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THE EFFECT OF CHEMICAL COMPOSITION ON THE PCT DURABILITY OF MIXED WASTE GLASSES FROM WASTEWATER TREATMENT SLUDGES*

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ABSTRACT

An experimental program has been designed to examine the chemical durability of a large glass composition space derived from the vitrification of simulated wastewater treatment sludges. These sludges represent the majority of low-level mixed wastes currently in need of treatment by the U. S. Department of Energy. The major oxides in these model glasses included SiO_2 , Al_2O_3 , B_2O_3 , Na_2O , CaO and Fe_2O_3 . In addition, three minor oxides, BaO , NiO , and PbO , were added as hazardous metals. The major oxides were each varied at two levels resulting in 32 experimental glasses. The compositions of these glasses represented the extreme vertices of a five-dimensional "hyperspace." The chemical durability was measured by the 7-Day Product Consistency Test (PCT). The normalized sodium release rates (NRR_{Na}) of these glasses ranged from 0.01 to $4.99 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. The molar ratio of the glass-former to glass-modifier (F/M) was found to have the greatest effect on PCT durability. Glass-formers included SiO_2 , Al_2O_3 , and B_2O_3 , while Na_2O , CaO , BaO , NiO , and PbO were glass-modifiers. As this ratio increased from 0.75 to 2.0, NRR_{Na} was found to decrease between one and two orders of magnitude. Another important effect on NRR_{Na} was the $\text{Na}_2\text{O}/\text{CaO}$ ratio. As this ratio increased from 0.5 to 2.0, NRR_{Na} increased up to two orders of magnitude for the glasses with the low F/M ratio but almost no effect was observed for the glasses with the high F/M ratio. Increasing the iron oxide content from 2 to 18 mole percent (4 to 35 weight percent) was found to decrease NRR_{Na} one order of magnitude for the glasses with low F/M but iron had little effect on the glasses with the high F/M ratio. The durability also increased when 10 mole percent Al_2O_3 was included in low iron oxide glasses but no effect was observed with the high iron glasses. The addition of B_2O_3 had little effect on durability. The effects of other composition parameters on durability are discussed as well. In addition, a strong positive

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linear relationship between pH and $\log \text{NRR}_{\text{Na}}$ was also observed when leachate pH was greater than 11.

BACKGROUND

The Mixed Waste Integrated Program (MWIP) at the U. S. Department of Energy (DOE) has taken a serious look at vitrification for treatment of low-level mixed waste streams. This was prompted, in part, by the fact that the EPA has declared that vitrification is the Best Demonstrated Available Technology for the disposal of high-level radioactive waste.¹ Among the low-level mixed waste streams within the DOE complex, which are under consideration for vitrification, are wastewater treatment sludges at the Savannah River Site (SRS), Oak Ridge Reservation (ORR), Rocky Flats Plant (RFP), and Los Alamos National Laboratory (LANL). These sludges typically contain low levels of radioactive and hazardous metals, water, and additives from the waste treatment process itself. The treatment additives normally include precipitating and flocculating agents such as sodium, calcium, magnesium, and iron compounds or siliceous filter aids from the dewatering process. These treatment additives tend to be soluble in silicate glass and are thus amenable to vitrification.

The compositions of these sludges vary depending upon the treatment processes employed. Stored in M-Area at SRS is a wastewater treatment sludge from their aluminum cladding and nickel cladding operations. Even though uranium and nickel are the chief radioactive and hazardous species in this waste, the sludge is primarily comprised of sodium hydroxide from the precipitation process and perlite and diatomaceous earth from the dewatering process.² These two filter aids are comprised chiefly of silica and alumina. Vitrification has already been chosen as the treatment for this sludge.³ Another candidate mixed waste is stored at the West End Treatment Facility (WETF) at ORR. Species targeted for immobilization include uranium and various hazardous metals but the majority of the waste consists of calcium and aluminum hydroxides from the precipitation process.⁴ An example of a RFP waste is the aqueous sludge from the plutonium recovery operations. In addition to small amounts of uranium, plutonium, and americium and several hazardous metals, this waste consists primarily of sodium, calcium, magnesium, and iron hydroxides from the treatment processes and some siliceous filter aid material from dewatering. The process water from decontamination operations at LANL contains small amounts of uranium, plutonium, and americium. The resulting sludge from the wastewater treatment process is comprised chiefly of calcium hydroxide from precipitation and alumina and silica from the spent filter aids.⁴ A summary of the major oxide constituents in these mixed wastes is shown below in Table I.

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Pilot-scale vitrification testing of these wastes is currently being carried out at Clemson University.⁵ To date, tests have been carried out on surrogates of the M-Area sludge and the WETF sludges. This resulted in the production of glasses which passed the Toxicity Characteristic Leaching Procedure (TCLP) as per the Land Disposal Restrictions.^{6,7} Formulations for the glass compositions used in these tests included glass-forming siliceous materials such as perlite, diatomaceous earth, and precipitated silica and fluxes such as sodium tetraborate or sodium carbonate. Results, so far, indicate that these sludges may be good candidates for vitrification.

A large glass composition space has been developed in these studies, which is intended to bracket most glass products that might result from the vitrification of wastewater treatment sludges currently in storage at DOE sites throughout the United States. Glasses have been prepared with these compositions and tested for chemical durability by the 7-Day Product Consistency Test. This should provide not only target composition ranges for each of these waste types but also a data base from which to predict the behavior of glassy products resulting from the vitrification of a wide variety of mixed wastes.

EXPERIMENTAL

Experimental Design

A glass composition space has been developed to serve as a simplified model for studying the durability of the products which might result from the vitrification of wastewater treatment sludges. This mixture is composed of six variable components SiO_2 , Al_2O_3 , B_2O_3 , Fe_2O_3 , Na_2O , and CaO . Three hazardous species, BaO , PbO , and NiO were also included at fixed levels. These components are divided into three groups depending upon their role in the glass structure. The first group, glass-formers (F), includes SiO_2 , Al_2O_3 , and B_2O_3 . The second group, glass-modifiers (M), includes Na_2O and CaO plus the hazardous species BaO , PbO , and NiO . Lastly, the iron oxides (Fe_xO_y) include FeO and Fe_2O_3 and are grouped by themselves. The sum of the six variable oxides always totals 95 mole percent while the BaO , PbO , and NiO levels are fixed at 2, 1, and 2 mole percent, respectively.

With the aid of ternary phase diagrams and exploratory experiments, a large glass-forming region was identified which is illustrated in the F-M- Fe_xO_y ternary phase diagram shown in Figure 1. The four vertices of the region represent the compositions given in Table II, labeled 1, 2, 3, and 4. Note that Fe_xO_y ranges between 2 and 18 mole percent. These correspond to about 4 and 35 weight percent, respectively. At the low iron level, the ratio of glass-former to glass-modifier (F/M), ranges from 42/56 to 63/35. At the high iron level, F/M ranges from 35/47 to 56/26. The compositions at these four vertices of the glass-forming region can then be represented by two independent compositional variables, the Fe_xO_y content and F/M. This two-dimensional composition space is further expanded by the substitutions of Al_2O_3 and B_2O_3 for SiO_2 , giving rise to two additional compositional variables. B_2O_3 is added at 0 and 17 mole percent of the glass-former composition while the level of Al_2O_3 is either 0 or 10 mole percent of the total glass composition. A final compositional variable, the $\text{Na}_2\text{O}/\text{CaO}$ ratio, is either 0.5 or 2.0. This increases the number of independent compositional variables to five, resulting in a

five-dimensional space consisting of 32 vertices. The target glass compositions of these 32 vertices are given in Table III, in oxide mole percent.

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The scheme used to identify these glasses is comprised of a number followed by three letters. Two of the compositional variables are identified by the number and the remaining three variables are identified by the three letters. The number refers to either of the four vertices of the two-dimensional space in Figure 1. But after expansion, these vertices become three-dimensional "subspaces." Subspaces 1 and 2 each contain 2 mole percent Fe_xO_y while the compositions in Subspaces 3 and 4 contain 18 mole percent iron oxides. Subspaces 1 and 3 contain the lower F/M ratios, 42/56 and 35/47, respectively, while subspaces 2 and 4 contain the higher F/M ratios, 63/35 and 56/26, respectively. These four subspaces are arranged in Figure 2 to illustrate the entire five-dimensional composition space.

PLACE FIGURE 2 HERE

Within each subspace, the Na_2O/CaO ratio, the B_2O_3/F ratio, and the Al_2O_3 content vary similarly. The first letter is either an *L* or *H* depending on whether the Na_2O/CaO mole ratio is low or high, i.e. 0.5 or 2.0. The second letter is either *l* or *h* depending on whether the B_2O_3/F mole ratio is low or high, i.e. 0 or 1/7. The last letter is either *0* or *H* depending on whether the Al_2O_3 content is 0 or 10 mole percent. This scheme is summarized in Table II and all 32 vertices of the five-dimensional composition space are shown in Figure 2. To illustrate this scheme, the compositional variables of Glass *ILOO* are given as follows: F/M, 42/56; Fe_xO_y , 2 mole %; Na_2O/CaO , 0.5; B_2O_3/F , 0; and Al_2O_3 , 0 %, while the hazardous metal oxides are always fixed at: BaO, 2 mole %; PbO, 1 mole %; and NiO, 2 mole %. The target oxide compositions for Glass *ILOO* are given in Table III. The glasses representing the compositions of all 32 vertices of this five-dimensional space were prepared in order to study their durability. Four of the compositions, *4LOH*, *4LHH*, *4HOH*, and *4HHH*, did not result in a homogeneous melt and their compositions had to be modified by lowering the iron content. The adjusted compositions for these glasses are indicated in Table III.

Glass Preparation

Glasses were prepared according to the target compositions in Table III. Reagent grade oxides or carbonates were mixed and then melted in high purity alumina crucibles for two hours at 1350°C in a Deltech, Inc. bottom-loaded glass melting furnace. Afterwards, each melt was quenched on a stainless steel plate. The resulting glass was milled to a -35 mesh

powder which yielded about 1 kg of glass. The resulting powders were then remelted in platinum crucibles at 1350°C for 2 hours and cast into small disks using graphite molds. The glass disks were immediately placed in an annealing furnace at 450° C and allowed to gradually cool to room temperature overnight.

Glass Analysis

The elemental composition of each glass disk was determined by wavelength dispersive XRF spectrometry. Each glass disk was first polished to a 600 grit finish. This analysis was performed on a Rigaku Model 3271 XRF spectrometer utilizing a "standardless" fundamental parameters software routine developed by Rigaku. The instrument description and conditions have been previously described.⁸ Selected glasses were also analyzed by wet chemical techniques⁹ to confirm the XRF results.¹⁰ The redox nature of the glass was estimated by the determination of the Fe²⁺/Fe³⁺ ratio.¹¹ In this procedure, a powdered glass sample was mixed with ammonium vanadate to preserve the redox stoichiometry and then dissolved in hydrofluoric and hydrochloric acids. The Fe²⁺ content was determined colorimetrically after complexation with FerroZine® iron reagent. Total iron content was then determined the same way following reduction of any Fe³⁺ with citric acid.

Chemical durability testing was carried out by the Product Consistency Test.¹² This static test measured the concentrations of all nine cations released from the crushed glass (75-150 µm) into the leachate after heating in deionized water at 90° C for seven days. The normalized elemental release rate (NRR_i), in g·m⁻²·d⁻¹, was determined from Equation 1,

$$(1) \quad NRR_i = \frac{C_i}{f_i \left(\frac{SA_g}{V_L} \right) t}$$

where C_i is the concentration of element i in the leachate, in g·m⁻³, V_L is the volume of the leachate, f_i is the weight fraction of element i in the glass, SA_g is the surface area of the glass, and t is leaching time. The SA_g/V_L ratio is assumed to be 1950 m⁻¹. This PCT test was carried out in triplicate for each glass and so the average pH and elemental release results are reported.

RESULTS and DISCUSSION

The chemical oxide content of the glass products, representing the vertices of the composition space, were determined by XRF spectrometry and are presented in Table IV. These results were compared to results from the analysis of several glasses by wet chemical dissolution followed by ICP and AA spectroscopy. This comparison showed no statistical difference in the results between the two analytical methods which confirmed the accuracy of the XRF method. This appears to be one of the first reported uses of XRF Spectrometry for an extensive quantitative chemical analysis of waste glasses. The

simplicity of this technique over the more tedious wet chemical methods greatly facilitated waste glass analysis and should be exploited more in the future.

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The measured compositions are in close agreement with the intended target values from the experimental design. One minor exception is the higher alumina content which is presumably due to corrosion of the alumina crucibles during the first melting step. Since the actual glass analyses so nearly matches the target values, the original target compositional variables will be used in the following discussions. The five compositional variables are summarized below.

- glass-former to glass-modifier ratio (F/M)
- iron oxide content (Fe_xO_y)
- $\text{Na}_2\text{O}/\text{CaO}$ ratio
- B_2O_3 to glass-former ratio ($\text{B}_2\text{O}_3 / \text{F}$)
- Al_2O_3 content

The results from the 7 day Product Consistency Test are presented in Table V as normalized elemental release rate, in $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. The variability in the individual release rates (NRR_i) is due either to selective leaching of one element over another or reprecipitation. However, in phase separated glasses or glasses with crystalline phases, leaching variability can also result from the difference in durability of the different phases present. As expected, the highest release rates are for sodium (NRR_{Na}) and it is these values which probably best reflect the relative durabilities of the various glasses. The NRR_{Na} is presented again in Table VI.

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There is no PCT benchmark by which low-level mixed waste glasses are judged for chemical durability. In the absence of a durability criteria, comparisons can be made with high-level waste glasses, for which the PCT test was developed. The durability of several high-level waste glasses, including SRL 131 and SRL 165, have been studied extensively and appear to be quite durable. The NRR_{Na} for these glasses is 0.04 and 0.02 $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, respectively.¹³ The Environmental Assessment (EA) glass, which has a sodium release rate of about 1 $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ represents the minimum acceptable durability for HLW glass at the Defense Waste Processing Facility at the Savannah River Site.¹⁴

Relationship between pH and Normalized Sodium Release Rate

The relationship between leachate pH and $\log \text{NRR}_{\text{Na}}$ is plotted in Figure 3. Above a pH of 11, this glass system exhibits a strong positive linear relationship between these two parameters. Below a pH of 11, no such correlation existed and the line in the figure is not fitted to these points. This correlation is not surprising. The leachate pH is expected to increase upon dissolution of silicate glasses because the dissolution mechanism involves the exchange of protons from the leachate for sodium ions in the glass. This results in an increase in pH and an increase in the sodium content of the leachate.

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Effect of Glass-Former to Glass-Modifier Ratio on Durability

There are four F/M ratios examined in this composition space. For the low iron glasses, the glass-former to glass-modifier ratios are 42/56 and 66/35. The F/M ratios for the high iron glasses are 35/47 and 56/26. So there are glasses with both a low and high F/M for each level of iron oxide. When the corresponding sodium releases for low iron glasses are compared, one finds that the NRR_{Na} increases by up to two orders of magnitude as F/M decreases. Therefore, with low iron glasses, durability is quite sensitive to the F/M ratio and decreases significantly as F/M decreases, regardless of the other compositional variables. Examination of NRR_{Na} reveal that all compositions with low iron and high F/M have comparable durability to the HLW glasses. The NRR_{Na} values are all below $0.30 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. However, five of the eight glasses with low iron and low F/M ratio have release rates in excess of $1.0 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. Therefore, in the vitrification of low iron oxide-containing glasses, attention must be paid to the F/M ratio in order to ensure a consistent and durable product.

For the high iron-containing glasses, the effect F/M has on durability depends upon additional compositional variables, especially the $\text{Na}_2\text{O}/\text{CaO}$ ratio. The F/M ratio significantly affects NRR_{Na} when the $\text{Na}_2\text{O}/\text{CaO}$ ratio is high but the durability does not appear to be affected when the ratio is low. This suggests that sodium release rates would not be as sensitive to composition fluctuations in the F/M ratio if the glasses had both a higher iron oxide content and lower $\text{Na}_2\text{O}/\text{CaO}$ ratios.

The sodium release rates for all glasses with the high F/M ratios are all less than 0.30 and most are below $0.10 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. The durability of these glasses is comparable to the that of the HLW glasses such as SRL 131 and SRL 165.¹³ The NRR_{Na} for glasses with low F/M ratio, on the other hand, are more variable and many are much less durable. For instance, the glasses with high $\text{Na}_2\text{O}/\text{CaO}$ ratios have release rates between 0.39 and $4.99 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$.

Effect of Iron Oxides (Fe_xO_y) on Glass Durability

The majority of glasses in this composition space had iron oxide contents of either 2 or 18 mole percent. The FeO and Fe_2O_3 content in these glasses are given in Table IV. The resulting FeO to Fe_xO_y ratio in these glasses ranged from 0.08 to 0.49 indicating that the

glasses were mostly oxidized. No attempt was made to examine the effect of iron redox state on glass durability.

The NRR_{Na} values for the glasses with high iron content were all below $0.10 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, except for the glasses that had both low F/M and high $\text{Na}_2\text{O}/\text{CaO}$ ratios. These four glasses had sodium release rates near or above $1.0 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. The low iron glasses displayed a similar trend; the majority of the release rates were below $0.29 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, again, however, the glasses with both a low F/M ratio and a high $\text{Na}_2\text{O}/\text{CaO}$ ratio all had NRR_{Na} values above 2.5. In addition, the low iron glasses, *ILOO* and *1 LHO*, had NRR_{Na} values of 1.16 and 0.65, respectively.

The effect of increasing the iron content on release rates is discussed. For the glasses with a high F/M ratio, i.e. Subspaces 2 and 4, the iron content has little effect on NRR_{Na} . The only measurable effect is with the high $\text{Na}_2\text{O}/\text{CaO}$ ratio glasses, but the effect is minimal. For the glasses with a low F/M ratio, i.e. Subspaces 1 and 3, the durability does show a significant dependency on iron content, the NRR_{Na} decreases as the iron content increases. So increasing the iron content from 2 to 18 mole percent does significantly reduce leaching if the F/M is 0.75; but there is little effect if the F/M ratio is up around 2.0.

Effect of $\text{Na}_2\text{O}/\text{CaO}$ Ratio

The Na_2O content in the 32 glasses of this study ranges from about 6 to 30 weight percent. The glasses with the Na_2O content between 6 and 12 weight percent, all have release rates below $0.1 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ while the glasses with higher soda content tend to have considerably higher release rates.

The glasses all have $\text{Na}_2\text{O}/\text{CaO}$ mole ratios of either 0.5 or 2.0. Glasses with the higher ratio tend to have lower release rates, as expected. The effect of the $\text{Na}_2\text{O}/\text{CaO}$ ratio on the NRR_{Na} is variable and depends upon the F/M ratio in the glass. When the F/M ratio is high, the $\text{Na}_2\text{O}/\text{CaO}$ ratio has little effect upon the release rate, i.e. all the glasses have relatively high NRR_{Na} . But when the glass-former content is low, the $\text{Na}_2\text{O}/\text{CaO}$ ratio has a strong influence on durability as discussed previously. Values for NRR_{Na} tend to increase one to two orders of magnitude as the $\text{Na}_2\text{O}/\text{CaO}$ ratio increases from 0.5 to 2.0.

Effect of B_2O_3

In half of the glasses in this study, B_2O_3 has been substituted for SiO_2 at levels between 6 and 10 weight percent; the other half contains no B_2O_3 . The addition of B_2O_3 appears to have no significant effect on durability. Since B_2O_3 has a tendency to lower glass viscosity, advantage can be taken of this to improve melt processing without sacrificing durability. At levels of B_2O_3 above 10 weight percent, glass durability is expected to decrease.

Effect of Al_2O_3

Aluminum oxide has been substituted for SiO_2 at levels between 11 and 18 weight percent. The glasses without added Al_2O_3 typically contain less than 2 percent, resulting from corrosion of the alumina crucible during the first melting procedure. The effect of added

Al_2O_3 on release rates is dependent upon the iron content in the glass. The durability is improved when Al_2O_3 is added to the low iron-containing glasses but shows no effect when added to the high iron-containing glasses.

CONCLUSIONS

A large glass composition space has been developed which is intended to bracket most glass products that might result from the vitrification of wastewater treatment sludges currently in storage at DOE sites throughout the United States. These surrogate glasses attempt to simulate the actual waste glasses with nine of the more representative oxides. The major oxides include SiO_2 , Al_2O_3 , B_2O_3 , Fe_2O_3 , Na_2O , and CaO . In addition, three minor oxides, BaO , NiO , and PbO , are included to represent hazardous metals. The levels of the six major oxides were varied in this mixture and, as a result, five independent variables were selected. These five composition variables included the glass-former to glass-modifier ratio (F/M), the iron oxide content (Fe_xO_y), the $\text{Na}_2\text{O}/\text{CaO}$ ratio, the $\text{B}_2\text{O}_3/\text{F}$ ratio, and the Al_2O_3 content. Glasses were made whose compositions corresponded to the 32 vertices of the resulting five-dimensional "hyperspace." The chemical durability of these glasses were determined by measuring the sodium release rates (NRR_{Na}) by the 7-Day Product Consistency Test.

A comparison of the normalized sodium release rates for these glasses showed that their chemical durability can be quite sensitive to changes in the F/M ratio, the Fe_xO_y content, and the $\text{Na}_2\text{O}/\text{CaO}$ ratio. This sensitivity necessitates the need for careful control of the glass composition because these waste streams can be quite inhomogeneous resulting in deviations from the target glass compositions. The F/M ratio had the greatest effect on durability for the glasses examined in this study. As F/M increased, the durability of all the glasses improved by one to two orders of magnitude. Raising the Fe_xO_y content from 2 to 18 mole percent (4 to 35 weight percent) increased the durability by about one order of magnitude. On the other hand, increasing the $\text{Na}_2\text{O}/\text{CaO}$ ratio from 0.5 to 2.0 decreased the durability about one order of magnitude. The B_2O_3 content had very little effect, while the effect of Al_2O_3 was mixed, with some glasses showing improvement in durability and others showing no change.

All of the glasses with the F/M ratios greater than one, had normalized sodium release rates below 0.3 and most were below $0.1 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. These release rates were comparable to the durable SRL 131 and SRL165 HLW glasses from the Savannah River Site. Glasses with the lower F/M ratios were much less durable, however, one durable composition region was detected for glasses with a low F/M ratio. It was found that relatively durable glasses could be produced with a low F/M ratio if they also had a low $\text{Na}_2\text{O}/\text{CaO}$ ratio and contained 10 mole percent Al_2O_3 (~14 weight percent).

This paper reports the first in a series of studies intending to fully characterize the durability of a large range of glassy products which might result from the vitrification of wastewater treatment sludges. Work is presently underway to prepare and test additional glass compositions within this space and to test these glasses after they have been heat treated to simulate slow cooling rates and greater devitrification. All of these glasses are

being further analyzed for phase composition in an effort to characterize the effect of cooling rates and devitrification on durability. Future work will also report on the TCLP results of these glasses. Finally, an attempt will be made to develop an empirical model to predict durability from glass composition and cooling rate.

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REFERENCES

1. U. S. ENVIRONMENTAL PROTECTION AGENCY, *Federal Register*, "Land Disposal Restrictions for Third Scheduled Wastes, Final Rule," 55 FR 22627.
2. J.B. PICKETT, J.C. MUSALL, and H.L. MARTIN, "Treatment and Disposal of a Mixed F006 Plating Line Sludge at the Savannah River Site," *Proc. 2nd Intern. Symp. Mixed Waste*, Aug. 17-20, 1993, Baltimore, MD, 1.3.1 (1993).
3. J. B. PICKETT, "GTS Duratek Awarded Contract to Treat M-Area Sludge," memo to J. L. Rice, November, 19, (1993).
4. W.D. BOSTICK, D.P. HOFFMAN, R.J. STEVENSON, A.A. RICHMOND, "Surrogate Formulations for Thermal Treatment of Low-Level Mixed Waste, Part IV: Wastewater Treatment Sludges," USDOE Report DOE/MWIP-18, Martin Marietta Energy Systems, Oakridge, TN, (1994).
5. D.B. BENNERT, T.J. OVERCAMP, T.N. SARGENT, JR., J.L. RESCE, and D.F. BICKFORD, "Pilot Scale Vitrification Laboratory for Treatability Studies on Hazardous and Mixed Wastes," *Ceramic Transactions, Environmental and Waste Management Issues in the Ceramic Industry*, p. 129, Ed. G. B. Mellinger, American Ceramics Society (1993).
6. D.B. BENNERT and D.F. BICKFORD, "Pilot Scale Demonstration of Vitrifications of Surrogate F006 Wastewater Treatment Sludges," *Proceeding of the International Topical Meeting on Nuclear and Hazardous Waste Management, Spectrum '94*, Atlanta, GA, August 14-18, 1994, p. 748 (1994).
7. K. J. HEWLETT, Thesis, "Vitrification Demonstration of West End Treatment Facility Mixed Waste Sludge," Clemson University, Clemson, SC, December (1994).
8. J.L. RESCE, R.G. RAGSDALE, T.J. OVERCAMP, A. JURGENSEN, D.F. BICKFORD, and C.A. CICERO, "XRF in Waste Glass Analysis and Vitrification Process Control, Part 1: Sample Preparation and Measurement Precision," Presented at the 96th Annual Meeting of the American Ceramics Society, April 24-28, 1994, Indianapolis, IN (1994).

9. Glass analysis performed by Corning Engineering Laboratory Services, Corning, NY.
10. **J.L. RESCE, R.G. RAGSDALE, T.J. OVERCAMP, D.F. BICKFORD, and A. JURGENSEN**, "Elemental Analysis of Waste Glass by X-Ray Fluorescence Spectrometry," Presented at this conference (February 1995).
11. **E.W. BAUMANN, C.J. COLEMAN, D.G. KARRAKER, and W.H. SCOTT**, "Colorimetric Determination of Fe(II)/Fe(III) Ratio in Glass, USDOE Report DPMS-87-18, Savannah River Laboratory, Aiken SC (1990).
12. **C.M. JANTZEN, N.E. BIBLER, D.C. BEAM, W.R. RAMSEY, and B.J. WATERS**, "Nuclear Waste Glass Product Consistency Test (PCT), Version 5.0," Report WSRC-TR-90-539, Rev. 2, Westinghouse Savannah River Co., Aiken, SC (1992).
13. **C.M. JANTZEN and D.F. BICKFORD**, "Leaching of Devitrified Glasses Containing Simulated SRP Nuclear Waste," Materials Research Society Symposium, Proceedings Volume 44 (1985).
14. **C. M. JANTZEN, et al.**, "Characterization of the Defense Waste Processing Facility Environmental Assessment (EA) Glass Standard Reference Material, WSRC-TR-92-346, Westinghouse Savannah River Co., Aiken, SC (1993).

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TABLE I. Estimated Major Oxide Content of Wastewater Treatment Sludges at Various DOE Sites

Site	SiO ₂ , wt. %	Al ₂ O ₃ , wt. %	Fe ₂ O ₃ , wt. %	Na ₂ O, wt. %	CaO, wt. %	MgO, wt. %
SRS	54	22	1	14	1	0
ORR	0	16	4	5	70	2
RFP	7	2	56	9	15	11
LANL	40	3	7	0	45	4

TABLE II. Description of Compositional Variables Used for the Glass Composition Space

Label	F/M, ^a mole ratio	Iron Oxides, mole %
1	42 / 56	2
2	63 / 35	2
3	35 / 47	18
4	56 / 26	18

Label	Na ₂ O/CaO, mole ratio	B ₂ O ₃ /F, mole ratio	Al ₂ O ₃ , mole %
LOO	1 / 2	0	0
LHO	1 / 2	1 / 7	0
LOH	1 / 2	0	10
LHH	1 / 2	1 / 7	10
HOO	2 / 1	0	0
HHO	2 / 1	1 / 7	0
HOH	2 / 1	0	10
HHH	2 / 1	1 / 7	10

^a Glass formers (F) include SiO₂, Al₂O₃, and B₂O₃; glass modifiers (M) include Na₂O, CaO, BaO, PbO, and NiO.

TABLE III. Target Oxide Composition of Glasses^a

Glass	Target Oxide Composition of Glasses, Mole % ^a					
	SiO ₂	Al ₂ O ₃	B ₂ O ₃	Fe ₂ O ₃	Na ₂ O	CaO
1LOO	42	0	0	2	17	34
1LHO	36	0	6	2	17	34
1LOH	32	10	0	2	17	34
1LHH	26	10	6	2	17	34
1HOO	42	0	0	2	34	17
1HHO	36	0	6	2	34	17
1HOH	32	10	0	2	34	17
1HHH	26	10	6	2	34	17
2LOO	63	0	0	2	10	20
2LHO	54	0	9	2	10	20
2LOH	53	10	0	2	10	20
2LHH	44	10	9	2	10	20
2HOO	63	0	0	2	20	10
2HHO	54	0	9	2	20	10
2HOH	53	10	0	2	20	10
2HHH	44	10	9	2	20	10
3LOO	35	0	0	18	14	28
3LHO	30	0	5	18	14	28
3LOH	25	10	0	18	14	28
3LHH	20	10	5	18	14	28
3HOO	35	0	0	18	28	14
3HHO	30	0	5	18	28	14
3HOH	25	10	0	18	28	14
3HHH	20	10	5	18	28	14
4LOO	56	0	0	18	7	14
4LHO	48	0	8	18	7	14
4LOH	48.8	10	0	11.6	8.2	16.4
4LHH	39.8	10	8.3	13.2	7.9	15.8
4HOO	56	0	0	18	14	7
4HHO	48	0	8	18	14	7
4HOH	49.5	10	0	10	17	8.5
4HHH	39.5	10	8.25	14	15.5	7.75

^a BaO, PbO, and NiO target values held fixed at 2, 1, and 2 mole %, respectively.

TABLE IV. Oxide Composition of Glasses Determined by XRF

Glass	Oxide Composition of Glass, Weight %									
	SiO ₂	Al ₂ O ₃	B ₂ O ₃	FeO ^a	Fe ₂ O ₃	Na ₂ O	CaO	BaO	PbO	NiO
1LOO	37.94	1.12	0	1.11	3.66	15.88	27.34	4.41	2.86	2.18
1LHO	32.24	1.60	8.24	1.00	3.75	15.79	26.96	4.45	3.10	2.18
1LOH	26.48	14.41	0	1.23	3.38	14.78	24.74	4.06	2.59	2.00
1LHH	22.03	14.83	8.53	1.38	3.24	15.10	25.31	4.15	2.70	2.04
1HOO	37.43	1.71	0	0.77	3.98	30.17	13.63	4.44	3.05	2.19
1HHO	31.78	1.21	7.01	0.77	4.06	30.78	13.77	4.57	3.17	2.20
1HOH	27.50	14.60	0	0.96	3.64	30.10	13.60	4.40	3.20	2.10
1HHH	21.37	13.90	10.44	^b	4.87 ^b	27.67	13.01	3.98	2.10	1.97
2LOO	46.83	0.46	0	1.93	3.02	9.49	16.61	4.41	3.28	2.27
2LHO	48.49	1.04	8.99	2.52	2.40	9.29	16.46	4.59	3.27	2.25
2LOH	44.73	14.73	0	1.73	2.95	8.91	15.46	4.30	3.04	2.10
2LHH	36.85	14.72	9.37	1.80	2.90	8.89	15.37	4.30	3.05	2.08
2HOO	56.92	0.37	0	2.45	2.56	18.77	8.41	4.58	3.30	2.30
2HHO	48.67	0.59	7.75	2.30	2.70	18.50	8.42	4.73	3.33	2.29
2HOH	44.46	14.62	0	1.94	2.78	17.78	7.86	4.35	3.09	2.13
2HHH	36.75	14.78	8.06	1.52	3.31	17.55	7.83	4.37	3.04	2.11
3LOO	57.06	1.57	0	2.63	29.92	10.72	17.97	3.60	2.41	1.66
3LHO	21.57	2.40	7.64	2.95	28.79	10.68	17.74	3.60	2.41	1.54
3LOH	24.36	17.12	0	3.64	22.94	8.97	14.94	3.01	2.06	1.13
3LHH	16.22	18.15	6.80	3.75	23.61	9.06	15.21	3.10	2.05	1.37
3HOO	25.71	1.14	0	2.22	28.58	20.53	8.68	3.35	2.31	1.52
3HHO	23.16	1.70	6.97	3.66	27.63	19.85	8.83	3.55	2.36	1.60
3HOH	17.50	11.90	0	2.54	30.86	20.20	9.10	3.60	2.60	1.70
3HHH	14.10	11.72	5.90	2.44	28.46	20.77	8.74	3.45	2.23	1.51
4LOO	40.16	0.54	0	5.89	25.79	5.34	9.28	3.61	2.56	1.37
4LHO	35.39	0.46	6.74	7.05	26.69	5.52	9.44	3.78	2.70	1.53
4LOH	38.41	13.88	0	4.16	14.73	6.98	11.85	4.01	2.61	1.26
4LHH	30.99	13.94	8.30	4.76	15.95	6.51	11.13	3.87	2.71	1.15
4HOO	40.77	0.29	0	4.51	25.58	10.91	4.85	3.84	2.62	1.70
4HHO	33.91	0.62	10.43	6.95	24.65	10.31	4.60	3.68	2.54	1.63
4HOH	38.71	12.32	0	2.95	14.39	14.66	6.25	3.99	2.51	1.65
4HHH	30.00	13.90	7.40	4.87	17.26	12.68	5.51	3.90	2.68	1.10

^a FeO determined by titration.^b Redox analysis not performed on this glass; reported as all Fe₂O₃.

TABLE V. Normalized Elemental Release Rates from Seven Day Product Consistency Test

Glasse	Normalized Elemental Release Rates, $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ^a							
	pH	Si	Al	B	Na	Ca	Ba	Pb
1LOO	12.9	0.03	0.04	n/a ^b	1.16	0.00	0.01	0.02
1LHO	12.6	0.01	0.02	0.30	0.65	0.00	0.02	0.01
1LOH	11.6	0.01	0.02	n/a	0.08	0.01	0.00	0.00
1LHH	11.7	0.01	0.02	0.02	0.10	0.02	0.01	0.00
1HOO	13.4	0.28	0.35	n/a	2.55	0.00	0.01	0.24
1HHO	13.6	0.73	0.13	4.40	4.99	0.00	0.00	0.11
1HOH	13.2	0.05	0.87	n/a	4.66	0.00	0.00	0.16
1HHH	13.2	0.07	0.69	0.88	3.31	0.00	0.00	0.01
2LOO	11.1	0.02	0.00	n/a	0.04	0.02	0.02	0.00
2LHO	10.5	0.02	0.00	0.03	0.04	0.02	0.02	0.00
2LOH	10.5	0.01	0.00	n/a	0.01	0.01	0.00	0.00
2LHH	10.2	0.01	0.00	0.01	0.01	0.01	0.00	0.00
2HOO	12.2	0.03	0.01	n/a	0.29	0.00	0.01	0.00
2HHO	11.5	0.04	0.01	0.07	0.17	0.01	0.01	0.00
2HOH	11.6	0.01	0.01	n/a	0.06	0.01	0.00	0.00
2HHH	11.1	0.01	0.01	0.01	0.04	0.01	0.00	0.00
3LOO	11.3	0.01	0.00	n/a	0.04	0.01	0.00	0.00
3LHO	11.2	0.01	0.00	0.01	0.03	0.01	0.01	0.00
3LOH	10.6	0.01	0.01	n/a	0.02	0.01	0.00	0.00
3LHH	11.2	0.01	0.02	0.01	0.04	0.01	0.00	0.00
3HOO	12.6	0.07	0.05	n/a	0.96	0.00	0.00	0.01
3HHO	10.2	0.05	0.06	0.05	0.99	0.00	0.00	0.00
3HOH	12.9	0.11	0.20	n/a	1.71	0.01	0.00	0.03
3HHH	12.8	0.05	0.30	0.47	1.53	0.00	0.00	0.04
4LOO	10.3	0.01	0.02	n/a	0.04	0.00	0.00	0.00
4LHO	10.0	0.01	0.00	0.01	0.03	0.01	0.00	0.00
4LOH	10.6	0.01	0.01	n/a	0.03	0.01	0.00	0.00
4LHH	10.1	0.01	0.01	0.01	0.02	0.01	0.00	0.00
4HOO	11.3	0.02	0.04	n/a	0.10	0.00	0.00	0.00
4HHO	11.1	0.03	0.02	0.02	0.09	0.00	0.00	0.00
4HOH	11.1	0.01	0.01	n/a	0.04	0.00	0.00	0.00
4HHH	10.6	0.01	0.01	0.01	0.03	0.00	0.00	0.00

^a NRR_i values for Fe and Ni are all less than or equal to $0.01 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$

^b Not applicable, samples do not contain B₂O₃

TABLE VI. Normalized Sodium Release Rates from Product Consistency Test

Glass ^a	Normalized Sodium Release Rate, $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$			
	Subspace 1	Subspace 2	Subspace 3	Subspace 4
<i>LOO</i>	1.16	0.04	0.04	0.04
<i>LHO</i>	0.65	0.04	0.03	0.03
<i>LOH</i>	0.08	0.01	0.02	0.03
<i>LHH</i>	0.10	0.01	0.04	0.02
<i>HOO</i>	2.55	0.29	0.96	0.10
<i>HHO</i>	4.99	0.17	0.99	0.09
<i>HOH</i>	4.66	0.06	1.71	0.04
<i>HHH</i>	3.31	0.04	1.53	0.03

a Refer to TABLE II for description of compositional variables.

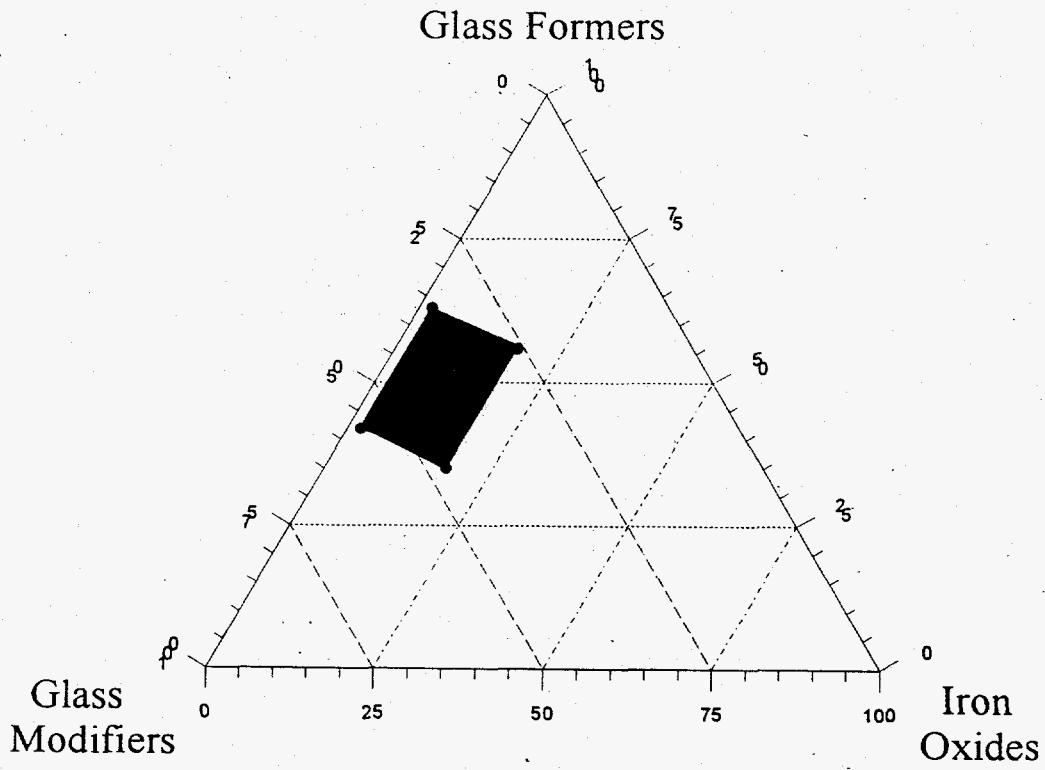


FIGURE 1. Glass-Forming Region in Ternary Phase Diagram (mole %)

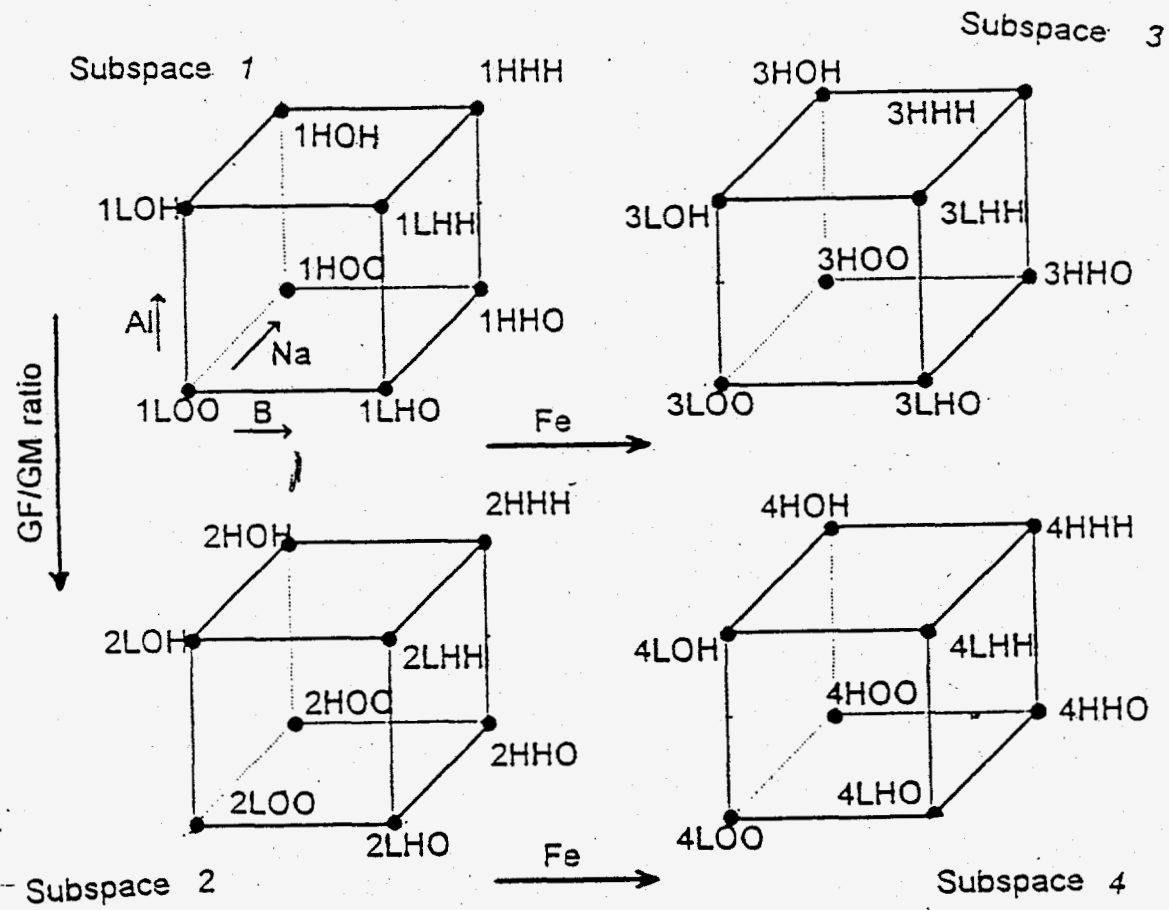


Figure 2. Representation of the 5-Dimensional Glass Composition "Hyperspace."

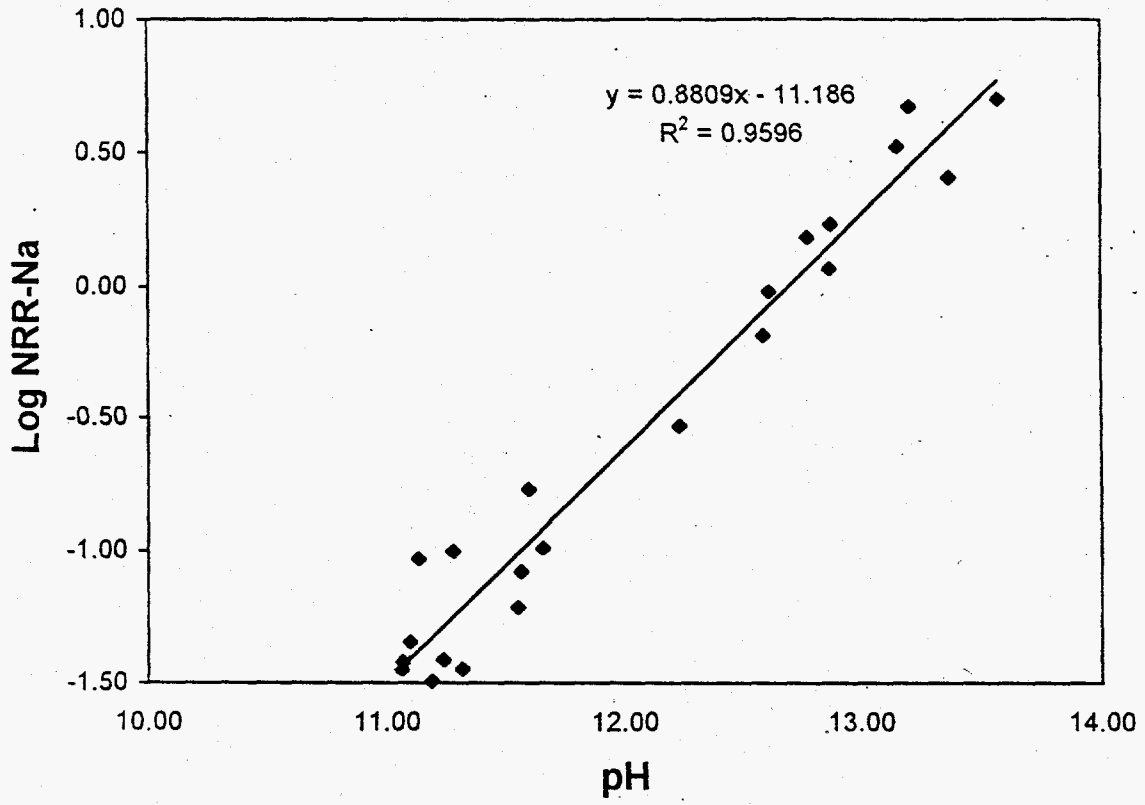


Figure 3. Plot of PCT Leachate pH versus Log NRR_{Na}.