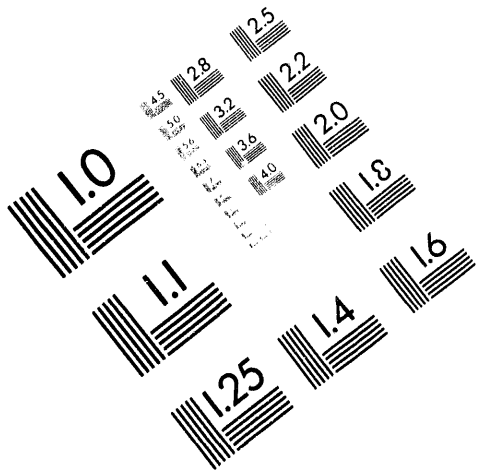
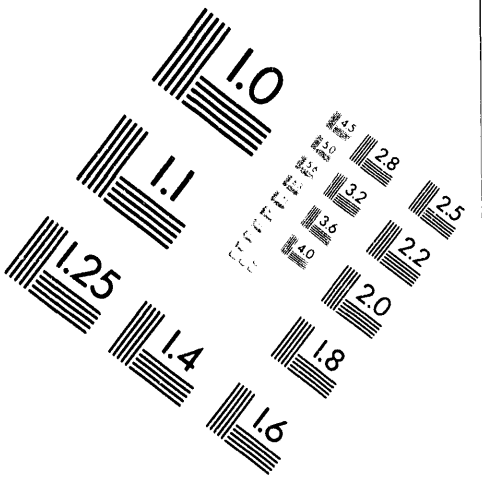
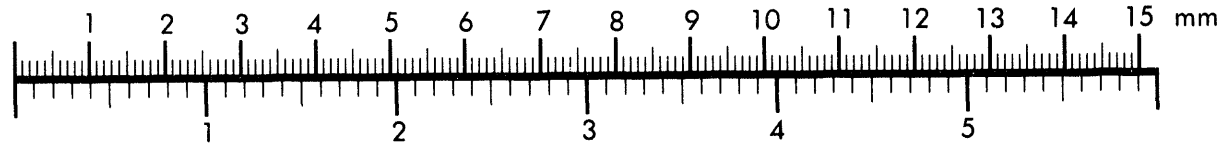


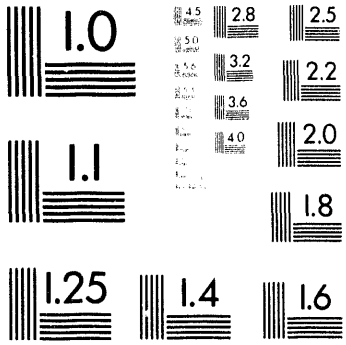
Association for Information and Image Management

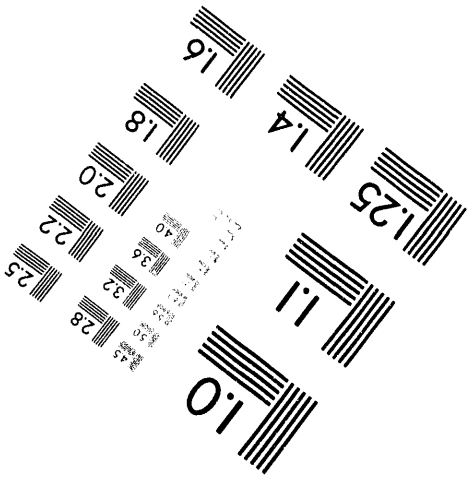
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910

301/587-8202

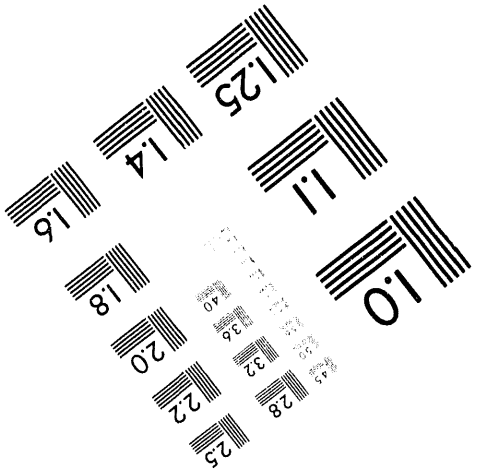








MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.



1 of 1

ANL/CMT/CP--80987
Conf-940225--64

AN EVALUATION OF VITRIFICATION TECHNOLOGY: APPLICATION TO MIXED WASTE AT ARGONNE NATIONAL LABORATORY

J. J. Mazer, J. S. Devgun, N. J. Beskid, and H. J. No

Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

For presentation at

Waste Management '94
Tucson, Arizona
February 27-March 3, 1994

*Work supported by the U.S. Department of Energy, Office of Technology Development, under contract W-31-109-ENG 38.

AN EVALUATION OF VITRIFICATION TECHNOLOGY: APPLICATION TO MIXED WASTE AT ARGONNE NATIONAL LABORATORY

J. J. Mazer, J. S. Devgun, N. J. Beskid, and H. J. No
Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439

ABSTRACT

Argonne National Laboratory-East (ANL-E) is evaluating the feasibility of using vitrification to treat mixed wastes. This program is in the process of identifying glass compositions that can be produced from mixed wastes and additives, with an emphasis on maximizing the waste loading in the glass, and the overall waste volume reduction. Preliminary crucible glass studies with surrogate mixed waste streams have produced a glass composition that could be produced in commercially available melters. This same glass composition, spiked with Resource Conservation Recovery Act (RCRA) metals, pass the Toxic Characteristic Leaching Procedure (TCLP) test. Thus, the final waste form is a low-level radioactive waste. Additional crucible melts with actual mixed waste streams are in progress and will define a compositional envelope of acceptable glasses that will eventually be produced during full-scale melter operations. Evaluations of the likely off-gases from vitrification indicate that the primary off-gases produced during vitrification will include compounds of SO_x, NO_x, and CO_2. These compounds are routinely treated in the off-gas portion of vitrification systems. The composition of the melter feed can be adjusted to control some of the off-gases produced, if necessary. The economics suggest that annual cost savings resulting from volume reduction and conversion of mixed waste to low-level waste may be substantial.

INTRODUCTION

Research activities at ANL-E produce radioactive and mixed waste, albeit in small quantities. Currently, ANL-E is shipping mixed waste to the Hanford site packaged in 55-gal drums with liners and an approved liquid absorbent. Approximately 750 L of mixed wastes suitable for vitrification is in storage awaiting disposal. Future mixed waste production is expected to continue at varying rates.

The commercial disposal options for mixed waste disposal are limited. Currently, the only operating commercial facility in the United States licensed to accept mixed waste for disposal is Envirocare's facility in Clive, Utah. While this facility is licensed under RCRA Part B and has received wastes from Comprehensive Environmental Response Compensation and Liability Act (CERCLA) response actions and some Department of Energy (DOE) cleanup projects, the facility is limited to accepting mixed waste with activity only emanating from naturally occurring radioactive materials (NORM), which are not covered under the Atomic Energy Act.

This project is planning to evaluate the feasibility of using vitrification to reduce the volume and stabilize some of the mixed waste streams at ANL-E. This report describes the results of tests using preliminary crucible melts of mixed waste surrogates and assesses the prospects for control of the likely off-gases that will be emitted during treatment. Further vitrification tests are in progress. These test results will form a technical basis for a

decision on whether to use vitrification for mixed waste treatment at ANL-E.

BACKGROUND

"Mixed waste" is defined as low-level radioactive waste (LLW), subject to the Atomic Energy Act, RCRA-regulated hazardous waste, based on 40 CFR 261. In 1986, the U.S. Environmental Protection Agency (EPA) formally issued notice subjecting mixed waste to RCRA regulations. Radioactive waste may be considered "mixed" due to characteristics of ignitability, corrosivity, reactivity, or toxicity, or it may be a listed waste on the F, K, P, or U lists in 40 CFR 261.

There are several strategies for managing mixed wastes. If the waste is classified as a mixed waste because of a characteristic, then attempts are made to eliminate that characteristic prior to disposal in a non-hazardous waste facility (e.g., LLW facility). If the waste is classified as a mixed waste because it contains a listed hazardous material, then the waste must be disposed of in a hazardous waste facility. Additionally, if the waste falls under land ban restrictions, then it must be treated first. With respect to the radioactive component of the mixed waste, the 10 CFR 61, administered by the U.S. Nuclear Regulatory Commission (NRC), covers shallow land disposal of low-level radioactive waste.

Section 105 of the Federal Facilities Compliance Act of 1992 (FFCA) is the main regulatory driver under which all DOE facilities are required to prepare an inventory of existing and planned mixed waste and to develop plans for mixed waste treatment. The DOE is required by Section 3021(b) of the RCRA, as amended by the FFCA, to prepare plans describing the development of treatment capacities and technologies for treating mixed wastes. The Act requires treatment plans (STP) to be developed for each site at which DOE generates or stores mixed waste. A recently drafted ANL-E STP provides information to other DOE sites with respect to common technology needs and options for mixed waste treatment. Recent major DOE initiatives related to mixed waste treatment include the Mixed Waste Integrated Program (MWIP) and the Minimum Additive Waste Stabilization (MAWS) Program. The objective of the former is to develop treatment technologies for mixed waste, and that of the latter is to develop and investigate the use of vitrification for mixed waste treatment.

This study reports on our initial findings on the feasibility of using vitrification for mixed waste treatment at ANL-E. In addition to RCRA compliance for leach resistance, the glass waste form must provide compositional flexibility, chemical durability, compressive strength, thermal stability, and radiation and biological stability. Potential glass waste forms include borosilicate glass (B_2O_3-SiO_2), aluminosilicate glass (Al_2O_3-SiO_2), phosphate glass (P_2O_5), and soda-lime silicate glass (Na_2O-CaO-SiO_2). For this program, ANL-E is considering borosilicate glass waste forms. Clearly defined mixed waste streams at ANL-E are being considered for vitrification, although the program may be expanded in the future to accommodate other waste streams.

MIXED WASTE STREAMS

Four candidate mixed waste streams are considered in this report: evaporator concentrator bottoms sludge, and Cu-sulfide sludge [1],

storage tank sludge, and High Efficiency Particulate Air (HEPA) filters. The actual waste streams at ANL-E are mixed waste as a result of their failure to pass the TCLP test with respect to toxic metal leaching. Surrogates for each waste stream were used for preliminary crucible melting tests to facilitate sample handling and analysis. Actual waste streams will be used later in the study.

The approximate concentration of each waste stream is presented in Table I. Evaporator bottoms sludge consists primarily of sodium salts and approximately 50 wt % water. The actual evaporator sludge bottoms are considered mixed wastes because of the presence of radioactive elements and the presence of RCRA metals above the TCLP limit, including Ag, As, Ba, Cd, Cr, Hg, Se, and Pb. The Cu-sulfide sludge was designed as a surrogate for an actual secondary waste that consists of RCRA metal sulfides and is produced during mixed waste treatment. The surrogate consists primarily of CuS, with minor amounts of Ca phases. The HEPA filters consist primarily of borosilicate glass. The spent HEPA filters from ANL-E are treated as mixed wastes because of the presence of radioactive elements and unacceptable release of RCRA metals during TCLP testing. The HEPA filters did not become available until late in this preliminary study, and this waste stream was not used in the initial crucible studies. However, it should be noted that the chemistry of HEPA filters and their contamination is very compatible for vitrification treatment. Estimates of the annual generation rate of these wastes are presented in Table II.

TEST RESULTS

Most of the crucible melts were performed with surrogate evaporator bottoms sludges and surrogate Cu-sulfide sludges. These sludges contained no hazardous metals, although one melt was spiked with hazardous metals. Each sludge was initially dried at 90°C, then blended with various amounts of silica sand and boric acid so that the resultant melt would form a vitreous product. The resulting blends each weighed approximately 150 g. These additives were selected because of their commercial availability. The blended waste was next preheated at 500°C in a hooded oven to volatilize the SO_x, NO_x, and CO_x compounds and to avoid foaming during vitrification. The crucible was next placed in a 1200°C furnace for one hour. At the end of this period the melt was removed from the furnace, and the melt viscosity was qualitatively assessed by attempting to pour the melt from the crucible. After cooling, the glasses were recovered, visually examined, and archived.

Four melts were produced. The first melt contained equal amounts of Na-sludge, silica sand, and boric acid. This blend (Melt #1) produced a clear glass with a slight yellowish tint and no visible crystallites. Melt #1 was easily poured from the crucible. This demonstration of homogeneity and low viscosity suggests that this melt composition should be considered a good candidate for the final waste form. Two other melts were produced with evaporator bottom Na-sludge, Cu-sulfide sludge, silica sand, and boric acid. These melts (Melts #2 and #3) were blended in proportions unrepresentative of any likely vitrification at ANL-E; however, they were intended to determine how much of the Cu-sulfide sludge could be incorporated into a glass. Additional analyses of these glasses are in progress. The high viscosity of each of these melts was evident from our inability to pour either melt from the crucibles. Melt #4 was essentially

identical in composition to Melt #1, except for the addition of approximately 0.2 wt % of As, Ag, Cd, Pb, Cr, Ni, and Ba. This blend produced an olive green glass with no visible crystallites, which was able to be easily poured from the crucible.

Leach testing with the TCLP procedure was performed on the glass from Melt #4. The results indicate that the glass passes the TCLP test and the RCRA metals are immobilized in the glass matrix; thus, the waste form can be considered a low-level radioactive waste, not a mixed waste.

The plan for future vitrification testing is to perform additional crucible melting to establish a compositional envelope for blends that produce glasses that pass TCLP testing and can be processed in a full-scale melter. We will identify blends that maximize waste loading and use inexpensive additives.

OFF-GAS AND METAL VOLATILITY CONSIDERATIONS

Based on an analysis of the materials in the waste streams, the following off-gases are anticipated in the vitrification system. From the evaporator bottom sludges, SO_x, NO_x, CO_2, Hg, and lesser amounts of F and Cl are anticipated. The amounts of these gases and metals will depend on the waste loading in the waste form. From the Cu-sulfide sludge, SO_x off-gases will need to be monitored and controlled. The HEPA filter waste stream is not expected to generate any off-gases. However, once the filter is removed from the housing, small amounts of cyanide may be produced from the residual neoprene adhesive on the filter media. Detailed characterizations of the storage tank sludge were unavailable for this study. When chemical analyses of this material are completed, its off-gas potential will also be evaluated.

The SO_x, NO_x, and CO_2 are commonly treated with off-gas systems that are commercially available. The extent that each of these compounds may need to be controlled will be experimentally estimated during the planned laboratory crucible studies. Preliminary studies of the ANL-E waste streams show that the primary off-gases produced during vitrification include SO_x, NO_x compounds, and CO_2. These compounds are routinely treated in the off-gas portion of vitrification systems. The composition of the melter feed can be adjusted to control some of the off-gases produced, if necessary. Initial correspondence with the Illinois EPA indicated that a vitrification system will not be subject to the same regulations and scrutiny as an incineration unit, rather it will be considered a thermal treatment unit. At this point, it appears that the likely off-gases can be treated with commercially available technology.

The air-pollution control systems typically employed to control toxic metal release in off-gases address those used for particulate and vapor phases [3]. Particulate fraction control is achieved with traditional particulate control devices, such as electrostatic precipitators, fabric filters, and wet scrubbers. The vapor phase fraction is controlled by cooling the off-gas and collecting the fine particulates that result. Control devices for vapor phase control include spray dryer absorbers, wet scrubbers, and condensing wet scrubbers.

Volatility of metals during vitrification may need to be addressed if we find that they are present in quantities of regulatory concern. It

is anticipated that most of the RCRA metals will be soluble in the designed final waste form. These metals are anticipated to be present in the waste streams at quantities less than 0.1 wt % (1000 ppm). Their concentration in the mixed feed delivered to the melter will be further reduced by the presence of additives or non-hazardous metal-bearing waste streams (several hundred ppm). Studies of solubilities of elements in silicate glasses (Table III) indicate that these concentrations of hazardous metals should be able to be vitrified. The elements that may not remain in the melt are Hg, Cd, and As. If so, they probably can be controlled by an off-gas system.

The constituents used to formulate Melt #4 included Cd metal and oxides of the remaining RCRA metals at a concentration of approximately 0.2 wt % of each metal. The composition of this melt was determined with scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) to evaluate whether any of these metals had been significantly volatilized during melting. These results are summarized in Figure 1. Semi-quantitative analyses made in conjunction with these microscopy analyses indicate that the RCRA metals are soluble in this glass. This issue will be further examined as the study continues and more vitrification tests are performed with actual waste streams.

PLACE FIGURE 1 HERE

Estimates of the efficiency of toxic metal control of an off-gas system are given in Table IV [3]. From these literature data, it appears that all of the RCRA metals found in the ANL-E mixed wastes, except for selenium, are addressed in this report, and that all metals except for mercury can be controlled at greater than 99% efficiency. The Hg collector efficiency can be improved to 95% by adding an adsorption enhancer in a spray dryer absorption system or a condensing wet scrubber following a dust collector.

VOLUME REDUCTION AND COST ESTIMATE

On the basis of limited laboratory studies and previous estimates for the potential mixed waste treatment with the MAWS Program, the volume reduction of the sludge waste is anticipated to range up to a factor of 70%, while a volume reduction of a factor of 100 is expected for HEPA filters. Volume reductions will be maximized as the waste loading is maximized through waste blending to minimize the addition of glass-forming fluxes. This aspect will be determined as all the waste streams to be vitrified are identified. Our initial cost estimates show that for ANL-E mixed wastes, the disposal costs of low-level radioactive wastes are lower than those for mixed waste disposal by a factor of two to three, although on-site mixed waste treatment may be mandated in the future. Thus, the potential cost benefits for use of vitrification technology appear to be substantial.

CONCLUSIONS

In conclusion, the prospects for application of vitrification to mixed wastes at ANL-E appear to be good. Our initial studies have demonstrated, in the laboratory with surrogate feeds, that all potential RCRA metals can be incorporated into glass melts, and that available commercial off-gas systems can treat gases expected to be produced during vitrification. The cost/benefit analysis suggests

that annual cost savings resulting from volume reduction and conversion of mixed waste to low-level waste glass may be substantial.

The strategy being used in the crucible glass studies is to maximize waste loading while ensuring that the final waste form meets TCLP criteria. The goal of this portion of the study is to devise a range of glass formulations that can successfully be vitrified. This is being accomplished by considering the chemical nature of each waste stream and synergistically blending the waste streams to minimize the need for glass-forming additives. The storage tank sludge and liquid waste streams require glass-forming additives to produce an acceptable vitrified waste form, and the maximum total waste loading would only be 30-40%. By blending these waste streams with the spent HEPA filter waste stream, which primarily consists of borosilicate glass, the maximum total waste loading approaches 100%. This strategy maximizes volume reduction, waste loading, and cost savings (for example, cost savings from vitrification and disposal). Additional waste streams are being evaluated to determine whether they can be incorporated into this vitrification scheme. As additional waste streams are identified, the system becomes more robust, and the overall economics of the system become more attractive.

The candidate mixed waste streams at ANL-E lend themselves to vitrification with relatively low temperature melters (<1200°C), such as joule-heated or microwave systems [4]. Final selection of a melter design will be made upon completion of these studies. One of the most important elements that will be a part of this system is an off-gas system that will satisfy the technical requirements, as well as regulatory requirements (federal, state, local). Included among the off-gas concerns are volatilized elements (potentially Hg, Cd, and As) and gases such as SO_x, NO_x, CO_2.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Technology Development, under contract W-31-109-ENG-38.

REFERENCES

1. G. F. VANDEGRIFT, C. CONNER, J. C. HUTTER, R. A. LEONARD, L. NUNEZ, J. SEDLET, and D. G. WYGMANS, "Preliminary Plan for Treating Mixed Waste," Argonne National Laboratory Report ANL-93/29 (1993).

2. M. B. VOLF, "Chemical Approach to Glass," Elsevier Science Pub., New York, NY (1984).

3. J. R. DONNELLY, "Metals Emissions Control Technologies for Waste Incineration," in Emerging Technologies in Hazardous Waste Management III, Eds., D. W. Tedder and F. G. Pohland, American Chemical Society, Washington DC (1993).

4. EPA HANDBOOK, "Vitrification Technologies for Treatment of Hazardous and Radioactive Waste," Office of Research and Development, Cincinnati, OH, EPA/625/R-92/002 (1992).

Table I. Reported compositions of surrogates for ANL-E mixed waste streams. All values are reported in wt %.

Constituent	Evaporator Bottoms Sludge	Cu-Sulfide Sludge	Storage Tank Sludge	HEPA Filters
SiO_2	0.1			57.0-69.0
Na_2O	36.0			8.0-12.5
B_2O_3	0.1			4.5-11.0
Al_2O_3				3.0-7.0
CaO	0.3			2.0-7.0
BaO				<5.5
MgO	0.8			<4.5
ZnO				<4.5
K_2O				<3.0
F_2	0.4			<1.0
Fe_2O_3				<0.2
CuS		93		
CaS		6		
$Ca(OH)_2$		1		
Li_2O	0.1			
SO_4^{2-}	14.4			
NO_3^-	4.2			
NO_2^-	5.2			
HCO_3^-	27.2			
Cl^-	8.1			
Carbonaceous Material			25	
Ash			66	
Other	3.1		9	
Total	100	100	100	100

Table II. Annual mixed waste generation rates at ANL-E (estimated)

Waste Stream	Generation Rate
Evaporator Concentrator Bottom Sludges	2.5 drums/year
Storage Tank Sludge	20 drums/year
HEPA Filter Media	14 bins/year

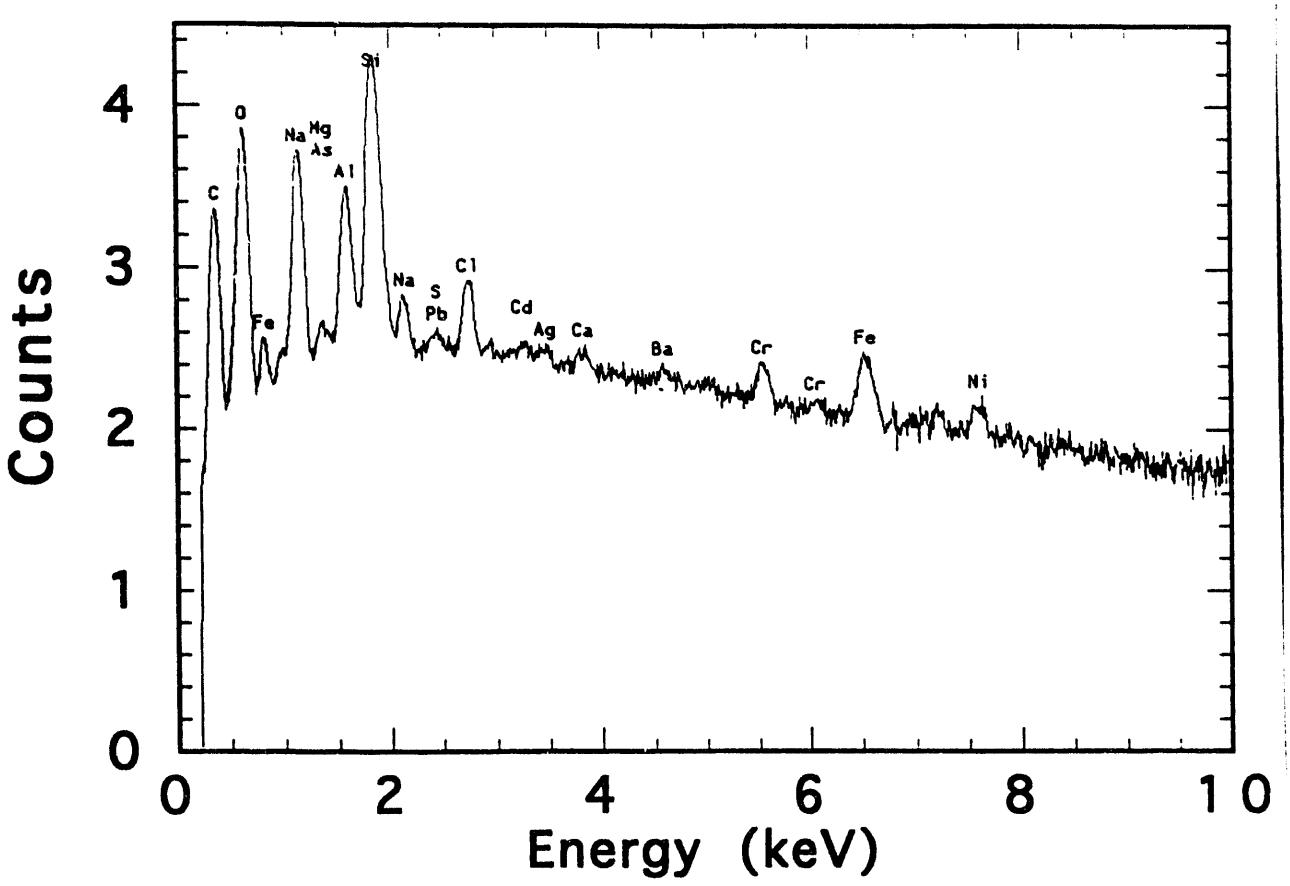
Table III. Approximate solubility of some elements in silicate glasses [2]

Solubility	Hazardous Elements in ANL-E Mixed Waste Streams	Other Elements in ANL-E Mixed Waste Streams	Other Elements Found in Silicate Glasses
< 0.1 wt %	Ag, Hg		Ar, Au, Br, H, He, I, Kr, N, Ne, Pd, Pt, Rh, Rn, Ru, Xe
1 to 3 wt %	As, Cr, Se	S, C, Cl	Sb, Sn, Tc, Te
3 to 5 wt %		Cu, Mn	Ni, Ti, Mo, Co, Bi
5 to 15 wt %		B, F, Th	Ce, La, Nd, Pr, Ge
15 to 25 wt %	Ba	Ca, U, Na	Al, Cs, Fe, Fr, K, Li, Mg, Ra, Rb, Sr, Zn
> 25 wt %	Pb	Si	P

Table IV. Hazardous waste incinerator estimates [3]

	EPA Conservative Estimated Efficiencies	Typical Actual Control Efficiencies	Typical Range of Emissions Rates
Particulate Matter	99+%	99.9+%	0.005-0.02 gr/dscf
Arsenic	95	99.9+	1-5 $\mu g/m^3$
Cadmium	95	99.7	0.1-5
Chromium	99	99.5	2-10
Barium	99	99.9+	10-25
Lead	95	99.8	10-100
Mercury	85-90	40-95+	10-200
Silver	99	99.9+	1-10

Figure 1. Typical SEM/EDS spectrum collected from an epoxy mounted cross-section of Melt #4 at 20 keV for 400 s. The data are presented on a logarithm counts scale. The carbon peak resulted from a carbon-coating applied to the sample.



DATE
FILMED
6/22/94
END