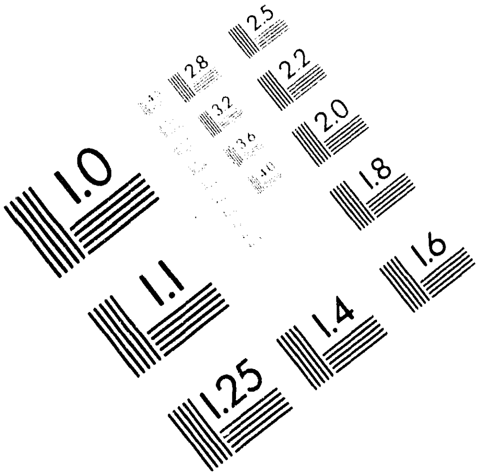

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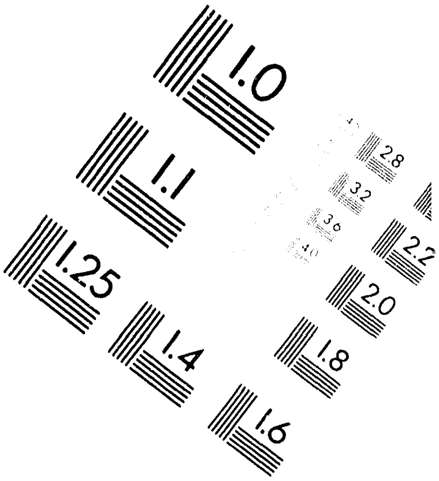

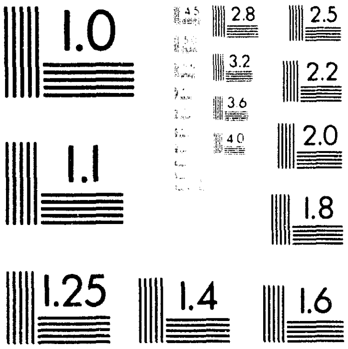

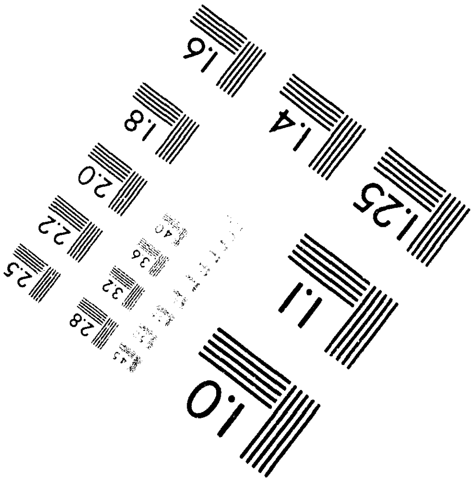

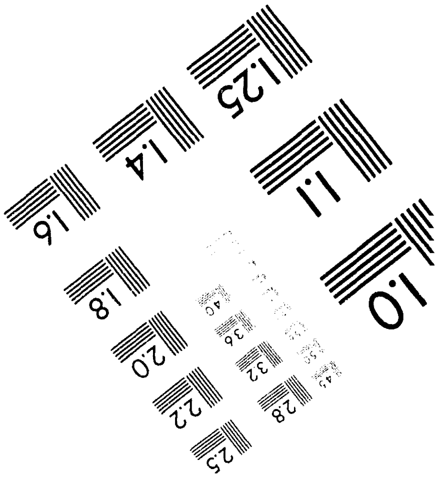

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TREATABILITY STUDIES ON MIXED (HAZARDOUS AND RADIOACTIVE) M-AREA F006 WASTE SLUDGE: VITRIFICATION VIA RASP

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TREATABILITY STUDIES ON MIXED (RADIOACTIVE AND HAZARDOUS) M-AREA F006 WASTE SLUDGE: VITRIFICATION VIA THE REACTIVE ADDITIVE STABILIZATION PROCESS (RASP)* (U)

by

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An extended abstract proposed for **presentation and publication** at Spectrum 94 Nuclear and Hazardous Waste Management International Topical Meeting, August 14-18, 1994 in Atlanta, GA

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Table II. Comparative Volume Reductions for M-Area Waste Stabilization.

Stabilization Options	Volume Reduction*
Base Case (CEMENT WITH SUPERNATE)	
1,200,000 gallons of M-Area supernate + sludge = 2,400,000 gallons cement	0%
Option 1 (CEMENT WITHOUT SUPERNATE)	
650,000 gallons sludge + spent filter aid + cement = 1,300,000 gallons cement	46%
Option 2 (FIST)	
650,000 gallons wastewater treated sludge/spent filter aid + cement = 325,000 gallons cement	86%
Option 3 (RASP)**	
650,000 gallons wastewater treated sludge + spent filter aid = 100,000 gallons glass	96%

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* Relative to original 2,400,000 gallons grout projected if the sludge is not wastewater treated

** assumes the glass is 75wt% waste on a dry calcine basis

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TREATABILITY STUDIES ON MIXED (RADIOACTIVE AND HAZARDOUS) M-AREA F006 WASTE SLUDGE: VITRIFICATION VIA THE REACTIVE ADDITIVE STABILIZATION PROCESS (RASP)†

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ABSTRACT

Solidification of mixed (hazardous and radioactive) waste sludges into glass is being examined at the Savannah River Site (SRS). The M-Area operations at the Savannah River Site (SRS) in Aiken, South Carolina, produced reactor components for nuclear weapons materials for the U.S. Department of Energy. The resulting waste is currently being stored in nine tanks. The total volume in storage was initially ~1,200,000 gallons of which ~1/3 is a gelatinous hydroxide sludge. Vitrification of the sludge into glass is an attractive option because it reduces the waste volume by ~85% and reduces final disposal volume by 96% compared to alternative stabilization technologies. The large volume reductions allow for large associated savings in disposal and/or long term storage costs.

I. INTRODUCTION

Technologies are being developed by the US Department of Energy's (DOE) Nuclear Facility sites to convert low-level and mixed (hazardous and radioactive) wastes to a solid stabilized waste form for permanent disposal. One of the alternative waste forms is vitrification. The Environmental Protection Agency (EPA) has declared vitrification the Best Demonstrated Available Technology (BDAT) for high-level radioactive waste[1] and produced a Handbook of Vitrification Technologies for Treatment of Hazardous and Radioactive Waste.[2] The DOE Office of Technology Development (OTD) has taken the position that mixed waste needs to be stabilized to the highest level reasonably possible to ensure that the resulting waste forms will meet both current and future regulatory specifications. Vitrification produces durable waste forms at volume reductions up to 97%.[3] Large reductions in volume minimize long-term storage costs making vitrification cost effective on a life cycle basis. The US DOE Savannah River Site (SRS), which is operated by Westinghouse Savannah River Company (WSRC), is currently investigating vitrification for disposal of various low-level and mixed wastes.[3,4] The first /mixed wastes vitrified in laboratory studies at SRS have been the M-Area nickel plating line wastes.

The M-Area operations at the SRS in Aiken, South Carolina, produced reactor components for nuclear weapons materials for the U.S. Department of Energy. The resulting mixed waste is a listed Resource Conservation and Recovery Act (RCRA) F006 waste which is currently being stored in the Process Waste Interim Treatment/Storage Facility (PWIT/SF). The total current volume in storage was initially ~1,200,000 gallons of which ~33% is a gelatinous hydroxide sludge containing nickel and uranium. It has been demonstrated[5,6] that a volume reduction of 65-70% of the M-Area waste can be achieved by wastewater treatment of the supernate, with the resulting effluent released via a National Pollution Discharge Elimination System (NPDES) outfall. About 450,000 gallons of spent SiO_2 rich filter aids (perlite/perflo) will be generated from the supernate treatment. The sludge and spent filter aid wastes are to be homogenized into a composite waste blend before final stabilization/solidification.

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† patent pending

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II. REACTIVE ADDITIVE STABILIZATION PROCESS (RASP)

The sludge and spent filter aid wastes are to be homogenized into a composite waste blend before final stabilization/solidification. The spent filter aid is a high surface area siliceous material. The high surface area of the spent filter aid, >50m^2/g, is very reactive and has been determined to enhance the kinetic reactions which dissolve hazardous, radioactive, and heavy metal species into glass at elevated temperatures, e.g.1150°C. Use of any reactive species[1] to enhance the kinetics of melting waste with glass formers, the Reactive Additive Stabilization Process (RASP), has been found to increase the solubility of the waste species in glass and minimize melt line corrosion of refractory melter linings.

The homogenized M-Area nickel plating line waste sludges plus the spent filter aid from the associated supernate treatment are examples of RASP stabilization.

III. GLASS FORMING SYSTEMS EXAMINED

Vitrification was achieved in four different glass forming systems:

- Soda-Boro-Silicate (SBS) glass
- Soda-Lithia-Boro-Silicate (SLBS) glass
- Soda-Lime-Silica (SLS) glass
- Soda-Lithia-Lime-Silica (SLLS) glass.

Waste loadings were varied between 70 to 90 wt%. Higher waste loadings were achieved at higher melt temperatures (Table I). Homogeneous glasses formed at 1150°C at waste loadings of 70 to 80 wt%. These high waste loadings correspond to volume reductions for the composite waste (650,000 gallons of sludge to 100,000 or 89,000 gallons of glass) of 85-86%, respectively, with large associated savings in storage costs. Melt temperatures were predicted from the process models developed for high level waste vitrification.[7] Melt temperatures were confirmed by experimentation and are given in Table I.

IV. WASTE VARIABILITY EXAMINED

The M-Area nickel plating line waste is high in glass forming SiO_2, Al_2O_3 and Na_2O. A nominal waste composition was determined by analyzing the sludge chemistry in each of the eight storage tanks (the main source of Al_2O_3 and Na_2O in the waste), analyzing the spent filter aid (the main source of SiO_2 in the waste) in one large storage tank, and calculating the weighted chemical contribution of each of the nine tanks according to the measured tank volume. In order to determine the flexibility of the glass formulations to potential variation in waste chemistry, e.g. inaccurate analyses or inaccurate tank volume measurement, three different waste mixtures were formulated

- a high silica waste
- a nominal waste
- a low silica waste

V. GLASS COMPOSITION FLEXIBILITY

The matrix of 44 glasses tested in the four different glass forming systems with the three different types of waste are shown in Table I. Fewer glasses were made with the high silica waste due to limitations in the amount of spent filter aid available.

The addition of only one additive, B_2O_3, borax ($Na_2O•2B_2O_3•10H_2O$), or $Na_2O•B_2O_3$ enabled the waste mixtures to be made into a Soda-Boro-Slicate (SBS) or Soda-Lithia-Boro-Silica (SLBS) glasses (Figure 1) while the addition of only $CaCO_3$ or a mixture of $CaCO_3$ and Na_2CO_3 or Li_2CO_3 allowed solidification into Soda-Lime-Silica (SLS) and Soda-Lithia-Lime-Silica (SLLS) glasses (Figure 2). The use of only one additive simplifies process control as only one component needs to be adjusted in order to optimize processability and waste loading (Figures 1 and 2). The use of reactive silica, in this case the spent filter aid that is part of the homogenized waste, was shown to extend the known glass forming region in the SLS and SLLS glass forming systems.[3]

VI. GLASS DURABILITY

To date the TCLP leaching procedure has been performed on one borosilicate glass and one SLS glass. Both of these glass formulations contained

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[1] reactive species include amorphous sources of silica with surface areas >50m^2/g such as waste waste water filter aids (perlite, perflo, diatomaceous earth, precipitated SiO_2, and rice husk ash, Na_2CO_3, $CaCO_3$, Li_2CO_3, $Na_2B_4O_7•10H_2O$ (borax), H_3BO_3, etc.

Table I. Glass Forming Systems Used to Vitrify M-Area Waste

		Soda-Boro-Silicate		Soda-Lithia-Boro-Silicate		Soda Lime-Silica		Soda-Lithia Lime-Silica	
Glass	Waste Type	Waste Loading (wt %)	Melt Temp (°C)	Waste Loading (wt %)	Melt Temp (°C)	Waste Loading (wt %)	Melt Temp (°C)	Waste Loading (wt %)	Melt Temp (°C)
MN-1	Nominal	90	1400	---	---	---	---	---	---
MN-2	Nominal	80	1260	---	---	---	---	---	---
MN-3	Nominal	70	1150	---	---	---	---	---	---
MN-4	Nominal	90	1400	---	---	---	---	---	---
MN-5	Nominal	80	1300	---	---	---	---	---	---
MN-6	Nominal	70	1150	---	---	---	---	---	---
MN-7	Nominal	90	1400	---	---	---	---	---	---
MN-8	Nominal	80	1150	---	---	---	---	---	---
MN-9	Nominal	70	1200	---	---	---	---	---	---
MN-10	Nominal	---	---	90	1200	---	---	---	---
MN-11	Nominal	---	---	80	1150	---	---	---	---
MN-12	Nominal	---	---	70	1150	---	---	---	---
MN-13	Nominal	---	---	85	1150	---	---	---	---
MN-14	Nominal	---	---	75	1150	---	---	---	---
MN-15	Nominal	85	1200	---	---	---	---	---	---
MN-16	Nominal	75	1150	---	---	---	---	---	---
MN 17	Nominal	---	---	---	---	90	1350	---	---
MN-18	Nominal	---	---	---	---	80	1150	---	---
MN-19	Nominal	---	---	---	---	70	1150	---	---
MN-20	Nominal	---	---	---	---	---	---	90	1200
MN-21	Nominal	---	---	---	---	---	---	80	1150
MN-22	Nominal	---	---	---	---	---	---	70	1150
MN-23	Nominal	---	---	---	---	90	1400	---	---
MN-24	Nominal	---	---	---	---	90	1400	---	---
MN-25	Nominal	---	---	---	---	80	1150	---	---
MN-26	Nominal	---	---	---	---	70	1150	---	---
MHSi-1	High Si	90	1400	---	---	---	---	---	---
MHSi-2	High Si	80	1300	---	---	---	---	---	---
MHSi-3	High Si	70	1150	---	---	---	---	---	---
MHSi-4	High Si	90	1400	---	---	---	---	---	---
MHSi-5	High Si	80	1150	---	---	---	---	---	---
MHSi-6	High Si	70	1200	---	---	---	---	---	---
MHSi-11	High Si	---	---	80	1200	---	---	---	---
MLSi-1	Low Si	90	1350	---	---	---	---	---	---
MLSi-2	Low Si	80	1300	---	---	---	---	---	---
MLSi-3	Low Si	70	1150	---	---	---	---	---	---
MLSi-4	Low Si	90	1400	---	---	---	---	---	---
MLSi-5	Low Si	80	1150	---	---	---	---	---	---
MLSi-6	Low Si	70	1150	---	---	---	---	---	---
MLSi-7	Low Si	90	1400	---	---	---	---	---	---
MLSi-8	Low Si	80	1150	---	---	---	---	---	---
MLSi-9	Low Si	70	1150	---	---	---	---	---	---
MLSi-10	Low Si	---	---	90	1200	---	---	---	---
MLSi-11	Low Si	---	---	80	1150	---	---	---	---

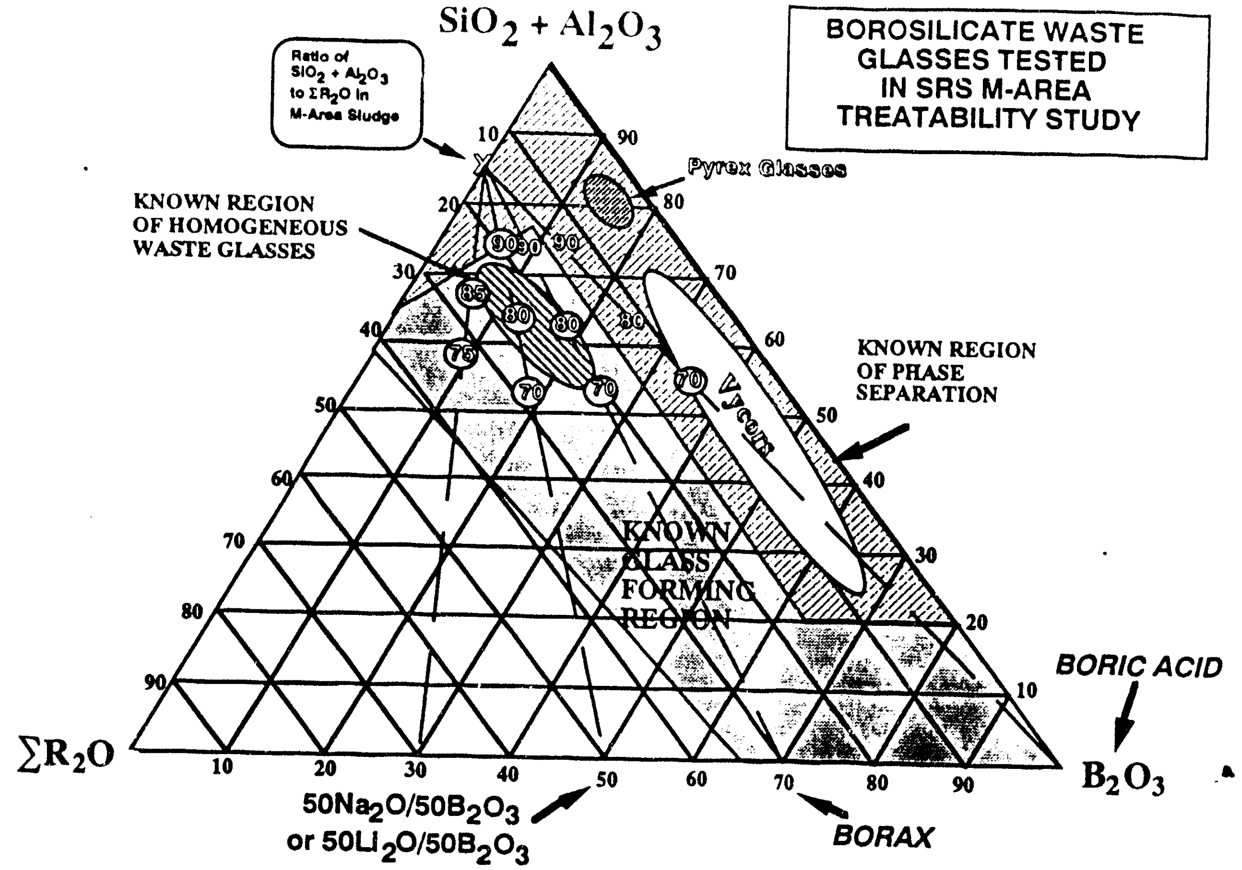

Figure 1. Ternary phase diagram for the system R_2O-B_2O_3-SiO_2 with the M-Area glasses superimposed (wt%). The "X" indicates the ratio of SiO_2 + Al_2O_3 to the alkali oxides (R_2O) in the M-Area homogenized sludge and filter aid.

70 wt% waste on a dry basis. 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. The SLS glass did not meet the Land Disposal Restrictions for Ni but the borosilicate glass did.[3]

Additional TCLP leaching tests and Product Consistency Tests (PCT)[8] are being generated for all 44 waste glasses. Results of the TCLP testing will be compared to the durability of the glasses tested with the high-level waste glass leaching procedure, the PCT. M-Area glass durability will be compared to the high-level waste glass benchmark Environmental Assessment (EA) glass.[9]

VI. VOLUME REDUCTION

Comparisons of the overall waste volume reduction achieved by vitrification as a stabilization technology for M-Area waste is compared to alternative stabilization strategies in cement (Table II). Assuming a waste loading of 70 wt%, vitrification of M-Area sludge and spent filter aid (Option 3 in Table II) reduces the stabilized waste volume by 96% relative to the base case cement stabilization where both supernate and sludge would have to be stabilized. Vitrification of wastewater treated sludge and spent filter aid (Option 3 in Table II) reduces stabilized volume by an additional 50 volume % relative to Option 1 (cement stabilization of wastewater treated sludge and spent filter aid) and by an additional 10 volume % relative to Option 2 (FIST (<u>FI</u>ltration and <u>ST</u>abilization) stabilization in cement).

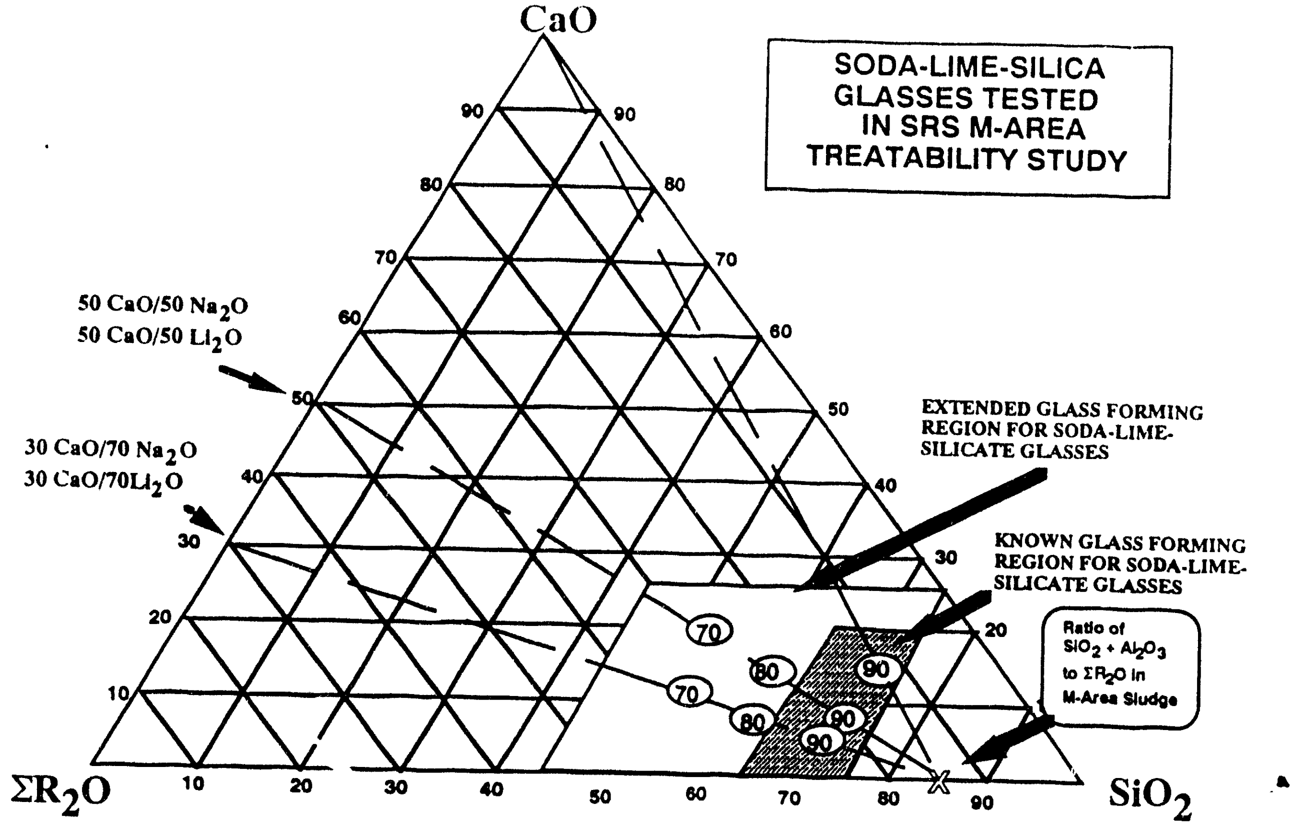

Figure 2. Ternary phase diagram for the system R_2O-CaO-SiO_2 with the M-Area glasses superimposed (wt%). The "X" indicates the composition of SiO_2 + Al_2O_3 to the alkali oxides (R_2O) in the M-Area homogenized sludge and filter aid.

VII. CONCLUSIONS

Laboratory scale studies have demonstrated that vitrification of hazardous/mixed wastes at the Savannah River Site is viable for nickel plating line (F006) sludges. Vitrification of these wastes using high surface area additives, the Reactive Additive Stabilization Process (RASP), was shown to enhance the dissolution and retention of hazardous, mixed, and heavy metal species in glass. Vitrification was achieved in four different glass forming systems at waste loadings up to 90 wt%. RASP vitrification was shown to enlarge the known region of glass formation in two of the glass forming systems, e.g. the Soda-Lime-Silica (SLS) and Soda-Lithia-Lime-Silica (SLLS) glass systems. Nominal waste loadings of ~75% correspond to volume reductions of ~96% compared to alternative stabilization strategies with large associated savings in long term storage costs.

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