DP-MS-84-67

INTERNATIONAL WASTE GLASS STUDY — COMPOSITION AND LEACHABILITY CORRELATIONS

by

George G. Wicks, W. Duncan Rankin*, and
Sherry L. Gore**

E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina 29808

* Co-op student from Clemson University
** Co-op student from Mississippi State University

A paper proposed for presentation at the
1984 Meeting of the Materials Research Society
Boston, MA
November 26-30, 1984

and for publication in the proceedings

This paper was prepared in connection with work done under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

DISCLAIMER

INTERNATIONAL WASTE GLASS STUDY — COMPOSITION AND LEACHABILITY CORRELATIONS

by

George G. Wicks, W. Duncan Rankin*, and
Sherry L. Gore**

E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina 29808

* Co-op Student from Clemson University
** Co-op Student from Mississippi State University

ABSTRACT

The International Waste Glass Study found important similarities, based on correlations of composition and leaching performance, among many different defense and commercial waste glass compositions being studied world-wide. In addition, the beneficial effect of waste on glass performance was confirmed for the systems evaluated.

INTRODUCTION

As part of an effort to assess and understand the performance and chemical durability of Savannah River Plant (SRP) waste glass, an International Glass Study was undertaken. Important objectives of this program were to determine if correlations could be made between SRP defense waste glass compositions and leaching behavior and the compositions and leaching performance of other waste glass systems derived from other countries. In Part I of this study, frit and waste glass formulations from nine different countries were defined from available literature. This includes a commercial waste glass, several defense waste glasses from the United States, and additional compositions from France, West Germany, Japan, the United Kingdom, Sweden, Italy, and India. The compositions selected often represented well-studied borosilicate glasses, but do not necessarily reflect the best or most recent formulations that are now available. In addition, glasses chosen represented relatively wide ranges in important glass components and, when specific waste compositions were not available, a generic waste and loading were selected. Therefore, while potential correlations in the many different waste glass systems were investigated, direct quantitative comparisons among glasses representative of the countries involved were not attempted. Seven different ternary diagrams were constructed and evaluated for representing eleven waste glases. The plotting procedures used in these ternarys were based on elemental leaching behavior, oxide bonding energies, and elemental roles in the glass structure. Since composition often dictates important glass properties, leaching behavior might be expected to be relatively similar if correlations in composition exist.

In Part II of the program, glass frits and waste glasses were leached using MCC-1 leaching tests. Relative comparisons were then made between frit and waste glass systems derived from each of four countries; the United States, France, Germany, and Japan. This was performed in order to see if the effects of waste on glass performance are similar to the beneficial effects previously determined for SRP glass.[1] Another objective was to determine whether similar mechanistic considerations might exist for the different glass systems. The leachability results of the waste glasses were then grouped into convenient categories and leaching contours were superimposed on the compositional ternaries to evaluate potential correlations between the many different waste glass compositions and leachability. If such correlations can be shown to exist, this would emphasize the similarities between the large variety of glasses studied and further link U.S. and international waste glass research efforts.

EXPERIMENTAL PROCEDURES

Frit and Waste Glass Compositions

Five frit and fifteen waste glass compositions were obtained from the literature and are summarized in Table 1. The frit and waste compositions were sometimes significantly different. There were also differences in waste loadings. For glass systems from two countries, exact waste compositions were unspecified, so PNL's standard waste formulation PW-8A was used. Therefore, waste glass systems selected represented relatively wide ranges in composition, and although based on waste glass efforts from each country, were not intended to represent the best formulations that can currently be achieved.

Leaching Tests and Glass Characterization

Glass systems derived from each country were leached using standard MCC-1 static leaching procedures.[2] Samples were fabricated by diamond core-drilling cast glasses and cutting the glasses into slices with 400 mm^2 surface area. Surfaces were finished to 600 grit. The samples were cleaned in an ultrasonic bath, dried, and weights recorded. Glass slices were then placed in Teflon® vessels containing 50 mL of leachant with a ratio of surface area to volume of leachant (Sa/V) of 0.1 cm^{-1}. The glasses were leached in duplicate using deionized water at 90°C for 28 days. Initial and final pH values were recorded and weight loss was measured. Solid samples and leachate solutions were analyzed using inductively coupled plasma spectroscopy (ICP) to determine the concentrations of Si, Na, B, Sr, Mn, Mg, Al, and Fe. Leached glass surface layers are also being investigated by optical microscopy, electron microprobe analysis, and Fourier Transform Infrared Reflection Spectroscopy.

Compositional Representations

All twenty glass and waste glass systems are represented on a single compositional ternary diagram in Figure 1, based on leaching behavior of individual elements in the 'as-mixed' compositions. In addition to this representation, seven additional approaches were selected for representing the eleven waste glass systems that were subsequently leached. These approaches involve plotting of weight percent frit and waste oxides instead of elemental concentrations and are shown in Figures 2 and 3. These diagrams were constructed based on both simplified and analytically determined glass compositions. The bases for constructing all seven of these diagrams are summarized in Table 2 and are described below:

Leaching Behavior Approach

A plotting approach for representing compositions of leached waste glass systems is shown in Figure 2a, based on the leaching behavior of major elements in the glasses. Silicon, one of the best measures of overall glass durability, was placed at the top apex of the ternary diagram, while elements typically exhibiting higher leach rates, such as boron and sodium, were placed on the right point. Elements exhibiting lower leach rates, such as aluminum, iron, and magnesium, were placed on the left axis of the diagram.

Elemental Leaching/Gel Layer Approach

In the next types of ternary diagrams, Figures 2b and 2c, waste glass compositions were plotted according to the primary role elements play during the leaching process. The major network formers, silicon and boron, were placed on the top of the ternary, while those elements most likely to be leached by ion exchange with hydronium ions were placed on the right apex. Elements which are typically retained in the surface layers of many waste glass systems during leaching were placed on the left apex. The exact roles of aluminum and boron during the leaching process are still not precisely defined, so two possible ternary diagrams resulted from this approach.

Oxide Bonding Energy Approach

A third type of ternary diagram was constructed based on oxide bond energies of the glass elements (Figures 2d and 2e). Work by Sun summarized by Kingery et al.[3] has shown that elements tend to fall into three categories based on oxide bonding energy: network formers, network modifiers, and intermediates. Atoms in a particular category tend to play similar roles in the glass structure. Silicon and boron are network formers, aluminum and zirconium are intermediates, and alkali and alkaline earth elements are typically network modifiers. Iron can fall into both the intermediate and network modifier categories, so two possible ternary diagrams of the oxide bond energy type were constructed based on the structural role of iron.

Structural and Leaching Characteristics Approach

The final class of ternary diagrams used for compositional comparisons are shown in Figures 2f and 3, and were based on a combination of structural and leaching characteristics of the glass forming elements. Sun's work on oxide bonding energy and glass structure produced three categories for classifying elements in a wide variety of glass types. However, this three category classification could be modified to two categories when discussing a particular class of elements. Intermediate atoms can tend to take on either a network forming or a network modifying role in the glassy structure, depending upon what other elements are present and, thus may not always have a unique third structural role of their own. Therefore, one could group silicon, boron, and the important intermediate atom aluminum as relative network formers in the waste glass systems under consideration, while the remaining major elements are typically network modifiers. Due to the solubility of some of the glass components, surface layers rich in particular species form and these elements were grouped to make up the third point of the ternary diagram. Two diagrams resulted due to the dual roles of the minor glass constituents.

RESULTS AND DISCUSSION

Frit and Waste Glass Compositions

In Part I of this study, the use of seven different plotting methods to represent a wide range of glass systems were investigated. The most obvious observation was that for almost any plotting technique used, waste glass compositions were generally very closely clustered in the ternary representations. This is perhaps best illustrated in Figure 1 in which five frit compositions and fifteen waste glass formulations derived from nine different countries are shown in terms of elemental percentages and plotted in terms of leaching behavior. This finding is consistent with a similar representation obtained by Hench et al. for a variety of additional compositions.[4] This close clustering of compositions emphasizes the inter-relationships that exist in the many different waste glass systems studied. Because of the tightness of this type of diagram and due to the properties of interest, ternary plots were also constructed based on weight percent oxides for the waste glass formulations.

The leach rates were then grouped arbitrarily into three main categories of increasing leachability. Leachability countours were then constructed and superimposed on the analytically determined waste glass compositions. From the seven different ternary representations, the best fit occurred using an oxide bonding energy approach. In this plot, the optimum composition for maximum glass durability would be expected to be focused in the center of the contour rings.

Frit Versus Waste Glass Leaching Performance

In Part II of the program, a variety of frit and waste glasses were leached using MCC-1 static leaching procedures. The mechanisms of glass dissolution for pure frits can differ from waste glasses as seen from previous studies. For four of the countries considered, both frit and corresponding waste glass were emphasized. These countries included the United States, France, Germany, and Japan. Normalized elemental mass losses for each of these pure frits were generally within a factor of two or three of each other. Since the absolute leaching numbers are not necessarily representative of the best or most realistic compositions that currently exist, direct comparisons of waste glass performance between each of the countries involved was not performed. The important point is that waste glass compositions were significantly more durable than the corresponding pure frit for each system and country involved. This is illustrated in Table 3. Therefore, consistent with earlier studies on leaching of SRP waste glasses,[1,4] the addition of the waste to the system improves the durability of the product. This result has now been confirmed for systems from three additional countries.

Composition and Leachability Correlations

The leachability results for the waste glass systems were then investigated for each of the seven compositional ternary representations. Leach rates based on boron extraction were emphasized due to the extreme solubility of this species and the unlikely possibility of precipitation of a boron compound or phase. The leaching data were grouped into three categories ranging from low leaching systems (0.43 - 0.54 g/m^2*d) to intermediate leaching (0.77 - 1.19 g/m^2*d) to higher leaching systems (1.32 - 11.95 g/m^2*d). Three leachability contours were then constructed and superimposed on the various compositional diagrams to determine the best correlation of composition with observed leachability. Table 4 summarizes the results of the MCC-1 leaching tests and the leachability groupings. In general, the leachability of the most realistic waste glass systems studied were within about a factor of two of each other. The highest leach rates observed occurred for the systems in which the generic waste was used so that the frits were not specifically tailored for the waste composition used. While these leaching results may not necessarily represent the durability of the best waste glasses that may currently be available from the countries considered, they do provide a relatively wide range of composition and leachability results. This therefore provides a good test of composition and leachability correlations. The best fit between leachability and composition occurred for plots based on bonding energy considerations as shown in Figure 3.

CONCLUSIONS

A variety of frit and waste glass compositions derived from nine countries were investigated. When described by any of a variety of methods, the compositions of the simulated defense and commercial waste glass systems were very similar. All could be represented conveniently by single ternary diagrams. From leaching tests of pure frits and corresponding waste glasses from four of the countries, the beneficial effects of adding waste to the frit were clearly seen and consistent with other studies. Finally, a general correlation between the compositions of the eleven waste glass systems derived from the nine countries and MCC-1 leachability results was observed and best represented by bonding energy considerations.

In summary, this study emphasizes the similarities among the compositions and performance of the many different defense and commercial waste glass systems that have been studied worldwide.

ACKNOWLEDGEMENT

The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

REFERENCES

1. Rankin, W. D. and Wicks, G. G. "The Chemical Durability of Savannah River Plant Waste Glass as a Function of Waste Loading." Journal of the American Ceramic Society, 66(6), pp. 417-420, June 1983.

2. Nuclear Waste Materials Handbook, MCC-1P Static Leach Test Method, Materials Characterization Center — Pacific Northwest Laboratories, DOE/TIC-11400, January 1982.

3. Kingery, W. D., Bowen, H. K., and Uhlmann, D. R. Introduction to Ceramics, Second Edition, Wiley and Sons, New York, p. 99 (1976).

4. Hench, A. A. and Hench, L. L. "Computer Analysis of Compositional Effects in Nuclear Waste Glass Leaching." Nuclear and Chemical Waste Management (in press).

5. Clark, D. E., Maurer, C. A., Jurgensen, A. R., and Urwongse, L. "Effects of Waste Composition and Loading on the Chemical Durability of a Borosilicate Glass." In: Scientific Basis for Nuclear Waste Management V (W. Lutze, ed.) 11, pp. 1-13 (1982).

TABLE 1

International Glass Study* (As-Mixed Compositions — wt % Oxides of Major Components Only)

Country	Composition	SiO_2	B_2O_3	Na_2O	Cs_2O	SrO	Al_2O_3	Fe_2O_3	MnO_2	MgO	CaO	ZrO_2
USA	Frit 131	57.9	14.7	17.7	-	-	-	-	-	2.0	-	-
	Frit 165	68.0	10.0	13.0	-	-	-	-	-	1.0	-	1.0
	131/HiAl	41.4	10.2	13.8	1.	0.	14.1	3.4	3.2	1.	-	-
	131/HiFe	40.4	10.0	14.0	1.	0.	0.4	17.6	1.2	1.	-	-
	76-68	39.8	9.5	12.5	1.0	0.4	-	9.8	-	-	3.0	1.8
France	F-son	43.6	19.0	9.4	1.79	0.66	0.1	0.6	-	-	-	3.12
	M7 Frit	52.1	16.0	14.1	-	-	5.6	3.3	-	-	4.6	-
	M7 Glass	46.1	14.2	14.3	0.4	0.1	5.0	6.5	-	-	4.1	0.6
Germany	Pamela-based	42.2	6.92	9.43	-	0.2	10.4	1.7	0.3	0.1	-	-
	98/12 Frit	56.7	12.4	17.5	-	-	2.6	-	-	2.1	4.1	-
	98/12 Glass	48.2	10.5	14.9	0.7	0.3	2.2	0.2	0.2	1.8	3.5	1.4
Japan	Tokai Works Frit	61.0	19.8	1.4	-	-	5.0	-	-	-	2.8	-
	Tokai Works Glass	43.2	14.1	8.4	1.0	0.4	3.5	7.4	0.3	-	2.0	2.0
UK	UK 209	50.9	11.1	8.3	0.8	0.3	5.1	2.7	-	6.3	-	1.4
Sweden	ABS 41	52.0	15.9	9.4	0.9	0.3	2.5	3.6	0.8	-	-	1.3
Italy	LRR-ECM	50.9	11.2	12.7	0.2	0.1	2.1	12.5	0.2	-	-	0.6
India	FA_2 Glass**	47.3	12.4	20.0	0.4	0.1	-	3.6	7.4	-	-	0.6
Canada	204 Glass**	52.6	7.6	11.7	1.0	0.4	-	9.6	-	-	-	1.7

* Compositions based on simplified and sometimes doped waste glass formulations.

** Exact waste composition not available so PNL's PW-8A waste formulation was used.

TABLE 2

Bases for Ternary Representations

Representation Approach	Figure Number	Elemental Roles		
		Si	B, Na	Al, Fe, WP
• Leach behavior (wt % as-mixed elements)	1	Good measure of long term durability	High leachability elements	Low leachability elements
		Si	B, Na	Al, Fe, WP
• Leach behavior (wt % oxides)	2a	Good measure of long term durability	High leachability elements	Low leachability elements
		Si, B	Na, Cs, bal	Fe, Mn, Mg, Al
• Elemental leaching rate/ gel layer (wt % oxides)	2b	Matrix dissolution elements	Ion exchange elements	Surface layer elements
		Si, Al	Na, B, bal	Fe, Mn, Mg
	2c	Matrix dissolution elements	High leachability	Major surface layer elements
		Si, B	Na,Mg,Fe,bal	Al, Zr
• Oxide bonding energy (wt % oxides)	2f	Major network formers	Modifiers & balance	Intermediates
		Si, B	Na, Mg, bal	Fe, Zr, Al
	3	Major network formers	Modifiers % balance	Intermediates
		Si, B, Al	Na, Cs	Fe,Mn,Mg,bal
• Structural and leaching characteristics (wt % oxides)	2d 5A	Network formers	Modifiers	Surface layer elements and low leachability elements
		Si, B, Al	Na, Cs, bal	Fe, Mn, Mg
	2c	Network formers	Modifiers & balance	Surface layer elements

TABLE 3

Normalized Elemental Mass Losses (NLi) for Frit Versus Waste Glass Systems from Four Different Countries

		Waste		NL(i) (g/m^2)									
Country	Frit	Glass	m	Si	B	Na	Cs	Sr	Al	Fe	Mn	Mg
1	X		59	63	38	62	0	0	0	0	0	48
		X	10	28	22	23	36	1	5	0	0	0
2	X		26	26	46	47	0	0	6	0	0	0
		X	10	11	13	14	0	6	7	0	0	0
3	X		55	54	140	196	0	0	1	0	0	2
		X	19	25	33	38	0	6	4	0	6	0
4	X		34	28	76	66	0	0	7	0	0	0
		X	8	13	13	16	0	5	9	0	0	0

TABLE 4

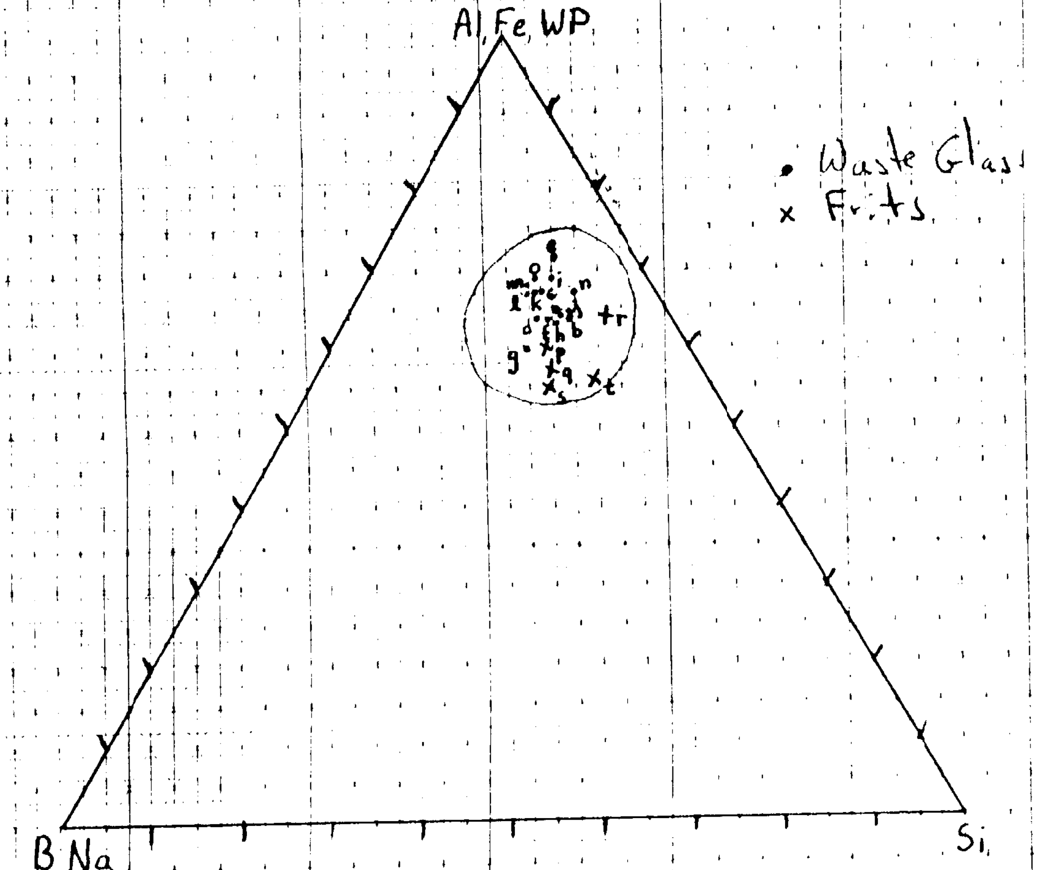
Leachabilities and Plotting Contours for Eleven Waste Glass Systems

Waste Glass I.D.	Leaching Coutour Grouping	Leach Rates (g/m^2*d) B	Mass	Si	Na	Cs	Sr	Al	Fe	Mn	Mg	Final pH
a	I	0.43	0.26	0.35	0.24	0.52	0.57	0.42	0	0	1.2	9.05
b		0.48	0.37	0.37	0.50	0	0.20	0.26	0	-	-	9.26
c		0.48	0.27	0.35	0.58	0	0.17	0.33	0.02	0.01	-	9.06
d		0.54	0.46	0.70	1.19	0.57	0.04	0.41	0.03	1.68	0.04	9.72
e	II	0.77	0.35	0.56	0.82	1.28	0.04	0.18	0.01	0	0	9.60
f		0.83	0.40	0.49	0.97	1.13	0.88	0.74	0.02	0	-	9.00
g		1.12	0.99	1.07	1.22	0	0.22	1.20	0.27	0.07	-	9.90
h		1.19	0.67	0.90	1.36	0	0.23	0.14	0	0.21	0	9.45
i	III	1.32	0.46	0.78	1.27	1.00	0.05	0	0	0	0	9.46
j		3.08	3.33	1.83	2.97	0	0.02	0	0	0	0	9.60
k		11.95	4.89	5.57	12.97	0	0.05	0	0.01	0.02	0	10.03

FIG. 1

COMPOSITIONAL TERNARY FOR WASTE GLASS AND FRIT SYSTEMS

[Based on 'Leaching Behavior' of As-Mixed Compositions]



WASTE GLASS SYSTEMS

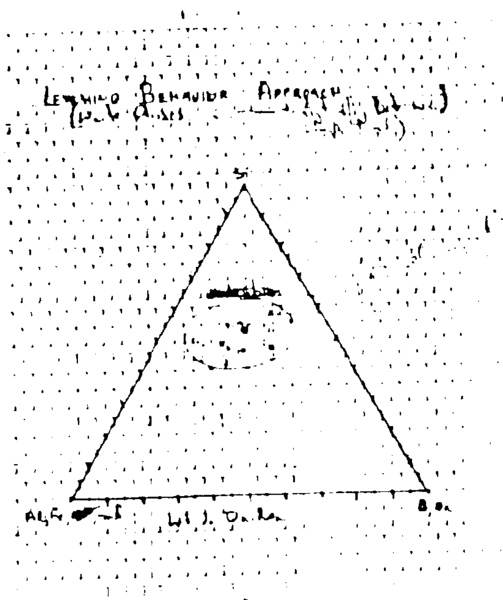
a - British; UK 209
b - Candian; 204 + Waste
c - French; F-SON
d - French; M7
e - German; Pamela
f - German; 98/12
g - Indian; FA2 + Waste
h - Italian; LRR-ECM
i - Japanese; Tokai Works
j - Swedish; ABS 41
k - USA; 131/TDS SRP
l - USA; 131/Hi Al SRP
m - USA; 131/Hi Fe SRP
n - USA; 165/TDS SRP
o - USA; 76-68 PNL

FRITS

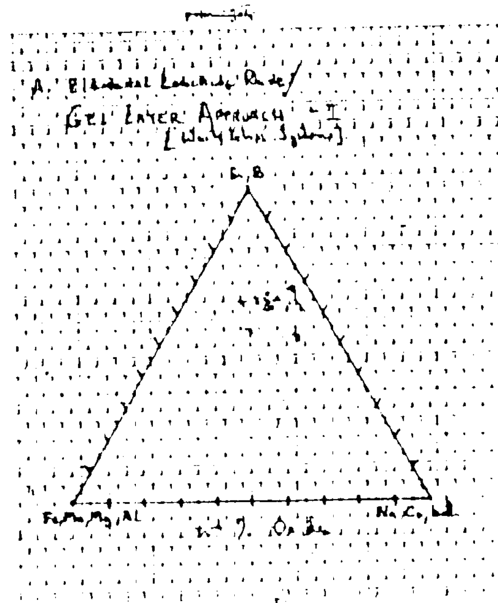
p - French; M7
q - German; 98/12
r - Japanese; Tokai Works
s - USA; SRP 131
t - USA; SRP 165

FIG 2

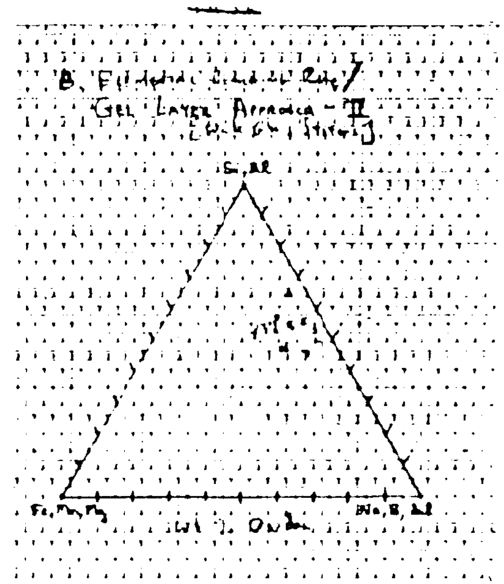
TERNARY REPRESENTATIONS



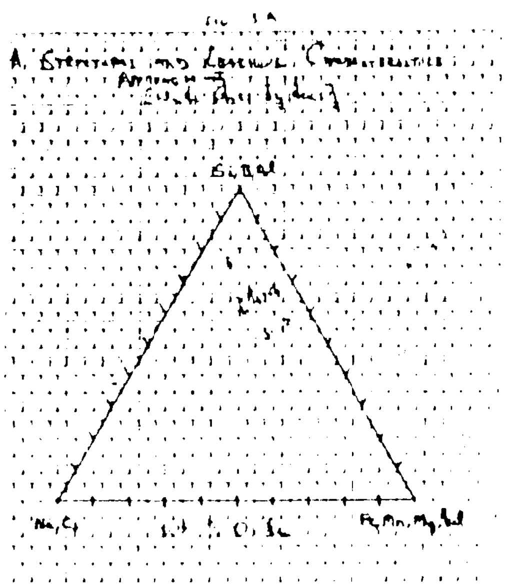
2A Leaching Behavior



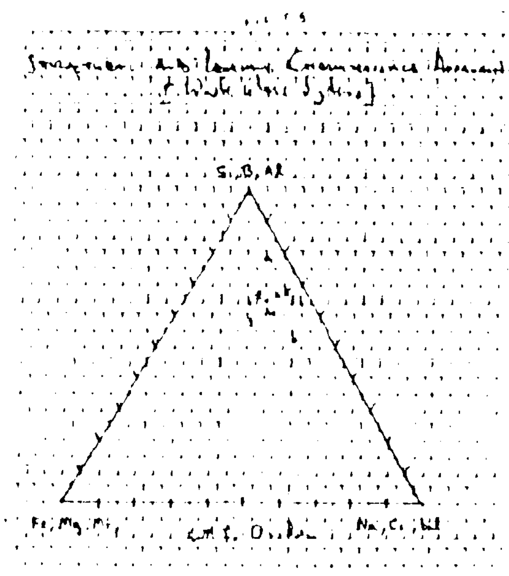
2B Elemental Leaching/ Gel Layer - I



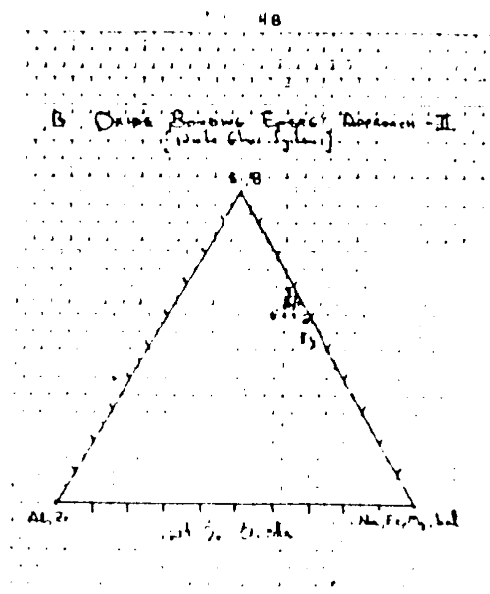
2C Elemental Leaching/Gel Layer II



2D Structural & Leaching Characteristics - I

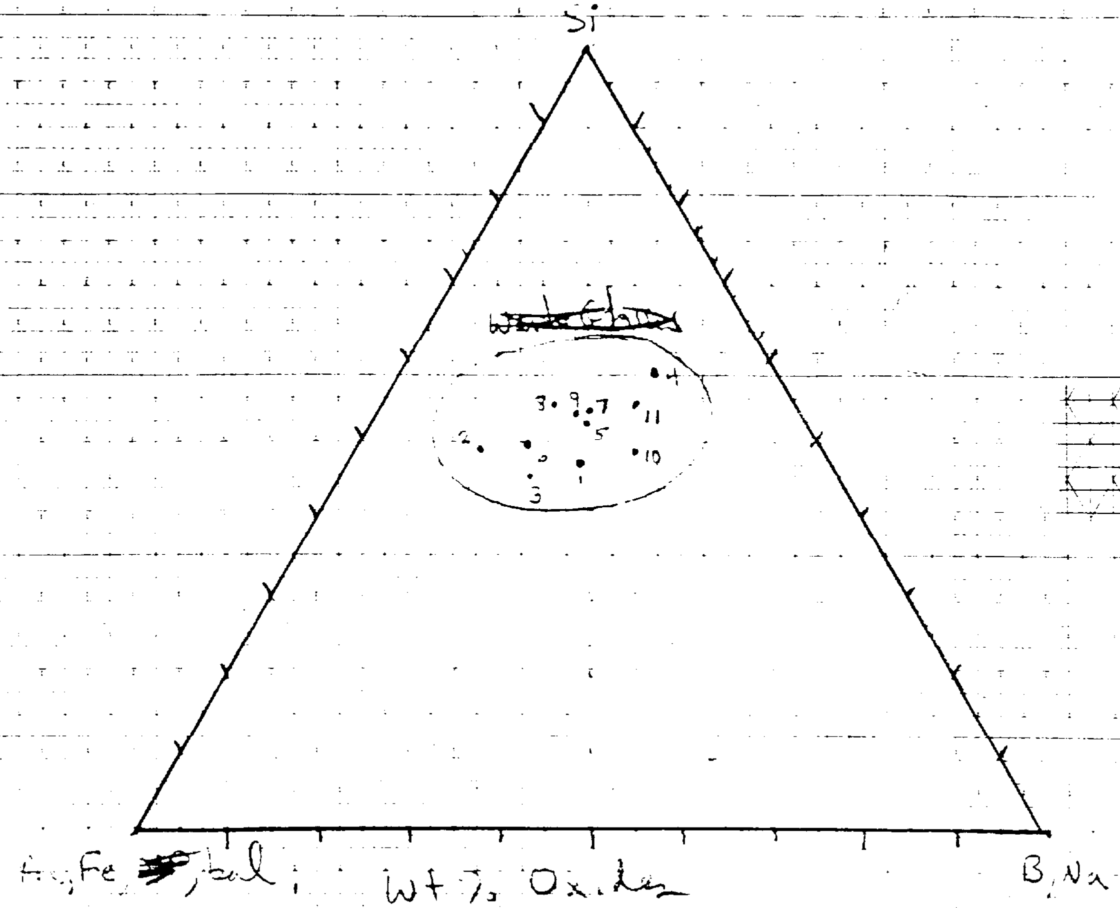


2E Structural & Leaching Characteristics - II

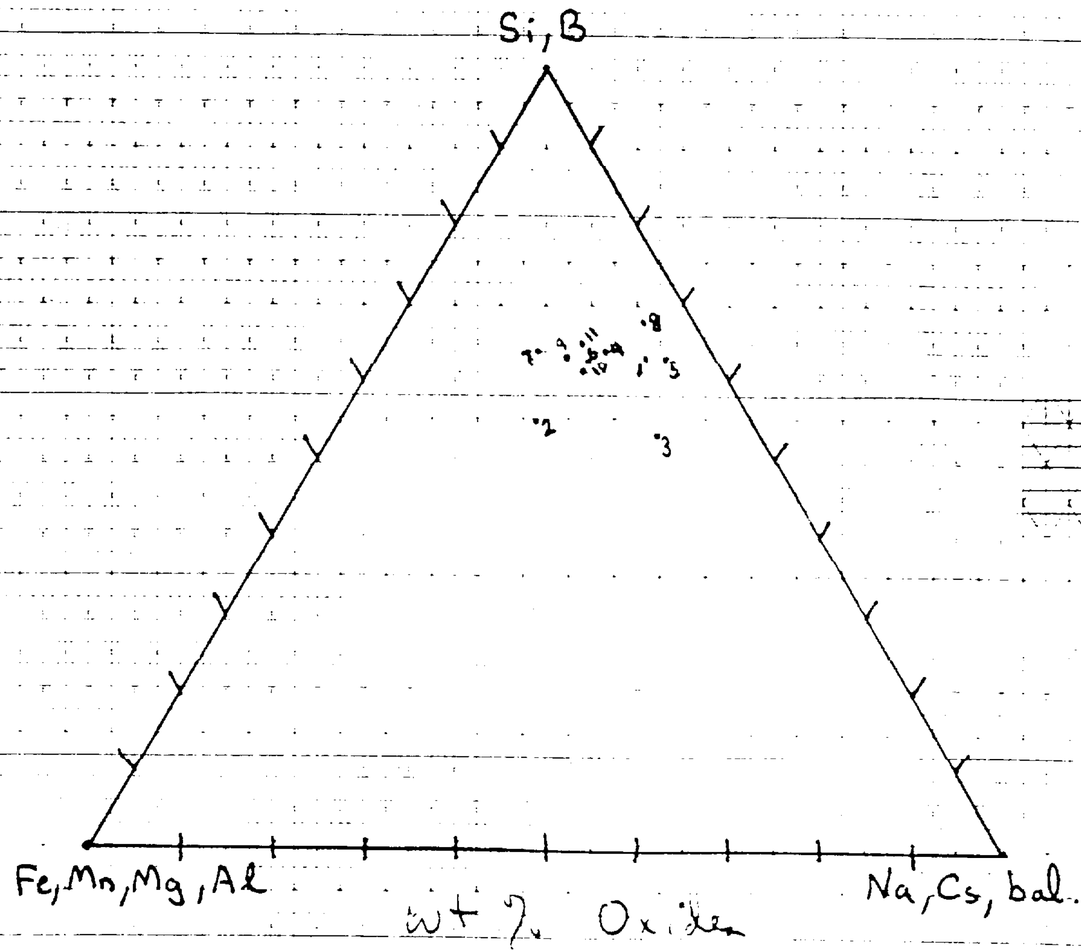


2F Oxide Bonding Energy - I

LEACHING BEHAVIOR APPROACH
(Waste Glasses — Analytically Determined Compositions)

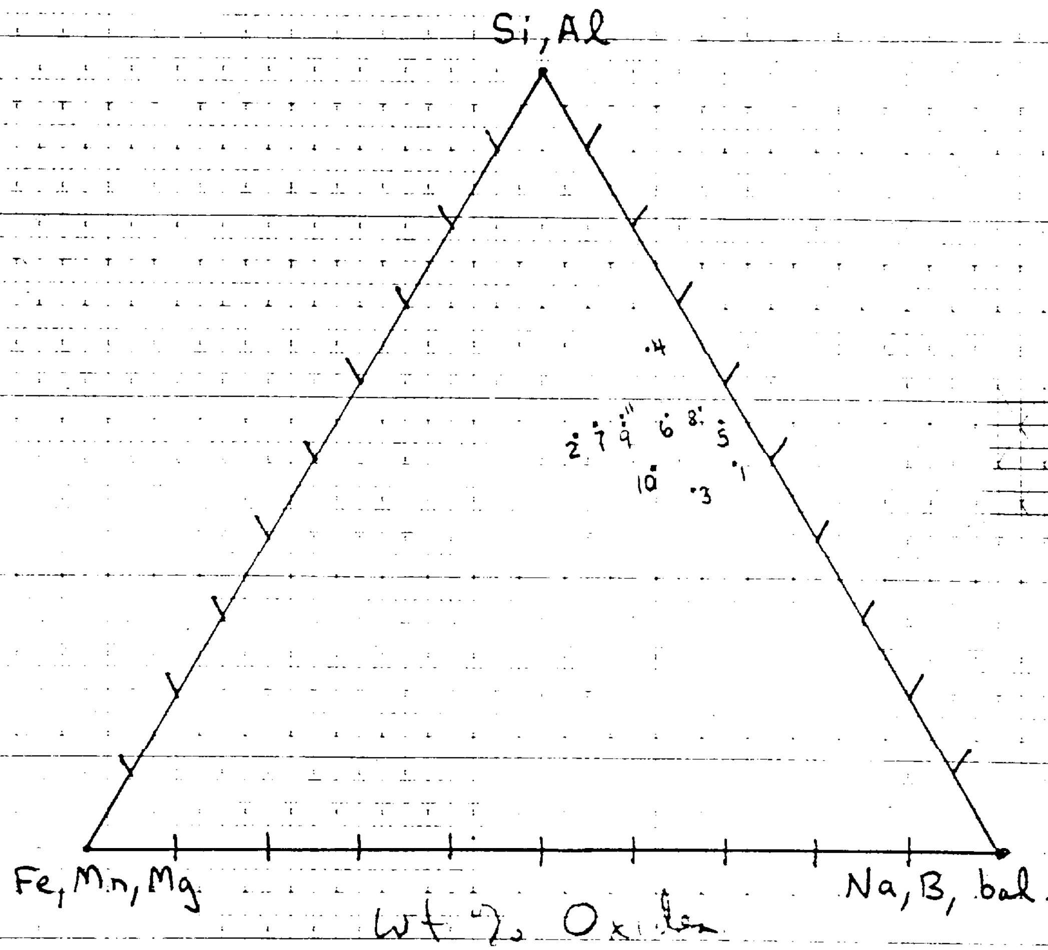


A, Elemental Leaching Rate / Gel Layer Approach – I [Waste Glass Systems]



F 22

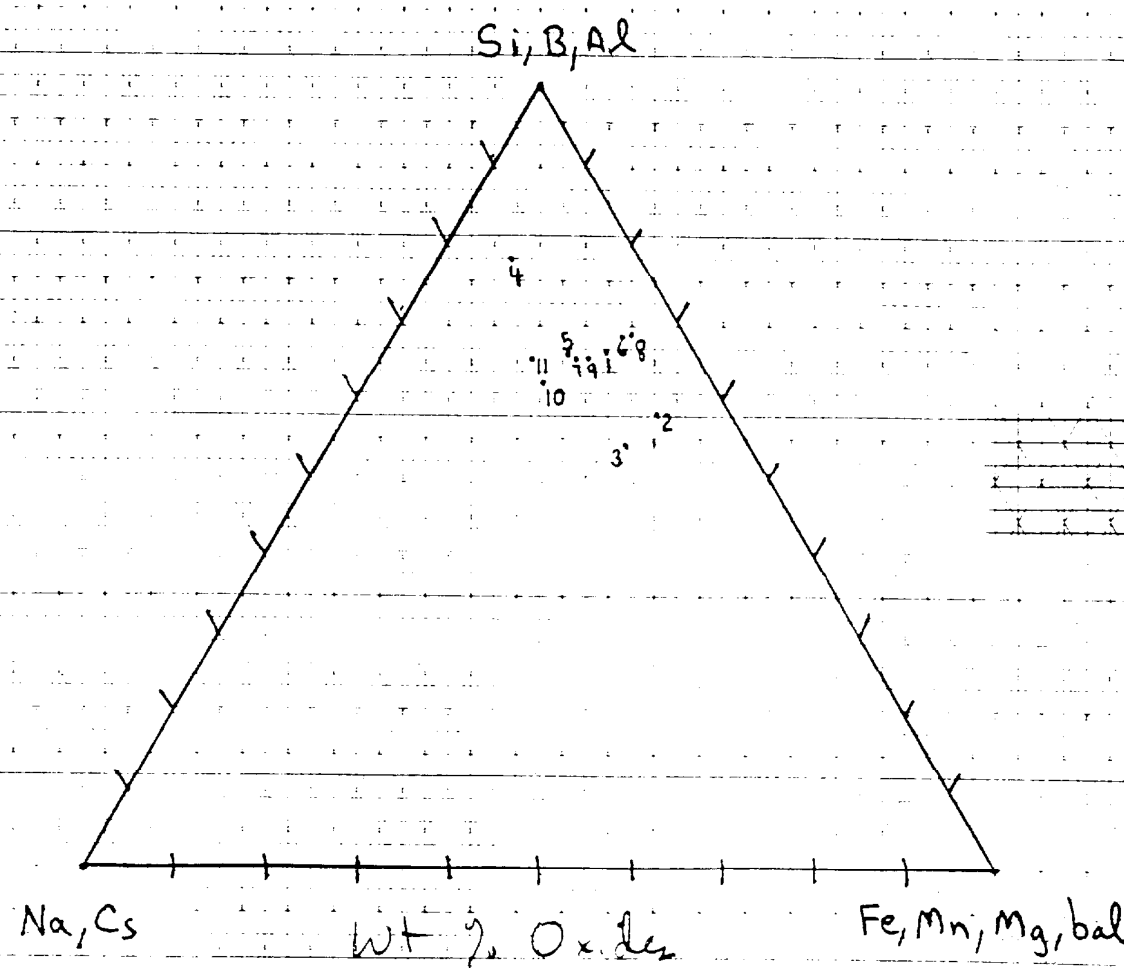
B. Elemental Leaching Rate / Gel Layer Approach – II [Waste Glass Systems]



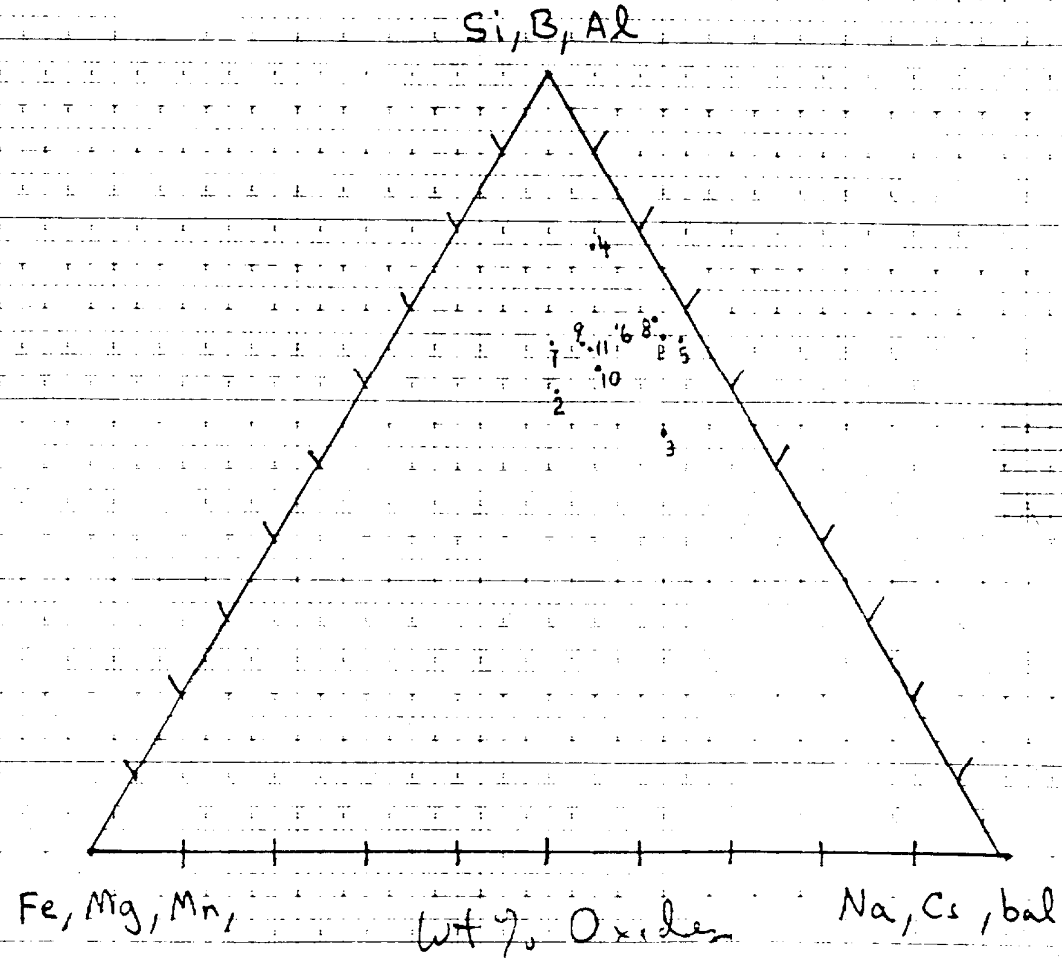
A. Structural and Leaching Characteristics

Approach – I

[Waste Glass Systems]



B. STRUCTURAL AND LEACHING CHARACTERISTICS APPROACH-II
[Waste Glass Systems]



B. Oxide Bonding Energy Approach - II
[Waste Glass Systems]

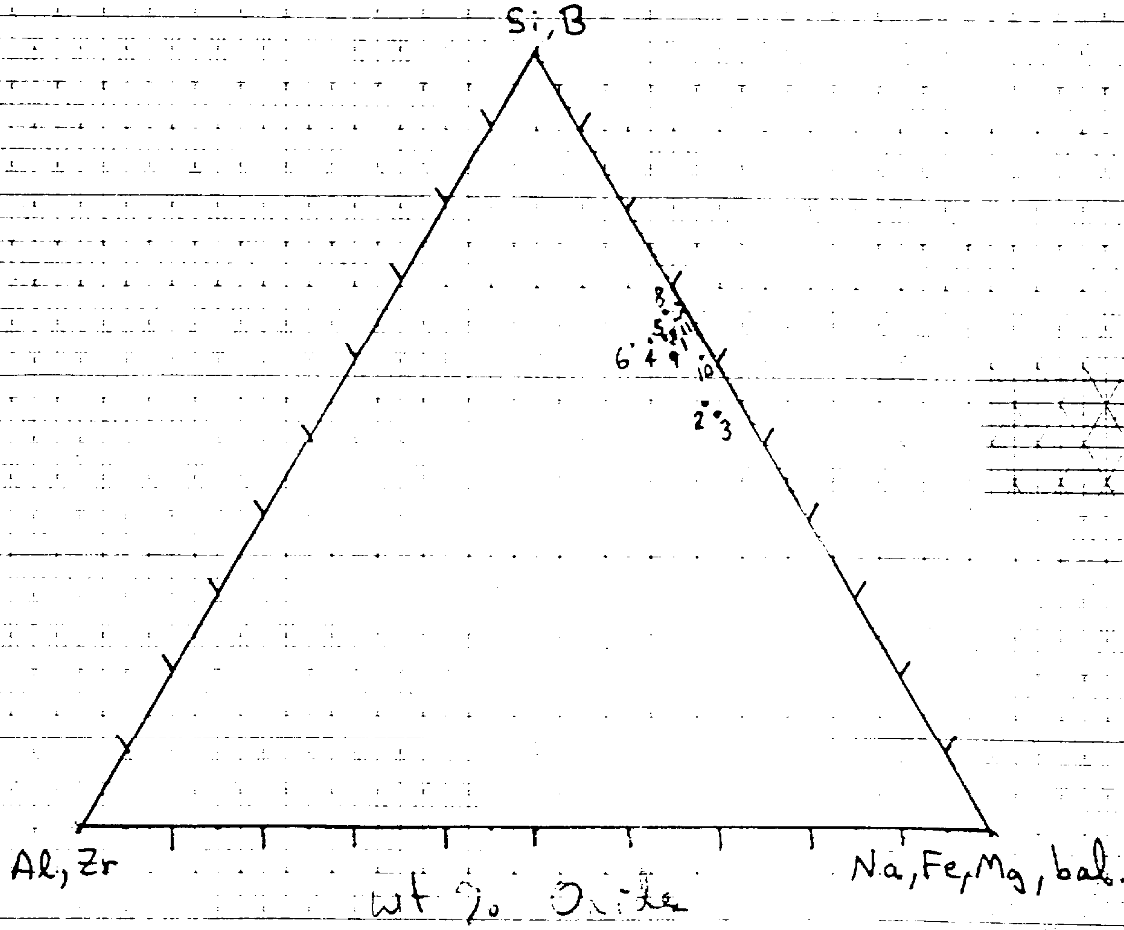


Fig 3

A Oxide Bonding Energy Approach - I
[Waste Glass Systems]