TWEAT: TERNARY WASTE ENVELOPE ASSESSMENT TOOL

Bob Robertus, and Pavel Hrma
Pacific Northwest Laboratory
Richland, WA

Ross Lambert
Ariel Publishing Inc.
Pateros, WA

ABSTRACT

TWEAT is a graphical visualization software tool used to support glass development for the Hanford Waste Vitrification Plant. It requires the user to input the chemical composition of streams that will be mixed to produce glass, along with the property limits that the glass must meet. Using built-in property models, TWEAT then displays on a ternary diagram an "acceptable composition region" and a "qualified composition region" where glass can be produced. The "qualified composition region" is the most restrictive area. It meets all specified property limits and does not extrapolate any property models.

NOMENCLATURE

- F = mass fraction of frit in final glass (oxide basis)
- R = mass fraction recycle in final glass (oxide basis)
- W = mass fraction waste in final glass (oxide basis)
- a_{ji} = i-th linear least squares coefficient for j-th transformed property
- f_i = mass fraction of i-th oxide in the frit
- g_i = mass fraction of i-th oxide in the glass
- $\rho_j\#$ = transform of j-th property
- ρ_j = j-th property value
- r_i = mass fraction of i-th oxide in the recycle stream
- w_i = mass fraction of i-th oxide in the waste stream

subscripts

- i = index for oxide components
- j = index for property of the glass

superscripts

- # implies a transformed value

GRAPHICAL VISUALIZATION TOOL

Background

As a by-product of defense related activities, many underground tanks at Hanford contain radioactive waste materials mixed with other hazardous chemicals. A clean-up effort is underway to first separate as much as possible the high level radioactive materials from low-level radioactive species. Then the concentrated radioactive wastes are to be fused with a glass frit to form a waste glass which solidifies inside a metal canister. The canisters will finally be housed in geologically isolated areas for safe long-term disposal.

The Hanford Waste Vitrification Plant (HWVP) is being designed to produce glasses from waste streams of varied compositions. Frit component weight fractions will depend on the composition of the waste being processed. The principal frit components are SiO_2, B_2O_3, Li_2O and Na_2O. Other oxides may be added. A recycle stream results from processing operations in the HWVP. The recycle stream, which is combined with the waste for vitrification, is expected to always be small and constitute 2% or less of the final glass product.

The Ternary Waste Envelope Assessment Tool (TWEAT) is a graphical visualization method developed for Macintosh™ computers to display the range of compositions that can be used to produce glass in the HWVP. TWEAT was developed by the Pacific Northwest Laboratory with assistance from Ariel Publishing Inc. It uses built-in empirical models for calculating glass properties as functions of oxide composition.

The database for the property models was generated by testing about 130 statistically selected glass samples of compositions believed to bracket composition ranges that will be produced by the HWVP. Processing characteristics for the melting operation and durability were measured for each sample. Processing characteristics included melt viscosity, melt electrical conductivity, and liquidus temperature. Limits on these characteristics are set by the design of the glass processing equipment.

Durability characteristics were normalized releases (in g/m^2) for Si, B, Li, Na, Mo, and Cs measured by two standardized dissolution tests: Materials Characterization Center(MCC-1) and the Product Consistency Test (PCT). The MCC-1 test uses a 6.3 x 6.3 x 12.5 mm glass monolith which is leached in de-ionized water at 90°C for 28 days. The PCT subjects 75-100 m glass powder to water at 90°C for 7 days. The waste glass must have release rates defined by the PCT lower than the Environmental Assessment (EA) glass which is currently used as a standard (1).

TWEAT Models

The experimental data have been fitted to a set of property equations which can be used to predict properties of any glasses within the experimental range of compositions studied. All of the property models in TWEAT are currently linear functions of nine specific oxides (see Fig. 1.) and a general category of "other oxides" . (Second-order models have also been generated but are not yet implemented in TWEAT.)

The present models used in TWEAT are of the form:

$$\rho_j^{\#} = \sum_{i=1}^{10} a_{ji} * g_i \qquad \text{(Eq. 1)}$$

With the exception of liquidus temperatures (for which $\rho_j = \rho_j^{\#}$), the property transforms in TWEAT are:

$$\rho_j^{\#} = \ln(\rho_j) \qquad \text{(Eq. 2)}$$

Glass from the HWVP will be formed from three classes of streams: waste, frit, and recycle. Material balance restrictions on each stream and the final glass require that:

$$W + F + R = 1 \qquad \text{(Eq. 3)}$$

$$\sum_{i=1}^{10} w_i = \sum_{i=1}^{10} f_i = \sum_{i=1}^{10} r_i = 1 \qquad \text{(Eq. 4)}$$

$$\sum_{i=1}^{10} g_i = 1 \qquad \text{(Eq. 5)}$$

$$g_i = W_i * W + f_i * R \qquad \text{(Eq. 6)}$$

Eq. (5) is a consequence of Eq. (3), Eqs. (4), and Eq. (6).

User Input

The first step in generating a ternary diagram is specifying compositions for the three streams that will be mixed to form glass. This is done in the "Vertex Data Entry" window shown in Fig. 1. (NCAW represents a plausible Neutralized Current Acid Waste stream.) The user must ensure that the conditions in Eqs. (4) are met. Otherwise, TWEAT will not generate a ternary diagram.

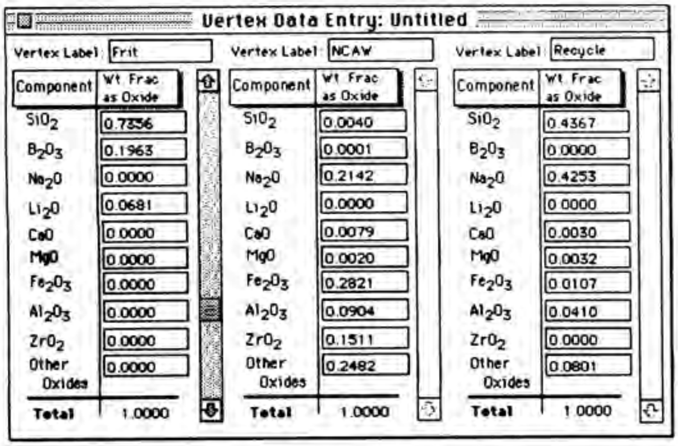

Fig. 1. Vertex data entry window.

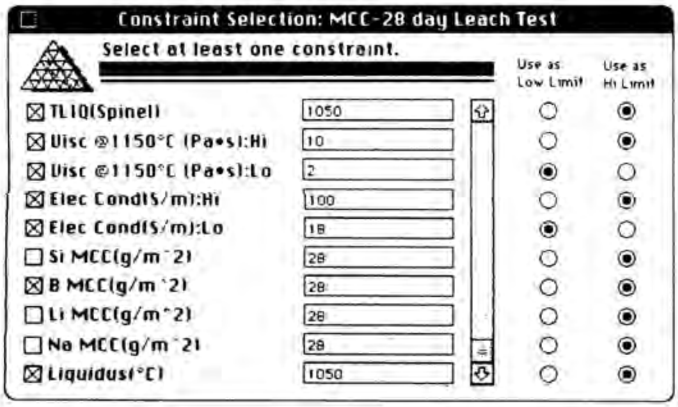

Fig. 2. Constraint input window.

Next, the user must specify which property limits are to be considered and what the numerical limit is for each selected property. This is accomplished by using the Constraint Input window shown in Fig. 2. Internally TWEAT decomposes the property models of Eq. (1) into lines of constant property values as dictated in Fig. 2.

Now the user can look at the information on a ternary diagram and can visualize other aspects of the data using menu selections in TWEAT.

Visualization of Information

Information in TWEAT is generally presented on a ternary diagram with the various processing and durability limits (constraints) forming boundaries of an "acceptable processing region". The ternary vertices represent waste, frit, and recycle streams.

TWEAT is an interactive tool that gives nearly immediate feedback to the user. When the user selects a point inside the ternary diagram, TWEAT calculates the glass composition as well as numerical values for all of the selected properties at that point. Fractions of waste, frit, and recycle are also indicated as shown in the small window of Fig. 3.

The experimental program that generated the property models examined only a portion of the total composition space. With linear models, it is easy to extrapolate beyond experimentally tested glasses. The "acceptable processing region" is sometimes bounded by property limit lines which are calculated using the models outside experimental composition ranges. Thus, another feature of TWEAT is an overlay boundary showing how much of the ternary diagram represents glass compositions where real experimental data are available. Extrapolation outside these boundaries (also shown in Fig. 3) is not recommended because the accuracy of the property calculations is unknown.

The composition boundary is generated by first determining the intersection points for each composition limit line with all other composition limit lines for all ten oxides. This array of intersection points is analyzed to see which ones fall inside the ternary diagram. Each of the vertices of the "qualified composition region" must individually satisfy simultaneously all of the composition limits.

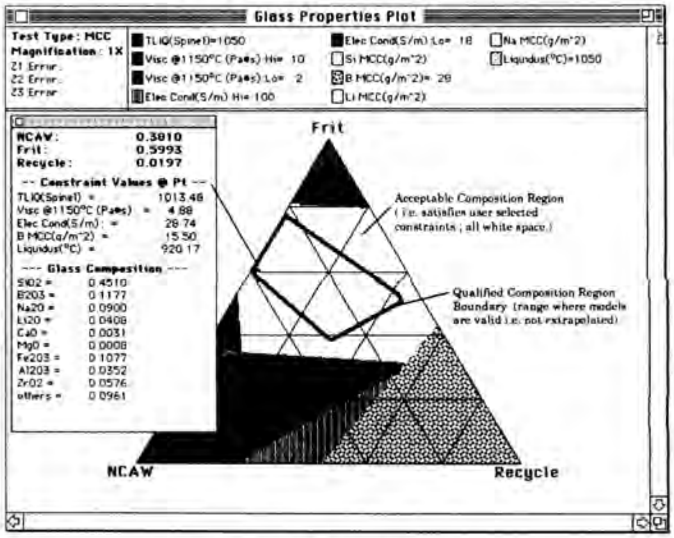

Fig. 3. Example ternary diagram.

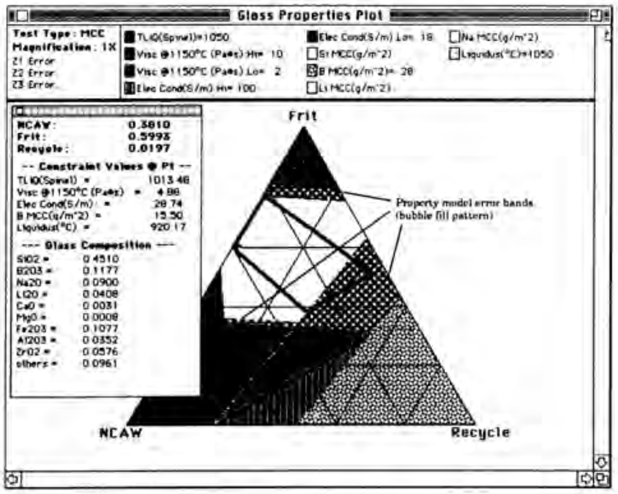

Fig. 4. Ternary plot with property error models.

TWEAT has an ability to display errors associated with the uncertainty of the property models. Covariance data for each of the models (except liquidus) have been generated from the experimental data. This covariance information is propagated through the property models to generate an estimate of the error associated with a particular model prediction. An example of the model errors is shown in Fig. 4. The error bands shown here are representative only and not necessarily the final values to be used. From Fig. 4, it is obvious that some models are subjected to a greater uncertainty than others. The viscosity and electrical conductivity models fit the data quite well and each has a narrow error band. The boron release rate model did not fit experimental data as well and shows a wide error band. These observations are motivating on-going efforts to develop models for normalized elemental releases that more closely fit the experimental data.

Exploring Options

The value of TWEAT is its ability to quickly respond to a users input. The user can:

- determine acceptable waste loadings using a particular frit;
- change frit composition to see its effect on waste loading;
- change waste, frit, or recycle compositions;
- change the number of constraints to be plotted;
- change the numerical values for a constraints;
- determine a glass composition and associated properties at any point on the ternary;
- determine which oxides are limiting the composition boundaries;
- examine consequences of blending two waste streams.

In Fig. 5 , different waste and frit compositions were entered into the Vertex Data Entry window. (The CC waste represents a plausible Complexant Concentrate stream.) The time required to make the changes and view a new ternary diagram was less than 3 min.

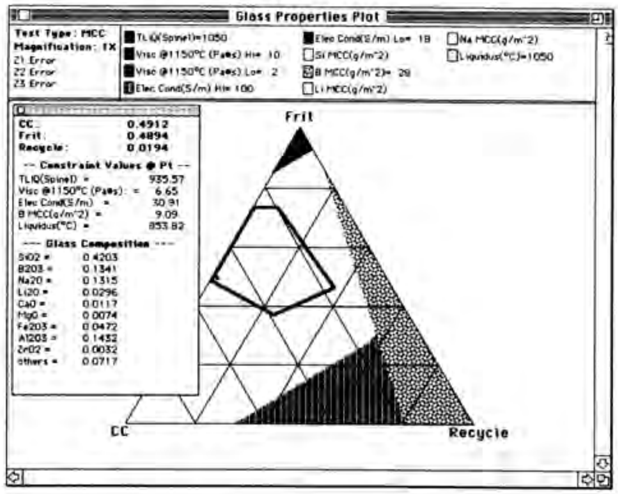

Fig. 5. Ternary diagram with new stream compositions.

Both Fig. 3 and Fig. 5 suggest that waste loading could be increased if we moved outside the composition range where the property models have been fitted, provided crystallization and phase separation would allow the move (phase behavior has not been implemented in TWEAT yet) . Hence, the diagrams are showing directions where more experimental work would be useful. That is, the experimental composition envelope could be expanded to develop models valid over larger composition spaces.

It is worth noting that information on the Vertex Data Entry window and the Constraint input window can be Saved to a file which TWEAT can Open at a later date, thus avoiding retyping the data. TWEAT can also accept composition information from EXCEL™ spreadsheets via Copy and Paste editing.

Figure 6 depicts the ability of TWEAT to mix two different waste streams simultaneously with one frit. This allows a user to examine the possibility of increasing waste loading by blending two different waste streams, rather than processing

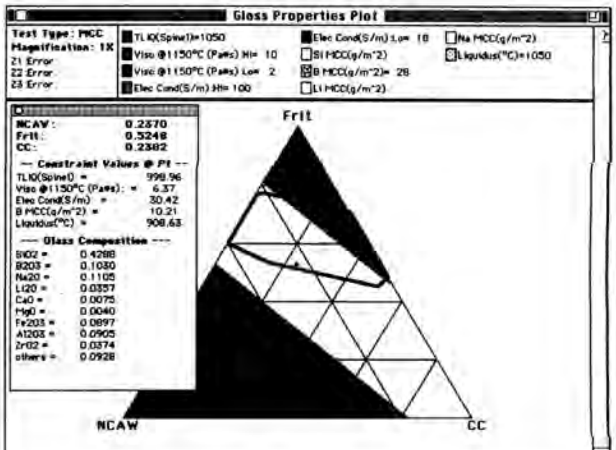

Fig. 6. Blending two waste streams.

each individually. Figure 6 shows plausible NCAW and CC wastes on the same ternary. In this particular example, the mass fraction of frit required to process a 50-50 blend is greater than that for the CC waste alone, but less than that required by NCAW alone. In this mode the recycle stream is neglected. As was the case in Fig. 5 and Fig. 6, increased waste loading with a 50-50 mixture appears possible outside of our experimental composition envelope provided phase behavior allows it.

TWEAT thus provides the capability of simultaneously visualizing many processing variables of importance to the HWVP. It gives users very specific data (e.g., glass composition and glass properties at a point) as well as general information (e.g., which property or composition limits are defining the "qualified composition region") The user can quickly observe the affect that changing one or more of the variables has on any of that information. Another value of TWEAT is its ability to show where more experimental work ought to be directed in order to increase the quality of the melt glass and the accuracy of its prediction.

ACKNOWLEDGMENTS

The property models and covariance matrices were developed at PNL. The experimental database was generated by P. Hrma, M. Schweiger, D. Smith, and C. Buchanan. The models and covariance information were generated by G. Piepel and P. Redgate.

This work was sponsored by the U.S. Department of Energy (DOE). Pacific Northwest Laboratory is operated for DOE by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

REFERENCE

1. C. M. JANTZEN, N. E. BIBLER and C.D. BEAM, "Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material". Westinghouse Savannah River Co. Report WSRC-TR-92-346, Rev. 0. (1992).