The Effect of Compositional Parameters on the TCLP and PCT Durability of Environmental Glasses

by

C. A. Cicero
Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

J. L. Resce
Clemson University
SC USA

T. J. Overcamp
Clemson University
SC USA

D. F. Bickford
WSRC
SC USA

A document prepared for I&EC SPECIAL SYMPOSIUM at Atlanta from 09/17/95 - 09/20/95.

DOE Contract No. DE-AC09-89SR18035

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.
THE EFFECT OF COMPOSITIONAL PARAMETERS ON TCLP AND PCT DURABILITY OF ENVIRONMENTAL GLASSES

by

James L. Resce and Tom J. Overcamp
Environmental Systems Engineering Department
Clemson University
Clemson, SC 29634

Connie A. Cicero and Dennis F. Bickford
Westinghouse Savannah River Company
Savannah River Technology Center
Aiken, SC 29808

A Paper Proposed for Presentation and Publication at the I&EC Special Symposium sponsored by the American Chemical Society, September 17 - 20, 1995, in Atlanta, Georgia.

This paper was prepared in connection with work done under the U.S. Department of Energy - Office of Technology Development Technical Task Plan No. SR1-3-20-04. By acceptance of this paper, the publisher and/or recipient acknowledges the U.S. Government's right to retain a non-exclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.
INTRODUCTION

The relationship between glass composition and the chemical durability of environmental waste glass is very important for both the development of glass formulations and the prediction of glass durability for process control. The development of such a model is extremely difficult for several reasons. Firstly, chemical durability is dependent upon the type of leach test employed; the leach tests themselves being only crude approximations of actual environmental conditions or long term behavior. Secondly, devitrification or crystallinity can also play a major role in durability, but is much more difficult to quantify. Lastly, the development of any one model for all glass types is impractical because of the wide variety of wastestreams, the heterogeneity of the wastestreams, and the large variety of components within each wastestream. Several ongoing efforts have been directed toward this goal, but as yet, no model has been proven acceptable.

If a successful model is to be developed, it need not cover such a large composition space nor be highly accurate. For regulatory purposes, the model need only be accurate enough to predict if the glass product will pass or fail the waste acceptance criteria. The accuracy is most important in the composition regions which border on low durability. Once the uncertainty of the model’s predictive capability in these regions are known, conservative limits could be set to insure quality control. Furthermore, the composition range for the model could be limited to a particular class of wastestreams, e.g. silicate glasses from wastewater treatment sludges. Other assumptions could be made which would greatly simplify the modeling effort. Trace metals in the glass generally have very little effect on durability because of their low levels, as a result, the model could either ignore their presence or group them with some other major component. Many minor or even major species could be grouped together if they are known to have similar effects on durability. On the simplest level, components could be grouped into three types: (1) glass-formers, (2) conditional glass-formers, and (3) glass-modifiers. Glass modifiers could be further divided into alkali and alkaline earth metal oxides. Many conditional glass-formers behave as glass-formers in certain silicate systems and could then be grouped with the glass-formers. Alumina is an example of this.

A large glass composition space has previously been developed to serve as a simplified model for studying the durability of glassy wasteforms which might result from vitrification. In this study, a subset of this space has been examined for chemical durability by both the PCT and TCLP tests. This subspace is composed of five variable components $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}$, and $\text{CaO}$ and four fixed-level components $\text{Fe}_2\text{O}_3$, $\text{BaO}$, $\text{PbO}$, and $\text{NiO}$. The sum of the five variable oxides always total to 95 mole percent, while $\text{Fe}_2\text{O}_3$, $\text{BaO}$, and $\text{NiO}$ levels are fixed at 2 mole percent each and $\text{PbO}$ is always 1 mole percent. These components are classified into three groups depending upon their role in the glass structure. Glass-formers (gf), include $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, and $\text{B}_2\text{O}_3$. The second group, glass-modifiers (gm), include $\text{Na}_2\text{O}$ and $\text{CaO}$ plus the hazardous species $\text{BaO}$, $\text{PbO}$, and $\text{NiO}$. Lastly, $\text{Fe}_2\text{O}_3$ is grouped by itself.
The five variable oxides, SiO₂, Al₂O₃, B₂O₃, Na₂O, and CaO have been transformed into four independent compositional variables. These are listed below along with the composition ranges examined in this study.

- Glass-former to glass-modifier mole ratio (gf/gm) 0.75 to 1.8
- M⁺⁺/M²⁺ cation mole ratio (M⁺⁺/M²⁺) 0.5 and 2.0
- B₂O₃ to glass-former mole ratio (B₂O₃/gf) 0 and 0.14
- Al₂O₃ content 0 and 10 mole %

**EXPERIMENTAL**

**Glass Preparation.** Glasses were prepared using reagent grade oxides or carbonates and melted in high purity alumina crucibles for two hours at 1350°C. Afterwards, each melt was quenched on a stainless steel plate. The resulting glasses were milled to -35 mesh, then remelted in platinum crucibles at 1350°C for 2 hours, and cast into graphite molds to produce disks, 40 mm in diameter. The glass disks were immediately placed in an annealing furnace at 450°C and allowed to gradually cool to room temperature. Each glass disk was polished to a 600 grit finish for later analysis by x-ray fluorescence spectrometry (XRF).

**Glass Analysis.** The elemental composition of each glass disk was determined by wavelength dispersive XRF spectrometry. This analysis was performed on a Rigaku Model 3271 sequential wavelength XRF spectrometer utilizing a "standardless" fundamental parameters software routine developed by Rigaku. The instrument description and conditions have been previously described. The XRF results closely agreed with the target oxide compositions except for Al₂O₃ which was found to be about 0.5 percent higher than the targeted composition due to leaching from the alumina crucibles.

Chemical durability testing was carried out by both the 7-Day Product Consistency Test and the TCLP test. The sodium normalized elemental release rate (NaNRR), in g·m⁻²·d⁻¹, was determined from Equation 1,

\[
\text{NaNRR} = \frac{C_{\text{Na}}}{f_{\text{Na}} \left( \frac{S_{\text{g}}}{V_L} \right) t}
\]

where \(C_{\text{Na}}\) is the concentration of elemental sodium in the leachate, in g·m⁻³; \(V_L\) is the volume of the leachate; \(f_{\text{Na}}\) is the weight fraction of sodium in the original glass; \(S_{\text{g}}\) is the surface area of the glass; and \(t\) is leaching time. The \(S_{\text{g}}/V_L\) ratio is assumed to be 1950 m⁻¹. The PCT test was carried out in triplicate. The TCLP results have not yet been received.

**RESULTS and DISCUSSION**

The results from the PCT tests are presented in Figure 1. There are four charts, each one showing the PCT durability as a function of both the M⁺⁺/M²⁺ and gf/gm ratios. The charts differ in that each one represents a different B₂O₃/gf ratio and Al₂O₃ contents. The results are summarized as follows:

- Glass-former to glass-modifier mole ratio (gf/gm) large positive effect
- M⁺⁺/M²⁺ cation mole ratio (M⁺⁺/M²⁺) large negative effect
- B₂O₃ to glass-former mole ratio (B₂O₃/gf) negligible effect
- Al₂O₃ mole percent minor positive effect
Figure 1. The Effect of Glass Compositional Parameters on the PCT Na-NRR Durability for a Subset of 32 Hyperspace Glasses.
ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Technology Development (Mixed Waste Integrated Program), under Contract No. DE-AC09-88R18035 and WSRC Subcontract No. AA00900T.

REFERENCES


DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.