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SODA-SILICA GLASS-FORMING SYSTEM

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WASTE VITRIFICATION: PREDICTION OF ACCEPTABLE COMPOSITIONS IN A LIME-SODA-SILICA GLASS-FORMING SYSTEM

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ABSTRACT

A model is presented based upon calculated bridging oxygens which allows the prediction of the region of acceptable glass compositions for a lime-soda-silica glass-forming system containing mixed waste. The model can be used to guide glass formulation studies (e.g., treatability studies) or assess the applicability of vitrification to candidate waste streams.

INTRODUCTION

Vitrification technology is used around the world for treatment of radioactive waste. Increasingly, it is being considered as the future baseline stabilization technology on U.S. Department of Energy (DOE) sites for the treatment of mixed wastes^{1,2}. At the present time, vitrification of mixed waste cannot be considered a mature commercially available technology. The expectation that it can become so, rests primarily on two assumptions: (1) glass making is a well-established technology/industry and the equipment and experience associated with it can be applied to the developing mixed waste vitrification technology; and (2) waste vitrification technology development and experience in the high-level waste arena will be applicable to low-level mixed wastes as well. This rationale is similar to that which led to the birth of cement-based waste-form technology, where it was assumed that equipment and experience from the construction and concrete industries could be applied to waste solidification and where technology development efforts concentrated initially on low-level radioactive waste and next progressed to hazardous and then to mixed waste. Based upon experience with the evolution of cement-based waste-form technology, it is reasonable to assume that vitrification can follow suit and that supporting its development is warranted.

Cement-based waste-form chemistry involves not only physical encapsulation but also chemical interaction of some waste constituents within the solid matrix and chemical reactions within the contained pore structure. The complexity of this chemistry and the lack of understanding concerning it have led to some unexpected problems in the application of the technology to some wastes across the DOE Complex. This, in turn, has led to increased emphasis on developing and defining an alternative waste-form technology such as vitrification. However, glass formation involves both the chemical interaction (i.e., reaction) of some waste constituents in formation of the glass matrix and the dispersion of waste constituents in the fluid glass, leading to their atomistic bonding (and possibly encapsulation, in some cases) by the glass matrix upon cooling. This complex chemistry, like that of cement-based waste forms, is not fully understood, particularly for mixed (i.e., low-level radioactive and chemically hazardous) waste vitrification, in which numerous constituents are present that may affect this chemistry. For this reason, the chemical behavior of mixed waste in a glass matrix cannot be quantitatively predicted.

GLASS FAMILIES OF POTENTIAL INTEREST

There are numerous glass families that have been developed and evaluated on a commercial scale. Examples of these families include soda-lime-silicate (SLS), borosilicate, lead silicate, aluminosilicate, halide, borate, phosphate, sulfide, chalcogenide, chalcobalide, oxyhalide, oxynitride, and oxycarbide glasses. Calcium is a major constituent (i.e., >1 wt %) in the majority of mixed waste sludges located throughout the DOE Complex. Consequently, the study presented herein focused on the SLS system. The SLS system has been evaluated previously for numerous mixed waste sludges² and has the advantage of utilizing the calcium content of the wastes as a needed additive.

Historically, the SLS system has used the three-component operating diagram with units of weight percent to illustrate regions of acceptable glass formulations. However, it is well known that the chemistry of any system occurs on a mole basis rather than a weight basis. The primary reason that units of weight percent can successfully illustrate regions within the SLS system is that the molecular weights of the three components are so similar. The molecular weights of Na_2O , CaO , and SiO_2 are 62, 56, and 60 grams/mole, respectively. Thus, a plot of composition in weight percent would accurately (to within a few percent error) reflect composition in mole percent. Obviously, as more components are introduced into the system, this comparison is no longer as accurate as the simple three-component system. This further emphasizes the need to better understand the effects of additional components on the basic system.

The Basic System

The phase diagrams for the basic SLS system, those of the related ternary systems that contain common major waste constituents (e.g., alumina [Al_2O_3]), and the accompanying literature permit useful comparisons to be made between the conditions of composition and temperature for equilibrium systems and those used to vitrify mixed waste. These comparisons lead, in turn, to an understanding of the fundamental chemical issues that operate in the processing of these wastes.

The structures of silicate glasses are based on the polymerizing tendency of SiO_4 tetrahedra, which derives, in part, from the bonding properties of Si(IV) and the small ionic size of silicon relative to that of oxygen. For the present purposes, the bonding properties are deemed to rely primarily on the electronic polarity of the Si-O bond and the coordination number of oxygen atoms that surround the silicon atoms. Based on electronegativity values³, the Si-O bond is approximately 88% ionic, indicating that the bond exhibits both ionic and covalent properties.

The 12%-covalent character helps to maintain the tetrahedra in the melt, making them the basic "building blocks" in silicate melts and glasses. If crystalline silicates precipitate from the melt, the high ionicity leads to the well-known variety of crystallographic packing arrangements for Si^{4+} and O^{2-} .

These concepts indicate that both the melt and its corresponding glassy state can be considered as differing only moderately from the crystalline silicates that possess similar chemical composition. Consequently, an improved understanding of silicate waste glasses can be gained from knowledge of the glass melt, the corresponding crystalline metal silicates, and the solidified glasses. Analogously, the structural properties of glasses that contain

elements such as aluminum and boron would respectively resemble the corresponding crystalline aluminosilicates and borosilicates.

One molecular restriction that applies to the glassy and crystalline states of silicate materials and to their melts is particularly noteworthy. Neighboring tetrahedra that are linked to one another can share only corners; sides and faces of tetrahedra cannot be shared. Hence, two tetrahedra are linked to each other by the sharing of an oxygen atom. This arrangement means that a tetrahedral unit may be linked to two, three, or four other tetrahedra. Two such links per silicon yield, locally and on the average if they predominate, a somewhat "linear" polymer or chain of SiO_4 tetrahedra. Analogously, three bridging oxygens per silicon produce two-dimensional arrays that resemble cross-linked polymers, and four would generate a three-dimensional network.

Clearly, the oxygen-to-silicon ratio is an important parameter for the polymeric and network structures in silicate melts, their corresponding glasses, and the formation of the various crystalline phases that can precipitate during processing. This ratio is 2:1 for unary SiO_2 systems. Thus, crystalline SiO_2 (e.g., quartz) can be understood as composed of tetrahedral arrangements of close-packed ions; this situation explains the relatively high density of quartz. The ionic radii of silicon and oxygen are 0.041 nm and 0.138 nm, respectively. Hence, the corresponding size ratio for Si:O of 0.34:1 leads to the establishment or retention of the SiO_4 tetrahedra in the crystalline state: 2.65 kg m^{-3} , as compared with that of the high-temperature crystalline forms of SiO_2 —tridymite (2.26 kg m^{-3}), cristobalite (2.32 kg m^{-3}), and amorphous silica (2.2 kg m^{-3}).

These considerations suggest that the establishment of SiO_4 tetrahedra in a melt requires an additional source of oxygen in order to achieve the oxygen-to-silicon ratio needed to stabilize the 2-dimensional and 3-dimensional networks. Normally, alkali and alkaline oxides are used to provide the needed oxygen while maintaining charge balance between positive and negative ions. Oxides of other metals, such as the transition metals and some of those in Groups IIIB and IVB, can also be used. This function underscores the variety of silicate minerals and the prevalence of complex compositions for tailored glasses and ceramics.

Minimum Bridging Oxygens

Recognizing that the number of bridging oxygens (oxygens which can bond covalently to produce the glass structure) is a critical parameter (above and beyond the simple oxygen-to-silica ratio) suggests a methodology by which one of the boundaries to the range of acceptable compositions can be predicted. The methodology is based upon Stevels'⁴ theory in which he calculated the mean possible number of bridging oxygens per SiO_2 based upon the oxygen-to-silica ratio. A minimum of one bridging oxygen is necessary for a plausible glass structure to form⁵; that is, at calculated bridging oxygens of less than one-ionic bonding is favored over covalent bonding. Consequently, there is, in effect, too much oxygen to promote the formation of the basic tetrahedral structure necessary for glass to form. Thus, the region of acceptable glass compositions would be predicted to be bounded by

$$F = 8 - 2(O/\text{Si}) \quad (1)$$

where

F = the mean possible number of bridging oxygens and has a value ≥ 1 ,

O = moles of oxygen within the glass melt,

Si = moles of silicon within the glass melt.

PREDICTING ACCEPTABLE COMPOSITION REGIONS

A treatability study of vitrification of West End Treatment Facility (WETF) sludge has been published previously^{2,6}. For this paper, the data set generated in the study is used solely for the purpose of applying and validating the bridging oxygen model. Consequently, only a brief description of the waste and treatability study is described herein.

Waste Composition^{2,6}

Historically tanks have been used for settling and storage of sludge at the Oak Ridge Reservation Y-12 Plant WETF and West Tank Farm. The sludge is composed primarily of WETF process metal hydroxide precipitate (copper, nickel, zinc, and aluminum), biodenitrification sludges (mainly $CaCO_3$) and ferric hydroxide with trace metal hydroxides. Depleted uranium at an average of approximately 0.42% ^{235}U vs 0.72% in natural uranium, is the primary radioisotope of concern. In addition to being low-level radioactive, the waste carries the following Resource Conservation and Recovery Act (RCRA) codes: F001, F002, F006, and F007. Treatability samples were obtained from Tanks 7 and 13, dried, and then homogenized. Characterization data for the two samples, designated as DH-TS02 and DH-TS03, on an oxide basis are presented in Table I.

With the waste contribution defined, the glass formulation or recipe of interest was selected. It should be noted that for the WETF study, the waste was the sole source of alkaline earths (e.g., CaO). Additives were SiO_2 and alkali (Na_2O and Li_2O , which was partially substituted for Na_2O). The ingredients were weighed, combined, and mixed. The material was then placed in a 99.8% pure $\alpha-Al_2O_3$ crucible with a loose-fitting lid. The crucible and contents were placed in a high-temperature furnace to achieve melting. The furnace was programmed to ramp to the desired melt temperature at $300^\circ C/h$ and hold at the melt temperature for 4 h, after which, the fluid glass was poured into a stainless steel pan and allowed to cool to ambient temperature. The resulting solidified glass product was then subjected to various types of characterization and analysis.

Operating Diagram

The resulting WETF data, shown in Figure 1, are presented in the traditional ternary diagram form described previously (i.e., alkalis, alkaline earths and glass formers). Line A-A represents calculated bridging oxygens of ≈ 1 . Thus, line A-A is one of the boundaries of acceptable glass compositions and, in effect, represents the maximum allowable oxygen content in the melt for this application. Compositions to the right of line A-A are those with calculated F values greater than one. The second boundary for acceptable glass compositions, also shown in Figure 1, is line B-B. Line B-B is particularly noteworthy, in that it represents a suspected phase-separation boundary based upon literature data for the $CaO-Na_2O-SiO_2$ system⁷: that is, compositions beyond this boundary that are "deficient" in alkali and alkaline earth tend to form unary rather than ternary phases. Compositions to the right of line B-B would be expected to

produce glass products characterized by phase separation and/or contained crystalline material. The region bounded by lines A-A and B-B represents the predicted region of acceptable compositions.

It should be noted that the use of the bridging oxygen calculations is not unique to the SLS system and should be equally applicable to other silicate systems such as borosilicate glass. However, the second boundary (line B-B) is unique to the SLS system and is not directly applicable to other silicate systems.

As shown in Figure 1, the WETF data compare favorably with the predicted region. Also presented on the operating diagram are acceptable composition regions for commercial SLS glass and the Reactive Additive Stabilization Process (RASP) for Hazardous and Mixed Waste Vitrification⁸. Both lie within the predicted region. Significantly, the predicted region is dependent on the waste composition. As such, it can be used to predict changes in the region of acceptable compositions as the waste or its composition changes. It should be noted, however, that the model is based solely on the bulk chemistry of the glass. As such, constraints like melt viscosity and regulatory performance requirements are not addressed.

CONCLUSIONS

A model using calculated bridging oxygens has been presented which enables the prediction of regions of acceptable glass compositions. The model can be used as a guide to determine glass formulations for evaluation in treatability studies or to assess the applicability of vitrification to a candidate waste stream.

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Table I. Normalized composition of DH-TS02
and DH-TS03 on an oxide basis

Oxide form	DH-TS02 composition (wt %)	DH-TS03 composition (wt %)
Ag ₂ O	0.0029	0.0044
Al ₂ O ₃	17.2095	16.1895
As ₂ O ₃	0.00000	0.0010
B ₂ O ₃	0.0486	0.1481
BaO	0.1084	0.0538
BeO	0.0048	0.0011
CaO	71.90000	59.20000
CdO	0.0101	0.0081
Cr ₂ O ₃	0.1284	0.1189
Fe ₂ O ₃	2.1246	10.6486
K ₂ O	0.1534	0.2923
MgO	3.1317	2.6808
MnO ₂	0.0680	0.0532
Na ₂ O	3.3953	8.2294
NiO	0.2672	0.2056
PbO ₂	0.0459	0.1300
SiO ₂	0.1278	0.1470
TiO ₂	0.0354	0.0397
Tl ₂ O	0.00000	0.0141
UO ₂	1.0665	1.5619
ZnO	0.0621	0.1126
ZrO ₂	0.1328	0.1359
	TOTAL = 100.0000	TOTAL = 100.0000

Figure 1. Operating diagram for SLS glass containing WETF sludge