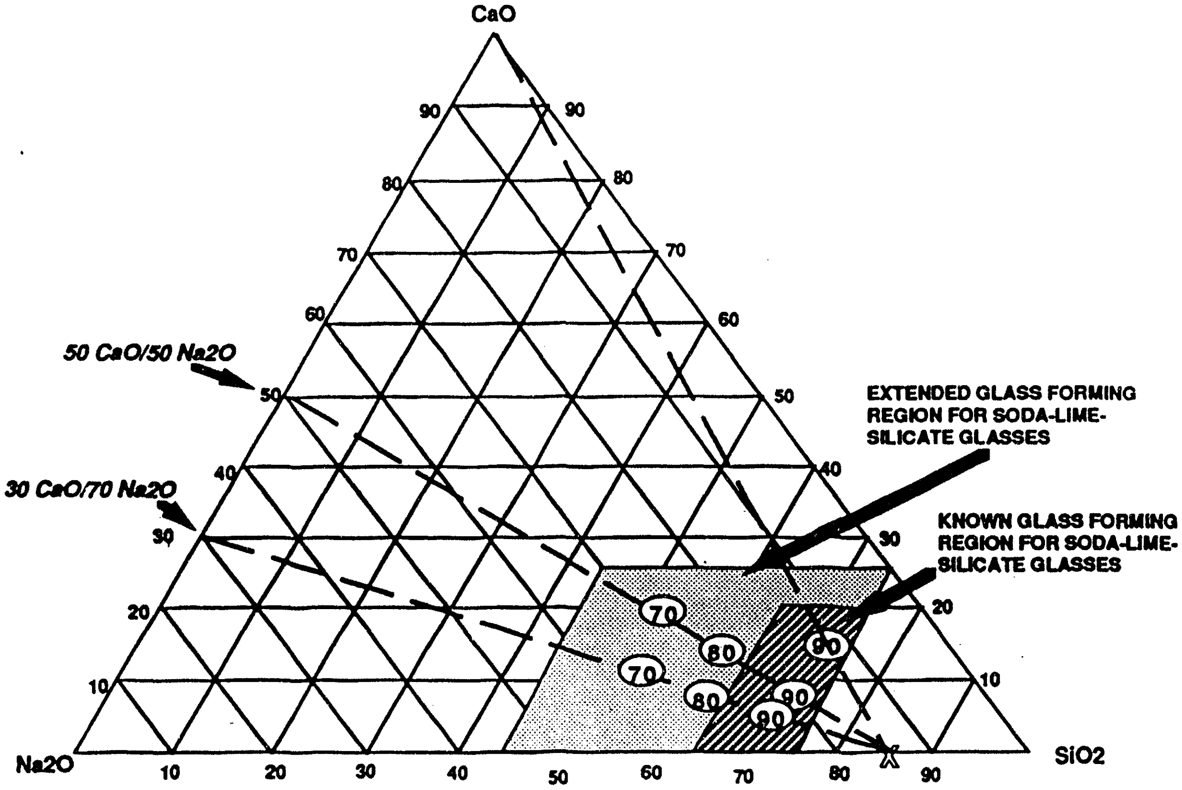

Figure 2. Ternary phase diagram for the system Na_2O-CaO-SiO_2 with the glasses formulated for M-Area sludge superimposed (wt%). The "X" indicates the ratio of SiO_2 + Al_2O_3 to the sum of the alkali oxides (R_2O) in the M-Area sludge + spent filter aid. The cross hatched parallelogram represents the known glass forming region in this system while the larger shaded parallelogram represents the extended glass forming region determined in this study by use of reactive silica additives.

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[12] R.A. Callow, L.E. Thompson, J.R. Weidner, C.A. Loehr, B.P. McGrail, and S.O. Bates, "In-situ Vitrification Application to Buried Waste: Final Report of Intermediate Field Tests at Idaho National Engineering Laboratory," U.S. DOE Report EGG-WTD-9807, Idaho National Engineering Laboraoty, Idaho Falls, ID (August, 1991).

[13] D.S. Janke, C.C. Chapman, and R.A. Vogel, "Results of Vitrifying Fernald K-65 Residue," Nuclear Waste Management IV,G.G. Wicks, D.F. Bickford, and L.R. Bunnell (Eds.), D.F. Bickford, and L.R. Bunnell (Eds.), Ceramic Transactions, V. 23, American Ceramic Society, Westerville, OH, 53-61 (1991).

[14] R. Kumar and J.E. Helt, "Improved Treatment/Disposal of Reactive Metals. Phase II: Technical Research and Development," U.S. DOE Report ANL-91/21, Argonne National Laboratory, Argonne, IL (May, 1991).

To date the TCLP leaching procedure has been performed on one borosilicate glass (M-6) and one SLS glass (M-9). Both of these glass formulations contained 70 wt% waste on a dry basis (Table 1). Both glass formulations had melted to a homogeneous glass at 1150°C. Both glasses passed the TCLP leachate limits for Pb, Ba, and Cr. The borosilicate glass formulation was superior to the SLS glass formulation for retention of Ni and U (Table 3). The SLS glass (M-9) did not meet the Land Disposal Restrictions for Ni but the borosilicate glass (M-6) did.

Table 3. Toxic Characteristic Leaching Procedure (TCLP) and Land Disposal Restriction (LDR) Limits and Response for M-Area Glasses.

						TCLP Leachate	
Element	Wt% Sludge	Wt% Glass M-6*	Wt% Glass M-9*	Waste Code	LDR Limit (ppm)**	M-6 (ppm)	M-9 (ppm)
Pb	0.10	0.074	0.074	F006	0.51	<0.2	<0.2
Ba	0.018	0.013	0.013	N/A	100	1.85	1.40
Ni	0.73	0.51	0.51	F006	0.32	0.17	0.74
Cr	0.007	0.005	0.005	F006	5.2	<0.04	<0.04
U	2.65	1.85	1.85	N/A	N/A	0.10	0.45

* M-6 and M-9 contained 70 wt% waste on a calcine oxide basis

** 40 CFR 148, et. al., Land Disposal Restriction for Third Third Scheduled Wastes Final Rule, 55 FR 22 250, June 1, 1990.

The RASP has been independently verified by a waste treatment company, which has been awarded the contract to vitrify the nickel plating sludge. A temporary wastewater treatment facility will be constructed in M-Area. The glass melter is now being designed, and full scale demonstration of the RASP will begin in 1995.

CONCLUSION

Reactive high surface area silica, as a waste form additive, was determined to greatly enhance the solubility and retention of hazardous, mixed and heavy metal species in glass. Highly reactive silica was found to increase the solubility and tolerance of Soda(Na_2O)- Lime(CaO)- Silica(SiO_2) glass (SLS) and borosilicate (B_2O_3-SiO_2) glass formulations to atomistically bond the waste species. Highly reactive silica lowers glassification temperatures, increases waste loadings which provides for large waste volume reductions, and produces EPA acceptable glasses.

The Reactive Additive Stabilization Process (RASP) can be used to vitrify the Metal Finishing Industry wastes of (1) filter cakes from wastewater treatment, (2) waste sludge, (3) filter media, (4) asbestos or glass fiber filters, (5) ion exchange zeolites, and (6) waste cement formulations in need of remediation into glass.

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