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Pacific Northwest National Laboratory
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Feed Variability and Bulk Vitrification Glass Performance Assessment

L. A. Mahoney
J. D. Vienna

January 2005

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

PACIFIC NORTHWEST NATIONAL LABORATORY
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Letter Report

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

The Low-Activity Waste (LAW) Supplemental Treatment Demonstration Project is pursuing testing and demonstration of several supplemental treatment technologies. One of these is bulk vitrification (BV), also known as in-container vitrification (ICV™)[(a)]. Because of the variability of the Hanford tank wastes, the supplemental treatment (ST) ICV process must be designed to handle a range of feed compositions. One purpose of this letter report is to describe the compositional variability of the feed to ST and determine which compositions should be included in an ICV testing program. The other is to support the Tri-Party Agreement M-62-08 milestone decision[(b)] by making initial estimates of the amount of glass that will be produced with ICV from the ST feed. These initial estimates will help establish whether ICV is a practical treatment methodology for all Hanford tank wastes.

Roughly nine-tenths of the ST LAW feed will come from the Waste Treatment Plant (WTP) pretreatment process. This portion of the ST LAW processed waste varies over time and is expected to consist of 1) a portion of the same LAW feed sent to the WTP melters and 2) a dilute stream that is the product of the condensate from the submerged-bed scrubber (SBS) and the drainage from the wet electrostatic precipitator (WESP), both of which are part of the LAW off-gas system. As in the preceding report,[(c)] the compositions of all WTP-supplied streams were predicted by the WTP program's dynamic process flowsheet model (G2™)[(d)] for the whole WTP campaign. This portion of the ST LAW feed consisted of 1451 batches of varying composition.

The interface between WTP and ST has not been determined. Therefore there is no set design for the methods of concentrating the off-gas product stream and of combining the excess LAW and off-gas product streams. One possible arrangement, the only one considered in this report, would add half of the total LAW to the off-gas product stream. (Total LAW equals that portion of LAW sent to the WTP LAW vitrification plant [WTP LAW] plus the LAW not currently treatable in the LAW vitrification plant due to capacity limitations [excess]).

The ST feed that does not come from WTP will come from single-shell tanks (SSTs) that have been determined to contain low-curie wastes. These wastes will not undergo separations within the WTP pretreatment facility; however, selective dissolution[(e)] will be applied to the wastes to reduce the soluble radionuclides (e.g., Cs-137, Tc-99 and I-129) that are processed by ST. The list of tanks designated as containing low-curie wastes has changed over time, a change which has an impact on the analysis of low-curie wastes in this report. The TFCOUP5A feed vector used to make the G2 run excluded waste from 20 SSTs; at the time the vector was generated, these tanks were considered to contain low-curie wastes that would be sent to ST without separations in the WTP pretreatment facility. These 20 tanks completed the set of predicted ST feeds, consistent with the assumptions that went into the feed vector. In addition, since the time the TFCOUP5A vector was generated, 16 tanks that were not part of the excluded set have

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(a) "ICV" is a trademark of AMEC Incorporated, Tempe, Arizona.
(b) HFFACO. 1988. Hanford Federal Facility Agreement and Consent Order as amended, informally known as the Tri-Party Agreement or TPA. This agreement is among the U.S. Department of Energy, the U.S. Environmental Protection Agency, and Washington State Department of Ecology.
(c) Mahoney, L.A. 2004. *Waste Simulant Formulation for Series-22 Bulk Vitrification Tests*, letter report ST05.004, Pacific Northwest National Laboratory, Richland, Washington. November 12, 2004.
(d) "G2" is a trademark of the GENSYM Corporation, Burlington, Massachusetts.

been determined to contain low-curie waste.[e] Although the wastes in these 16 tanks were part of the G2 model input and therefore made up part of the WTP-derived ST feed, this report also considers these wastes as potential contributors to the non-WTP-treated ST feed. The Best Basis Inventory (BBI) and the BBI water wash factors for the wastes in the 36 selected tanks, together with non-tank-specific selective dissolution factors defined by retrieval experience and modeling, were used to calculate a set of 36 feed streams to ST in addition to the 1451 batches predicted to come from WTP pretreatment.

All of the streams fed to ST were processed to express the compositions in terms of the concentrations of waste oxides and other constituents. Next, the WTP-derived streams were broken into three broad groups: those dominated by off-gas product composition, those dominated by LAW streams with high fluoride, and those dominated by LAW streams with low fluoride. Then statistical analysis software (JMP™ [f]) was used to subdivide the low-fluoride LAW-dominated streams into "clusters" of similar composition. To assess the properties of the glass, similarity was defined according to the three species with the strongest effect on glass durability and phase separation: Al_2O_3, P_2O_5, and SO_3. The oxides MoO_3 and CaO were omitted as similarity criteria because of the low predicted concentrations. The concentrations of certain other chemicals—Cl, NO_3, and NO_2—were not used as criteria in this cluster analysis but will be considered in defining simulants for engineering-scale melter tests because they relate to overall melter system performance and immobilization success rather than to the glass properties of concern in the crucible tests.

The following conclusions were drawn from the review of feed compositional variability:

- The low-curie tank waste compositions are frequently outside the concentration ranges of most of the LAW streams generated by the WTP pre-treatment facility. Several low-curie wastes are higher in nominal P_2O_5 and SO_3 than the WTP-derived LAW streams, and most are lower in nominal Al_2O_3 and Cl. (The "nominal" concentration of a constituent is that calculated on the basis of 20 wt% Na_2O.)

- The streams whose composition is dominated by off-gas product contain very little of the Na and Al but have high nominal concentrations of most of the significant anion species (Cl, F, NO_2, NO_3, and SO_3).

- The maximum nominal concentrations of CaO and SO_3 that, to date, have been tested in glasses are about equal to the Na-weighted averages for LAW streams.

- The maximum tested nominal concentration of NO_2 plus NO_3 is an upper bound for virtually all of the LAW streams.

- The concentrations of Al_2O_3, Cl, F, and P_2O_5 in most of the predicted LAW streams are well above the concentrations that have been tested in glasses.

The analysis showed that 16 cluster-average compositions would adequately describe the streams containing more than 99% of the Na that might be directed to ST from the WTP. These streams are

(e) Raymond, R.E. 2004. *Candidate Single-Shell Tanks for Low-Curie Feed to Supplemental Treatment*, letter report 7F300-04-RER-001 R1, CH2MHILL Hanford Group, Inc., October 20, 2004.

(f) JMP is a trademark of SAS Institute, Inc., Cary, North Carolina.

dominated by the contribution from pretreated LAW waste. The small percentage remaining is dominated by the off-gas product and would require considerably different handling for successful vitrification. One composition is provided to describe this type of ST feed, for a total of 17 compositions representing WTP-derived feeds. Eight additional cluster compositions were derived to describe the low-curie SST waste streams.

To estimate the effectiveness of ICV over the range of ST feed compositions, the glass mass produced for each waste cluster was calculated according to “conservative,” “best-estimate,” and “stretch” assumptions for acceptable glass compositions. The assumptions were based on a review of glass data that have been generated in support of the ST project along with data from other pertinent projects and general glass chemistry knowledge. Two different combinations of soil and additives were considered, one using standard Hanford soil (together with B_2O_3 and ZrO_2) and one with soil plus a SiO_2 supplement (together with B_2O_3 and ZrO_2). The following conclusions were drawn from these calculations:

- The present state of knowledge about the effects of glass composition on glass performance and processing can lead to uncertainties of roughly 45% in glass production, based on a comparison of the results for the “conservative” and “stretch” cases.

- The lowest waste loadings are the result of high sulfur and/or phosphorus concentrations.

- The extremes that are present in the composition of the waste fed to ICV increase the total glass mass by 10% to 30%, compared to the glass that would be produced if the waste was constantly at the overall-average composition of the feed.

- Adjusting the glass additives with pure SiO_2 to optimize waste loading may decrease the total ICV-produced glass mass by 10% to 15%.

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1.0 Introduction

The Low-Activity Waste (LAW) Supplemental Treatment Demonstration Project is pursuing testing and demonstration of several supplemental treatment technologies. Bulk vitrification (BV), also known as in-container vitrification (ICV), was one of the technologies evaluated for their potential to supplement the treatment capacity of the Hanford Waste Treatment and Immobilization Plant (WTP) for LAW. In 2003, CH2M HILL Hanford Group, Inc, made an investment decision to pursue a pilot-scale test and demonstration facility for bulk vitrification treatment of selected Hanford low-activity tank waste. The test and demonstration facility is planned to be operational late in 2005, and will produce up to 50 boxes of vitrified material to provide data to support final decisions on tank waste treatment. The tank waste for the test and demonstration facility will come from Hanford Tank 241-S-109 (S-109). This waste will be used directly in the initial boxes to define acceptable operational windows. Later testing will produce boxes with S-109 waste spiked with other chemicals to represent other tank wastes expected to be treated with ICV.

A number of smaller-scale simulant tests are planned to support the test and demonstration facility. The S-109 simulant used in these tests was described in earlier letter reports.[a] Other Supplemental Treatment (ST) tests require simulants that represent the range of compositions that might be present in waste fed to ST throughout the Waste Treatment Plant (WTP) campaign. The Series 33 tests to be performed in the engineering-scale melter (ESM) are limited to three to five simulants, one of which is the already-defined S-109 waste simulant. Before the Series 33 tests take place, the Series 22 tests will be performed at crucible scale to determine glass properties for a range of glasses that describe the ST feed. A preceding report[b] set out the information needed for the Series 22 tests, a set of 21 waste formulations expressed in terms of waste-oxide composition.

One purpose of this letter report is to describe the compositional variability of the feed to ST and show which compositions are most relevant to ICV testing. Much of the variability and feed composition information in this report was also presented in the preceding report; however, this study considers a larger set of feeds from low-curie single-shell tank (SST) wastes, and includes the effect of selective dissolution during retrieval. The other purpose of this report is to provide an initial assessment of the performance of ICV in handling the entire ST feed envelope. Such an assessment is needed to support the Tri-Party Agreement M-62-08 milestone decision by determining which wastes are likely to create difficulties for ICV. To this end, the amount of glass required to immobilize the ST feed is calculated for groupings of feed streams that represent the entire envelope of compositions.

Figure 1.1 diagrams the procedure used in defining the waste-oxides formulations that are one of the products of the current study. The ST feeds that originate in the WTP pretreatment facility are 1451 weekly streams calculated with the G2 model of the WTP facility. Half of the predicted total LAW is sent to the WTP melters and half is sent to ST, where it is combined with a stream produced by the WTP LAW off-gas process. The reason for using this particular combination is given in Section 2 of this report.

(a) Mahoney, L.A. and S.D. Rassat. December 5, 2003. *Tank 241-S-109 Cold Saltcake Simulant Formulation*, letter report ST04.007, Pacific Northwest National Laboratory, Richland, Washington.
Bagaasen, L.M. January 21, 2004. *Baseline S-109 Chemical Simulant Recipe for AMEC Tests*, letter report ST04.010, Pacific Northwest National Laboratory, Richland, Washington.

(b) Mahoney, L.A. November 12, 2004. *Waste Simulant Formulation for* Series-*22 Bulk Vitrification Tests*, letter report ST05.004, Pacific Northwest National Laboratory, Richland, Washington.

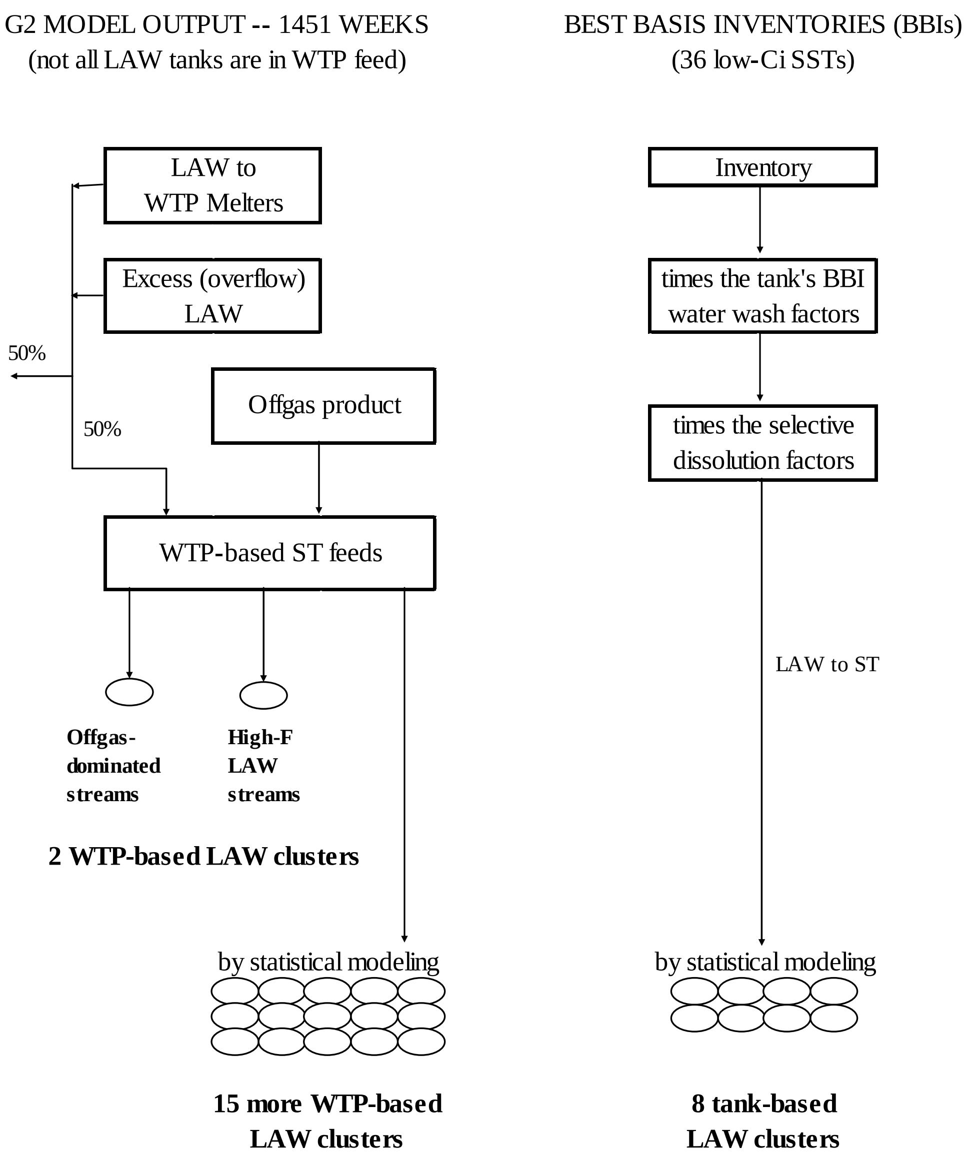

Figure 1.1. Diagram of Cluster Analysis Procedure

As described in Section 3, the WTP-derived feeds are subdivided into three parts – streams dominated by off-gas product, streams dominated by LAW waste with high fluoride, and streams dominated by LAW waste with low fluoride. This last part, which makes up most of the WTP-derived feed, is subdivided by statistical analysis into 15 clusters, as described in Section 4. These WTP-derived clusters contain the same streams and have the same compositions as in the preceding Series-22 report.[a]

Figure 1.1 also shows the procedure used for the 36 SST wastes that were assumed to be sent to ST after undergoing pretreatment outside of the WTP plant. The LAW streams from the 36 SSTs were calculated as being the water-soluble portion of the Best Basis Inventories (BBIs) that was retrieved from the tanks during the later part of retrieval, after selective removal of the relatively high-activity liquid had

(a) Mahoney, L.A. November 12, 2004. *Waste Simulant Formulation for Series-22 Bulk Vitrification Tests*, letter report ST05.004, Pacific Northwest National Laboratory, Richland, Washington.

taken place. The SST LAW wastes did not fit within WTP-based clusters; they were statistically subdivided into 8 clusters. These 8 clusters (identified as Y1 through Y8) replace the 4 low-curie waste clusters that were defined in the preceding Series-22 report (identified as X1 through X4).

The average compositions of the 25 clusters defined in this report were calculated in terms of waste oxide and are presented in Section 5. Then the mass of glass required for each cluster was determined for “conservative,” “best estimate,” and “stretch” formulations for each of two different mixtures of Hanford soil and additives. The results of these calculations are given in Section 6.

2.0 Background

The currently defined waste streams that are potentially directed to ST include the following:

- Some portion of the LAW stream produced by the WTP pretreatment process. LAW is strongly alkaline with a total Na concentration in the range of 5 to 10 M. It is not yet determined whether the LAW sent to ST will be 1) a fraction of what is sent to the WTP melters, thus having the same range of compositions as the WTP melter feed; 2) only the excess LAW over what can be stored, which will not be available to ST at all times and so will only include a subset of the WTP LAW compositions; or 3) the LAW streams whose compositions are the most challenging to the WTP melters (for example, high-SO_4 streams) but are not representative of LAW as a whole.

- The submerged-bed scrubber (SBS) condensate streams, which originate in the WTP LAW process off-gas system and are dilute alkaline solutions, relatively high in Cl, F, NO_3, NO_2, and SO_4.

- The wet electrostatic precipitator (WESP) streams, dilute and near-neutral pH solutions, which also come from the WTP LAW process off-gas system.

- Demineralized water used to adjust WTP LAW off-gas condensate chemistry.

- Low-activity waste from low-curie saltcake tanks that is sent to ST without being routed through WTP pretreatment. This type of waste will be similar in nature to the LAW, but with lower concentrations of Al and higher concentrations of SO_4 and PO_4.

Other as-yet undefined streams may also be included; for example, the liquids produced by the ST ICV off-gas system may be recycled into the ST feed. At this time, there is no information about the composition or volume of any such additional streams.

The interface between WTP and ST also remains to be defined. This report, like the preceding Series-22 report, considers an interface design in which 50 percent of the concentrated LAW is sent to ST during all periods when LAW is being produced. There the LAW is mixed with off-gas product (SBS condensate, WESP solution, and demineralized water) that has been separately concentrated by ST. Because LAW is not produced at all times, there are some periods when the ST feed is pure off-gas product.

The best available source of predicted WTP stream compositions is a recent run of the WTP G2 dynamic flowsheet model[a] (as described in 24590-WTP-MRR-PO-04-0011, Rev. 0). The run provided output at weekly intervals for the mass of each constituent that made up the WTP LAW, excess LAW,[b] and off-gas product streams. This resulted in 1451 discrete batches for each stream.[c] The first week of

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(a) Model run request 24590-WTP-MRQ-PO-04-0665, *Supplemental LAW Data Collection.* Run results were transmitted to the U.S. Department of Energy, Office of River Protection on September 16, 2004. The software run was the Dynamic (G2) Model, version 3.1 (with run-specific changes described in the run request).

(b) "Excess LAW" refers to the overflow from the storage tanks that supply the WTP melters. Adding excess LAW to WTP LAW gives the total LAW produced by pretreatment.

(c) The G2 model identifiers for the streams were V41001_V21001, V41001_V21002 (the two WTP LAW melter feeds), V41001_LAW-OVERFLOW-1 (the excess LAW to ST), and V25003_LAW-OVERFLOW-2 (the off-gas product coming from vessel RLD-VSL-00005).

output was December 7, 2009, and the last was September 28, 2037. The end-of-mission date was later than 2028, which was accepted because the run was intended only to predict the overall population of feed compositions, not to indicate the anticipated time period to treat all the tank waste.

The G2 run used the TFCOUP5A feed vector (Kirkbride et al. 2003) and its associated leach factors, together with run parameters that represent the latest dates of hot commissioning, hot operation, and ramp up, and the associated melter production rates (within the design limitations of the WTP). Some of the characteristics of the run that should be kept in mind in interpreting the predicted compositions are

- The TFCOUP5A feed vector excludes from LAW pretreatment the soluble wastes from the 20 tanks that at the time of the vector's generation were considered to contain low-curie wastes that could be sent directly to ST without pretreatment in the WTP plant. The excluded tanks were B-101, B-102, B-103, B-105, B-106, B-107, B-108, B-109, BX-103, BX-107, BX-108, BX-109, BX-110, BY-102, BY-105, BY-108, BY-111, BY-112, S-109, and TY-102.[a] Only the insoluble fraction of these tanks (i.e. sludge) is sent to the WTP for processing.

- Constituent concentrations that are derived from supplemental BBI information (including Ag, As, Ba, Cd, Mo, Sb, Se, and Tl) should be interpreted with great caution. The Se concentrations, in particular, were represented in the TFCOUP5A feed vector by minimum detection limits for the ICP analytical results. This resulted in very high upper bounds for the Se concentrations in the wastes for which ICP fusion digestions were used.[b]

- A new LAW glass model for waste loading was used to hold the Na_2O concentration in glass to 20 wt%, except when it had to be forced lower to keep the SO_3 concentration in LAW glass to a maximum of 0.8 wt%.

- The time necessary to process the feed was calculated with G2 as 28 years, with calculated average ILAW and IHLW production rates of 18.6 and 4.2 metric tons/day, respectively. Envelope C processing was not included in the run, which caused more Sr and TRU to be sent to LAW glass than would have been sent otherwise. In actual processing, the Sr and TRU will be removed from the Envelope C wastes.

- The SBS reactions were updated to adjust melter ammonia production such that the pH in the SBS would remain in the range of 6.5 to 7.5.

- The G2 model does not maintain charge balance. The results must be post-processed to balance cations and anions, if a full simulant recipe is required (rather than a waste-oxides mixture formulation).

To complete the TFCOUP5A feed vector, only the wastes from the 20 SSTs indicated above were needed. However, this set of 20 SSTs is not completely consistent with the current plans for low-curie

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(a) Personal communication, R. Kirkbride to L.A. Mahoney, regarding TFCOUP5A vector and excluded SSTs, telephone conversation on October 21, 2004.

(b) Personal communication, D.E. Place to L.A. Mahoney, regarding Se inventories as used in TFCOUP5A, e-mail on October 12, 2004.

feeds to ST. Current plans take into account improved tank waste characterization data, operations in the tank farms, and improved data on selective dissolution during retrieval.[(a), (b)]

The current set of low-curie waste tanks contains 27 SSTs: B-101, B-103, B-105, B-108, BX-111, BY-102, BY-103, BY-105, BY-108, BY-109, BY-111, BY-112, S-105, S-109, T-109, TX-103, TX-105, TX-108, TX-110, TX-111, TX-112, TX-114, TX-115, TX-117, TX-118, TY-102, and U-107. Eleven of these tanks are among those excluded from the TFCOUP5A feed vector. The other 16 current tanks contain waste that is already part of the WTP-derived waste streams because it was included in the feed vector. However, these 16 wastes also need to be considered under the assumption that they will not pass through WTP pretreatment (although they will be pretreated by solid-liquid separation and selective dissolution). Accordingly, in this report the wastes in these 16 tanks were considered as low-curie feeds, in addition to the 20 excluded SSTs whose wastes were used in the preceding Series-22 report. In some cases, as needed, this report refers to the 16 tanks as "double-counted" tanks and discounts their waste contribution to avoid double-counting.

The insoluble fraction of the waste in the 36 low-curie tank wastes is considered to be sent to the WTP for processing. Selective dissolution is assumed to be applied to the soluble fraction to reduce the soluble radionuclides transferred to the ST.

(a) Raymond, R.E. October 20, 2004. *Candidate Single-Shell Tanks for Low-Curie Feed to Supplemental Treatment*, letter report 7F300-04-RER-001 R1, CH2MHILL Hanford Group, Inc.

(b) Retrieval that depends on water dissolution of the waste is a partially selective process because the waste interstitial liquid originally present in the waste, with its burden of completely dissolved high-activity constituents such as ^{137}Cs and ^{99}Tc, is flushed out of the waste before most of the relatively low-activity solids are dissolved. Hence, the waste retrieved after the initial flushing phase has lower activity and a higher proportion of freshly dissolved salt constituents than does the waste from the initial phase of dissolution retrieval.

3.0 Composition Variability

The first step in developing simulants was to determine the variability of ST feed composition during the WTP campaign with respect to the waste constituents that most affect glass properties and melter system performance. These significant constituents, and the reasons for their significance, were the following:

- Al, in its oxidized form Al_2O_3, affects the durability of the glass
- Ca, in its oxidized form CaO, affects the durability
- Cl is primarily a melter off-gas concern, but may influence volatility and/or salt phase separation
- F can cause phase separation in glasses and is also a melter off-gas concern
- Mo, in its oxidized form MoO_3, can cause phase separation
- NO_2 and NO_3 affect the volatilization of Tc, the redox balance of the glass, and the off-gas system
- PO_4, in its oxidized form P_2O_5, can cause phase separation
- SO_4, in its oxidized form SO_3, can cause phase separation and may influence Tc volatility.

The approach taken to create a population of WTP-originated ST feeds was to assume a plant interface between WTP and ST that sends the off-gas product stream to ST for evaporation and mixes the off-gas concentrate with half the LAW to produce ST feed. The additional LAW feeds from the 36 low-curie tank wastes were calculated by multiplying the BBI of each constituent by its BBI water wash factor to reflect retrieval by water dissolution, and by a selective dissolution factor to account for the selective removal of initially dissolved constituents of the waste. The Appendix provides more detail about the method of calculating low-curie feed streams.

The total Na sent to the ST, including the 20 excluded low-curie tank wastes but excluding the 16 double-counted tank wastes, was 27 998 megagrams (Mg, or metric tons) of Na. Of this, 3168 Mg Na came from the excluded low-curie tank wastes alone, and 215 Mg Na came from the off-gas product alone. The double-counted tank wastes contained 4725 Mg Na.

For each ST feed stream, the waste oxide composition was calculated in terms of wt% Al_2O_3, CaO, Cl, F, MoO_3, NO_2+NO_3, P_2O_5, and SO_3 in a waste glass containing a nominal Na_2O oxide waste loading of 20 wt%. The wt% Na_2O was treated as constant in order to put all the streams on the same waste-loading basis. For the purpose of displaying composition variability, the cation and anion concentrations were used as supplied by the G2 model without imposing a charge-balance requirement.

Figures 3.1 through 3.8 show how much of the Na in all streams is associated with different nominal concentrations of each of the significant constituents: Al_2O_3, CaO, Cl, F, MoO_3,[(a)] NO_2+NO_3, P_2O_5, and SO_3. Note that to show the entire potential composition envelope, the 16 double-counted low-curie SSTs are included in these figures. The total Na represented in each figure is therefore 32 723 Mg Na, rather than the 27 998 Mg Na present in the ST feed alone.

In Figures 3.1 through 3.8, the columns (which are referred to the left y-axis) show the percentage of Na in each increment of nominal concentration of the constituent. The curves (which are referred to the right y-axis) represent the percentage of the total Na in the streams that is present below any given nominal concentration of the significant constituent. In cases where one tank or category of waste is the sole source of a concentration extreme, a note on the figure identifies the source(s) of waste.

For example, Figure 3.1 shows that, if the Na in all the streams is processed into a 20 wt% Na_2O glass waste form, about 25% of the Na can be found at nominal Al_2O_3 concentrations between 3.0 wt% and 4.0 wt% (the sum of the two tallest columns). The curve in the figure indicates that a 20 wt% Na_2O glass can hold a total of 85% of the Na while having a concentration of less than 5% Al_2O_3 from the waste.

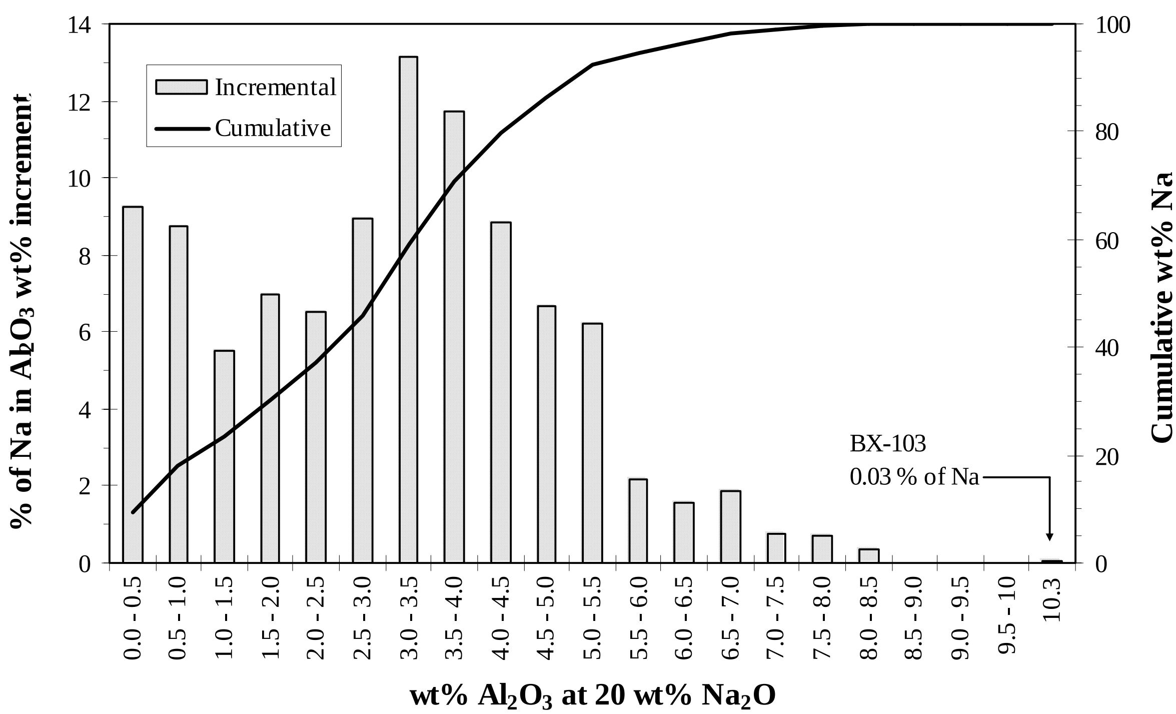

Figure 3.1. Relationship Between Al_2O_3 and Na

(a) Only 6 of the BBIs for the 20 excluded low-curie waste tanks included a Mo inventory: tanks B-106, B-107, BX-109, BY-105, BY-108, and S-109. The other 14 excluded SSTs, which contained 6.6% of the total Na in the ST feed, were assumed to contain no Mo for lack of data in their BBIs. Among the 16 double-counted low-curie waste tanks, only two (BY-109 and U-107) had Mo data in their BBIs; the others were assumed to contain no Mo.

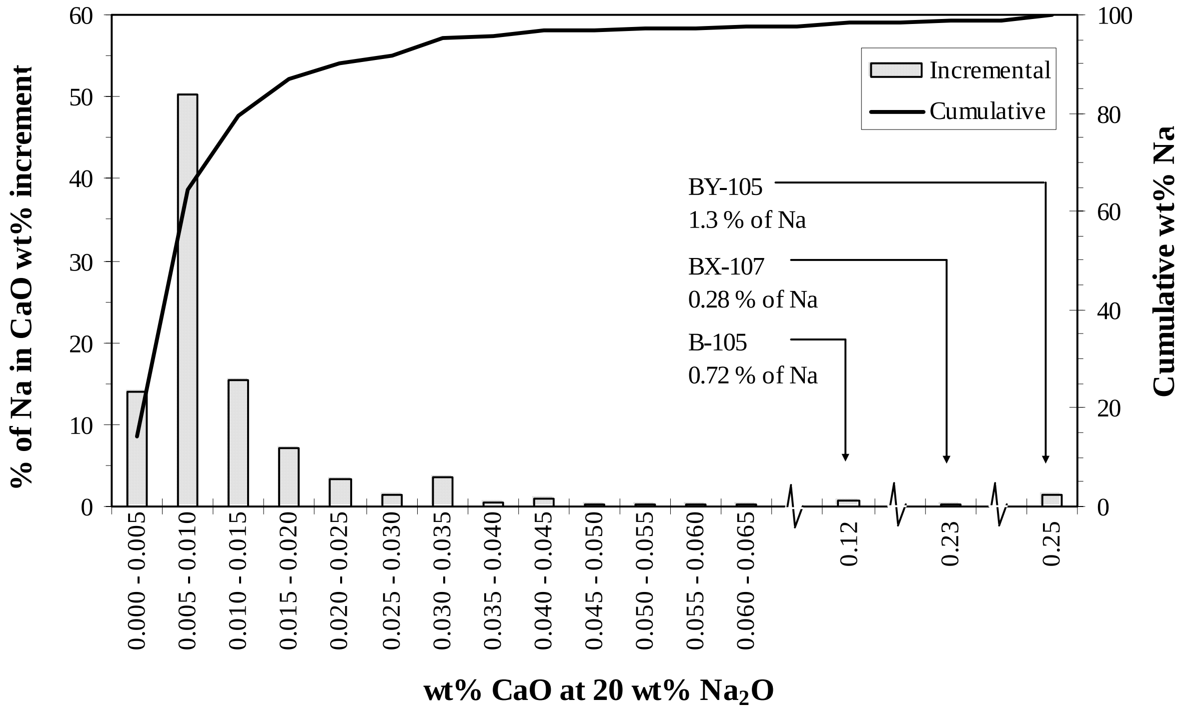

Figure 3.2. Relationship Between CaO and Na

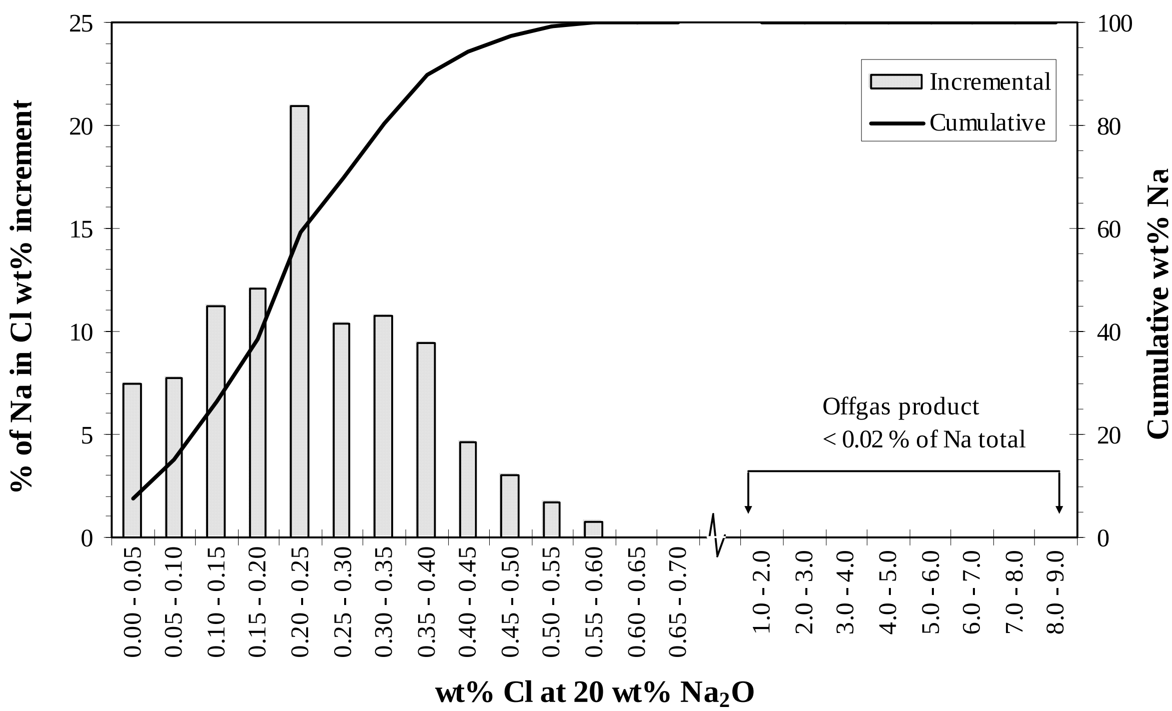

Figure 3.3. Relationship Between Cl and Na

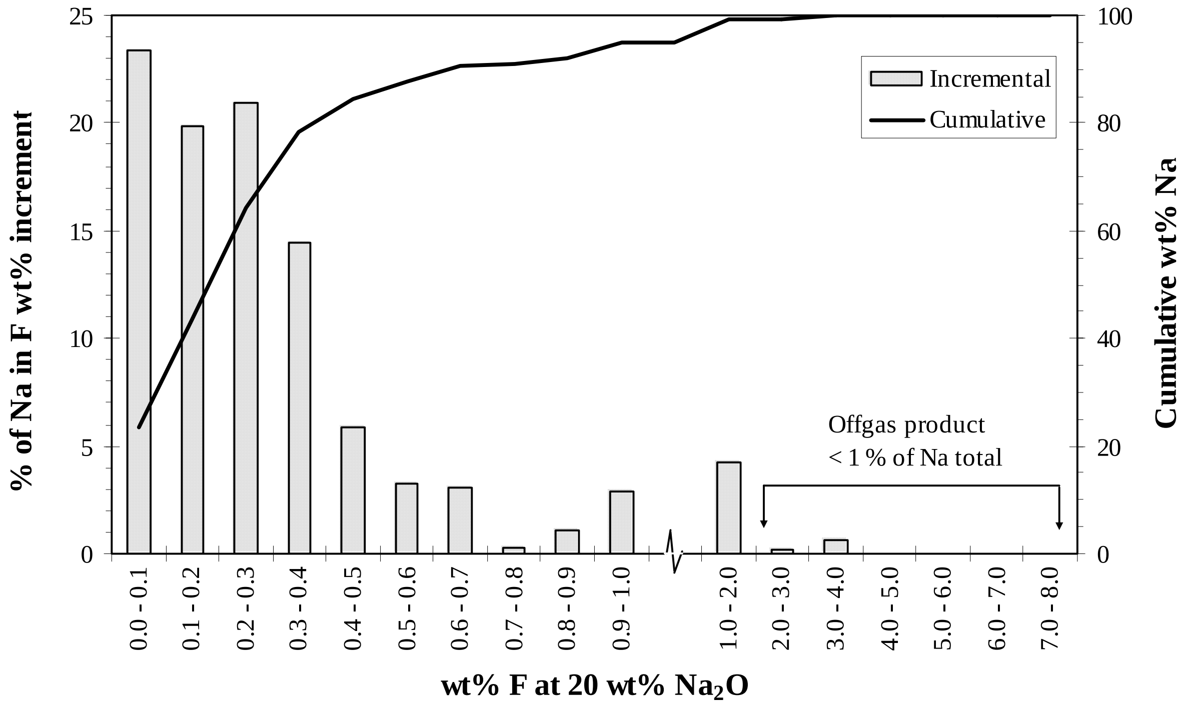

Figure 3.4. Relationship Between F and Na

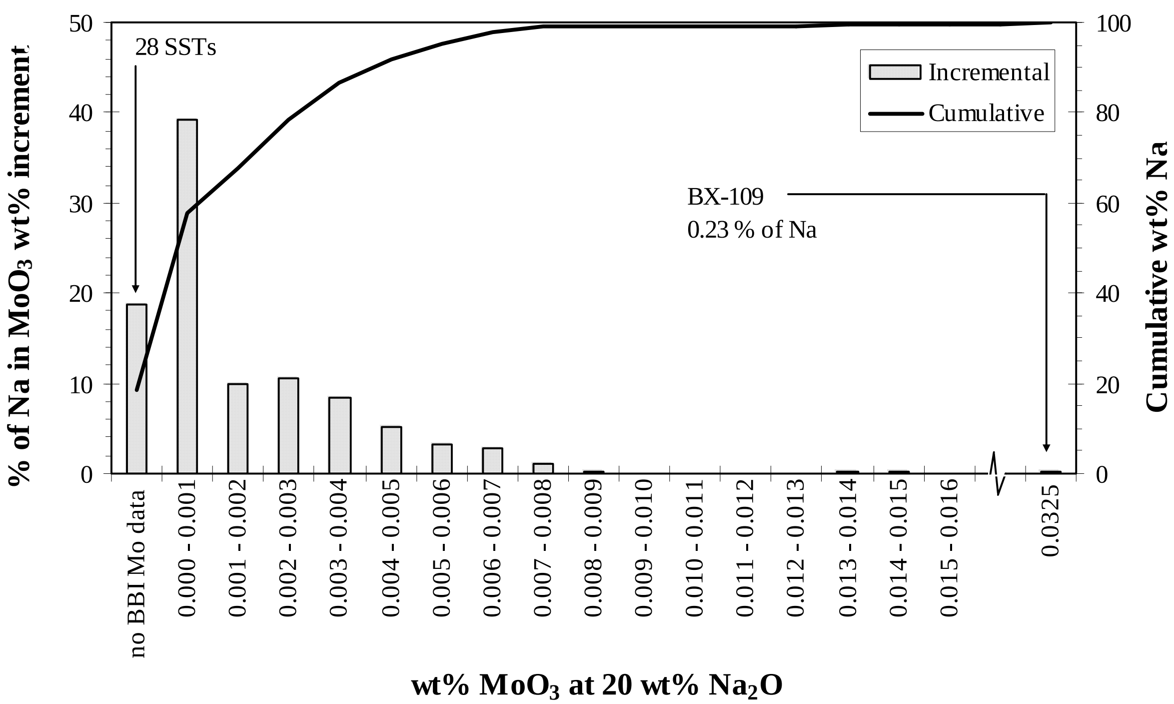

Figure 3.5. Relationship Between MoO_3 and Na

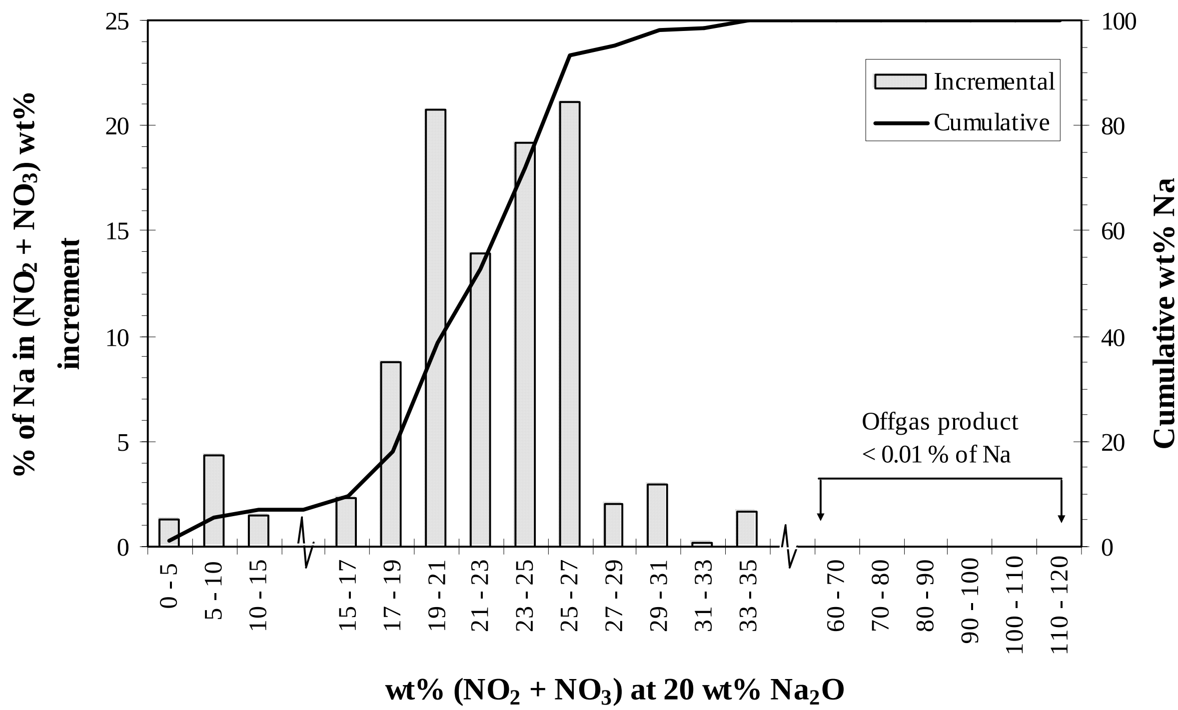

Figure 3.6. Relationship Between (NO_2+ NO_3) and Na

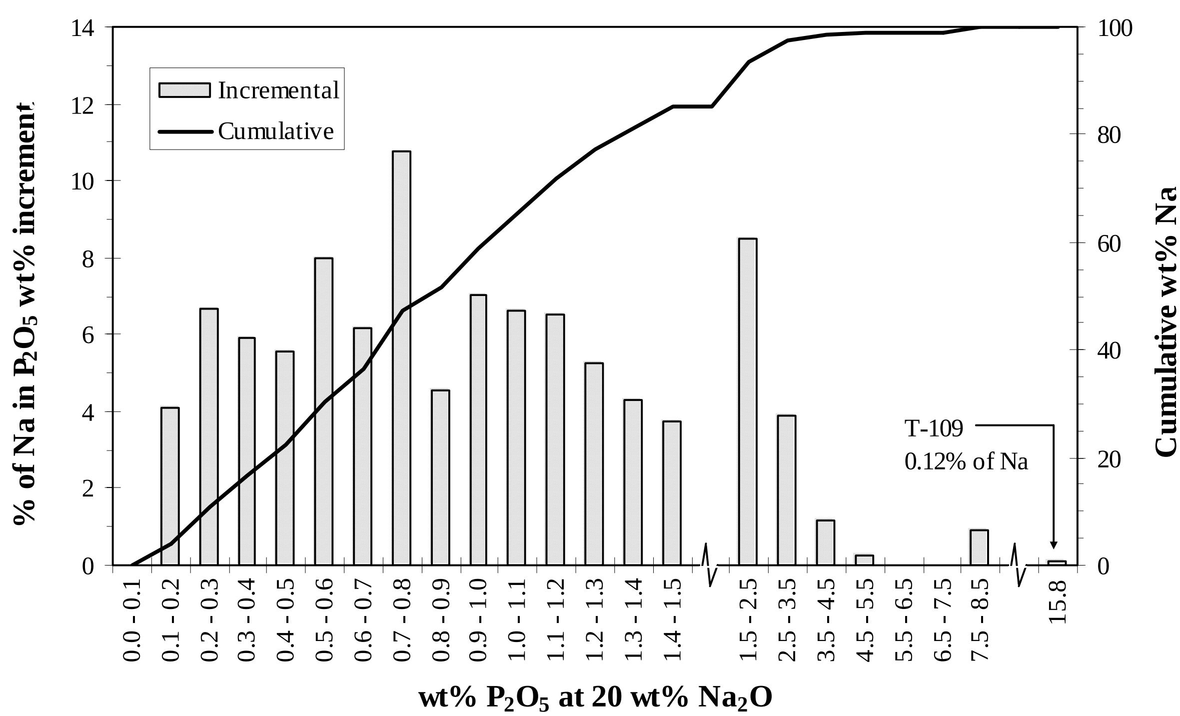

Figure 3.7. Relationship Between P_2O_5 and Na

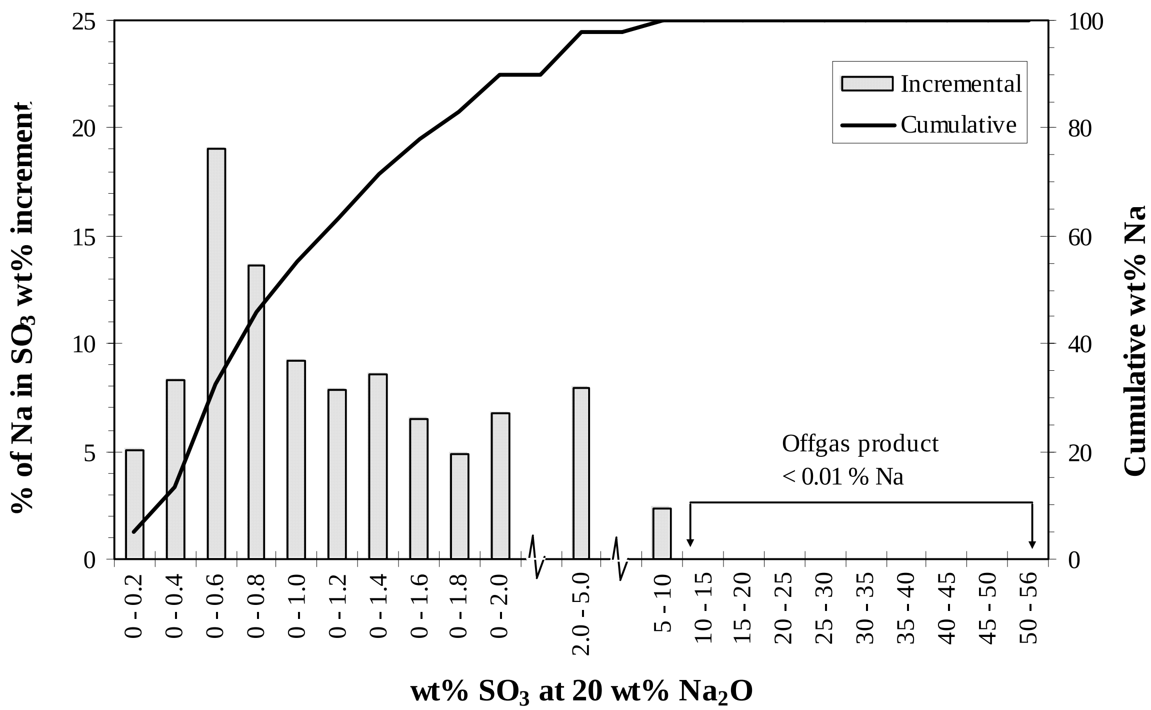

Figure 3.8. Relationship Between SO_3 and Na

Table 3.1. Summary of Significant Constituent Distributions

Constituent	Max. nominal wt% for 90% of the Na	Overall max. nominal wt%	Max. nominal wt% in ICV tests to date	% of Na that is above the tested maximum
Al_2O_3	5.2	10.3	0.77	82
CaO	0.024	0.25	0.0083	46
Cl	0.40	8.6	0.20	62
F	0.67	7.8	0.081	81
MoO_3	0.0044	0.032	---	---
NO_2+ NO_3	27	116	35.3	0.01
P_2O_5	1.7	16	0.50	78
SO_3	2.0	56	0.99	45

"Nominal" indicates that concentrations are based on an assumed 20 wt% Na_2O, although the waste-oxide compositions could contain less or more than that amount in practice.
The Na percentages are referred to the total Na in all LAW streams, including the wastes from the 16 double-counted tanks, a total sodium mass of 32 723 Mg Na.

Some aspects of the constituent distributions shown in Figures 3.1 through 3.8 are summarized in Table 3.1, from which the following conclusions can be drawn:

- The maximum nominal concentrations of MoO_3 and CaO are so low that although there may be reason to include these constituents in simulant recipes and glass formulations, there is no need to use them as criteria for defining "clusters."

- The maximum nominal concentrations of CaO and SO_3 that, as of November 2004, have been tested in glasses are about equal to the Na-weighted averages for all streams (a little less than 50% of the Na is associated with higher concentrations).

- The maximum tested nominal concentration of NO_2 plus NO_3 is an upper bound for almost all the LAW-dominated streams.

- The concentrations of Al_2O_3, Cl, F, and P_2O_5 in most of the streams are well above the concentrations that have been tested in glasses.

Figures 3.9 though 3.14 show the nominal concentrations of Al_2O_3, Cl, F, NO_2+NO_3, P_2O_5, and SO_3 in each of the nearly 1500 streams plotted against the mass of Na in each stream. These figures help to clarify which subsets of the feed streams contribute the significant species. The feed streams are subdivided into WTP streams that are dominated by off-gas-product, WTP streams that are dominated by LAW (which contain most of the Na), and streams derived from the 20 low-curie tank wastes.[a] (Note that the streams dominated by off-gas product may contain some pretreated LAW waste; similarly, the LAW-dominated streams usually contain some off-gas product.) The LAW-dominated WTP streams are further subdivided into a general set and a high-F set, based on the grouping that is evident in Figure 3.11.

The conclusions to be drawn from Figures 3.9 through 3.14 include the following:

- The low-curie tank waste compositions are frequently outside the concentration ranges of most of the LAW streams generated by the WTP pre-treatment facility. Several low-curie wastes are higher in nominal P_2O_5 and SO_3 than the WTP-derived LAW streams, and most are lower in nominal Al_2O_3 and Cl.

- The streams dominated by off-gas product contain very little Na and Al but have high nominal concentrations of most of the significant anion species (Cl, F, NO_2+NO_3, and SO_3).

- The streams with high nominal fluoride (defined as those that are not dominated by off-gas product but have F concentration of 0.745 wt% or higher at 20 wt% Na_2O) tend to be distinguishable from other LAW feed in other ways as well. Figures 3.9 and 3.14 show that the high-F LAW streams are lower than most in Al_2O_3 and SO_3.

(a) In Figures 3.9 through 3.14, the low-curie tank waste streams stand out artificially from the WTP-based streams because they are considered as whole-tank batches and not broken down into weekly batches. They therefore contain much more Na per "batch."

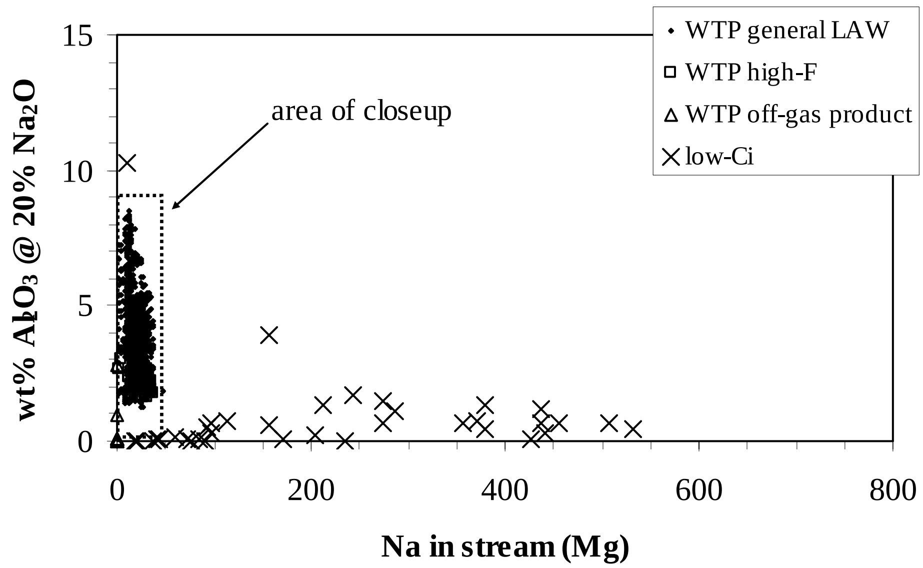

Figure 3.9a. Nominal Al_2O_3 Concentration Versus Na Mass, by Stream

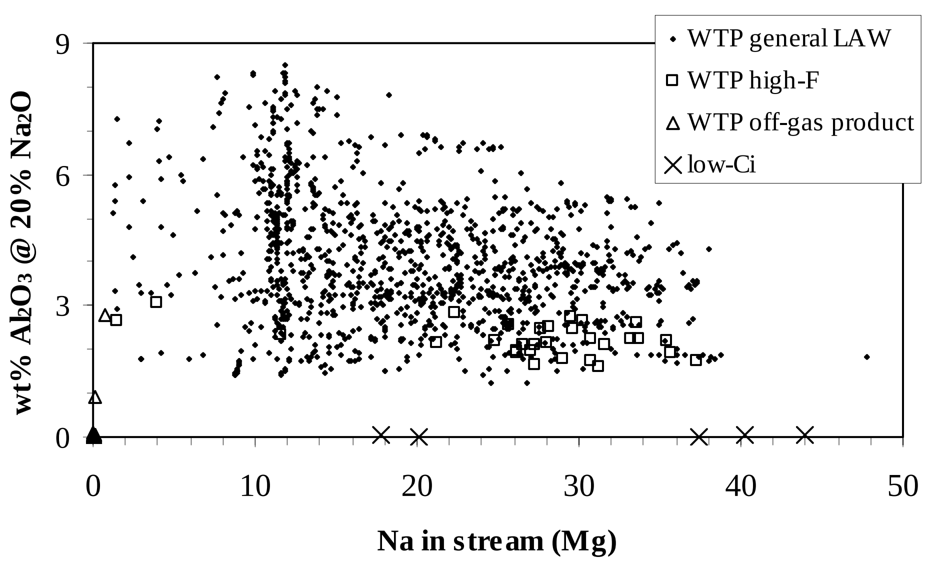

Figure 3.9b. Close-up of Nominal Al_2O_3 Versus Na Mass by Stream

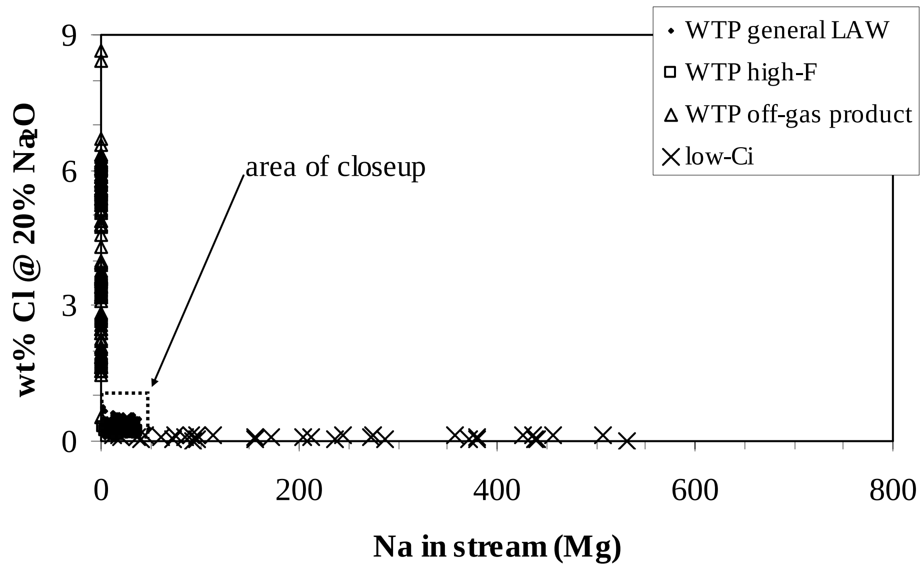

Figure 3.10a. Nominal Cl Concentration Versus Na Mass by Stream

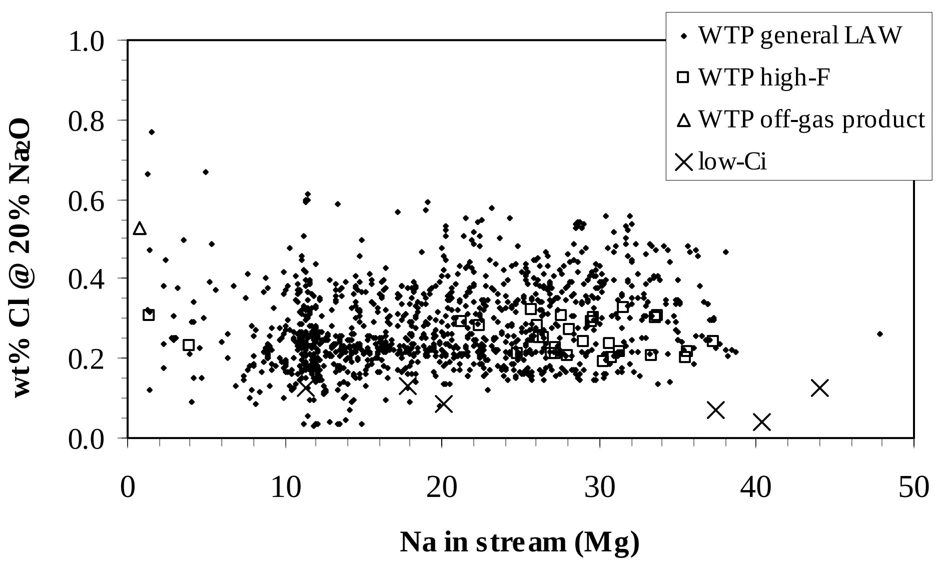

Figure 3.10b. Close-up of Nominal Cl Versus Na Mass by Stream

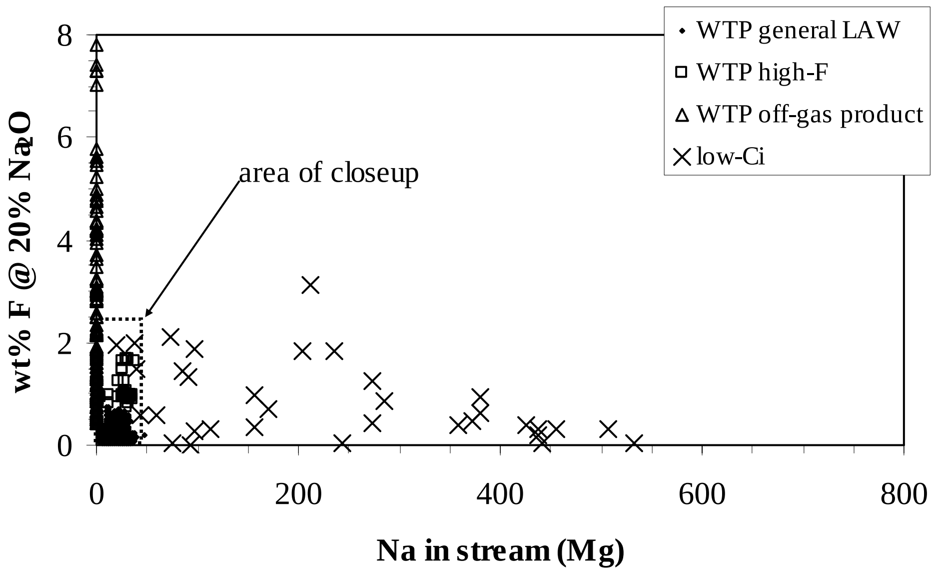

Figure 3.11a. Nominal F Concentration Versus Na Mass, by Stream

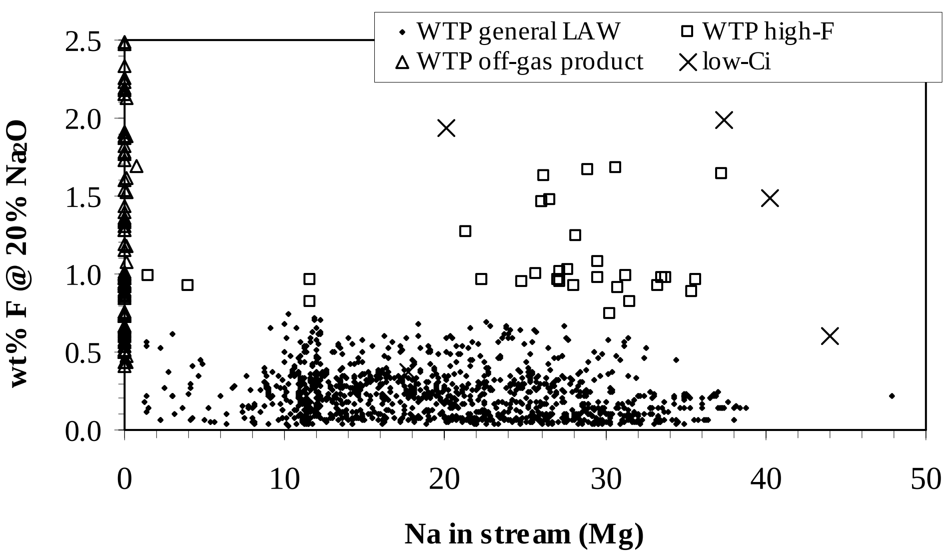

Figure 3.11b. Close-up of Nominal F Versus Na Mass, by Stream

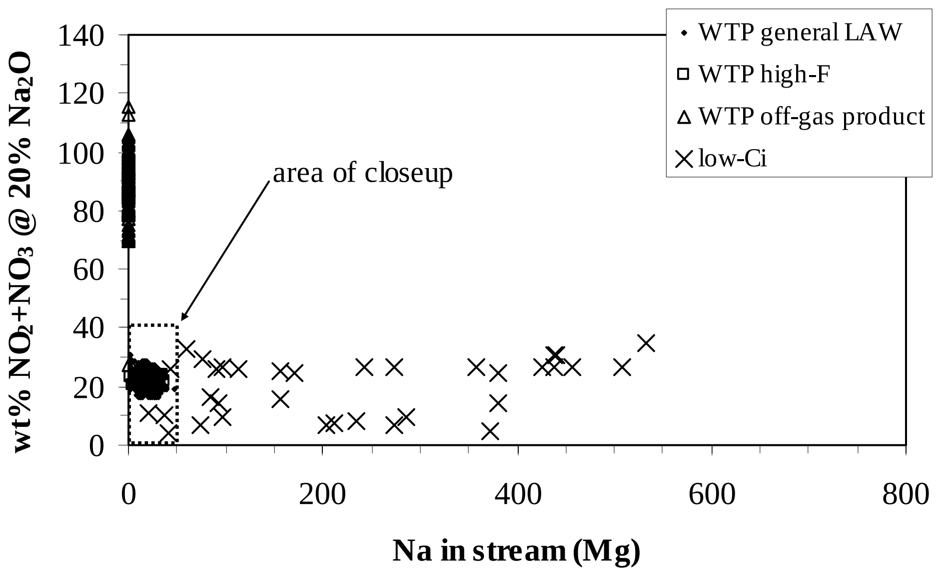

Figure 3.12a. Nominal (NO_2+NO_3) Concentration Versus Na Mass by Stream

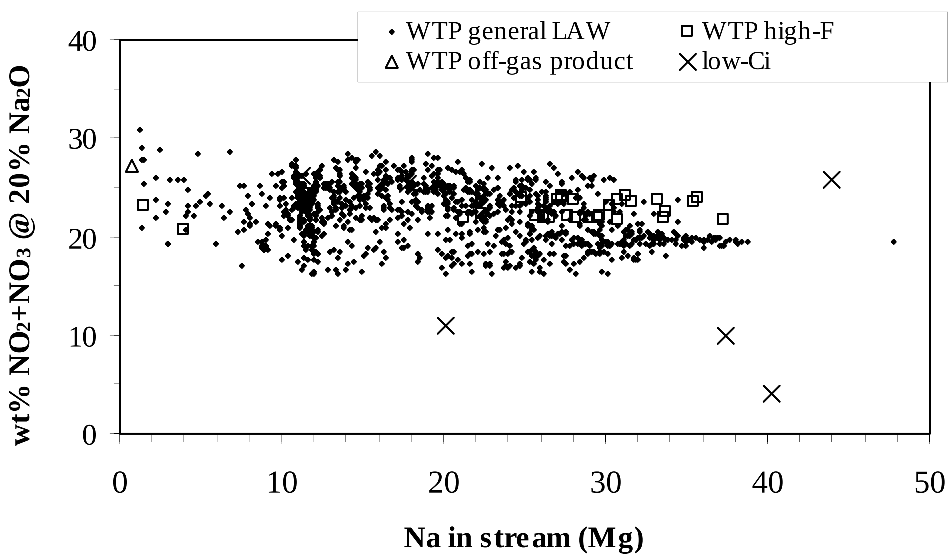

Figure 3.12b. Close-up of Nominal (NO_2+NO_3) Versus Na Mass by Stream

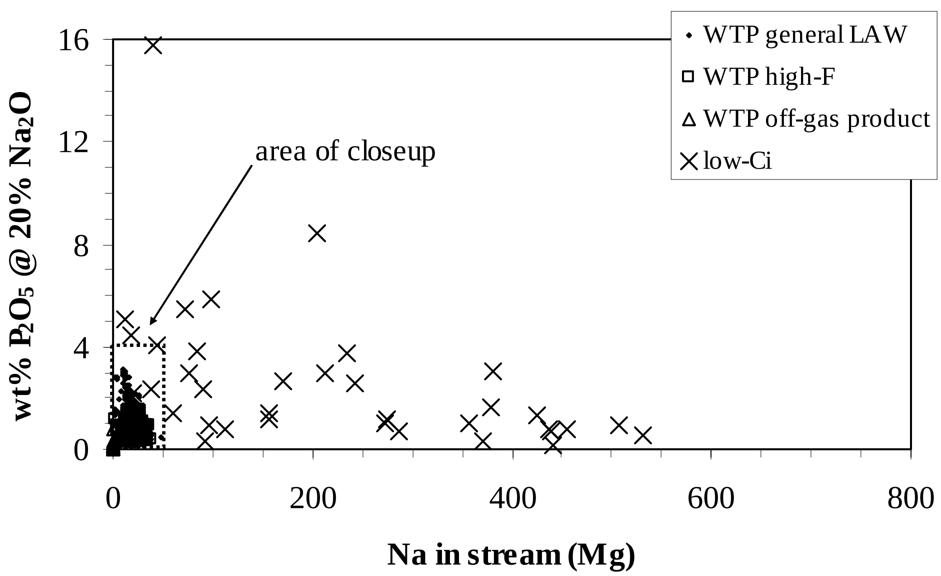

Figure 3.13a. Nominal P_2O_5 Concentration Versus Na Mass by Stream

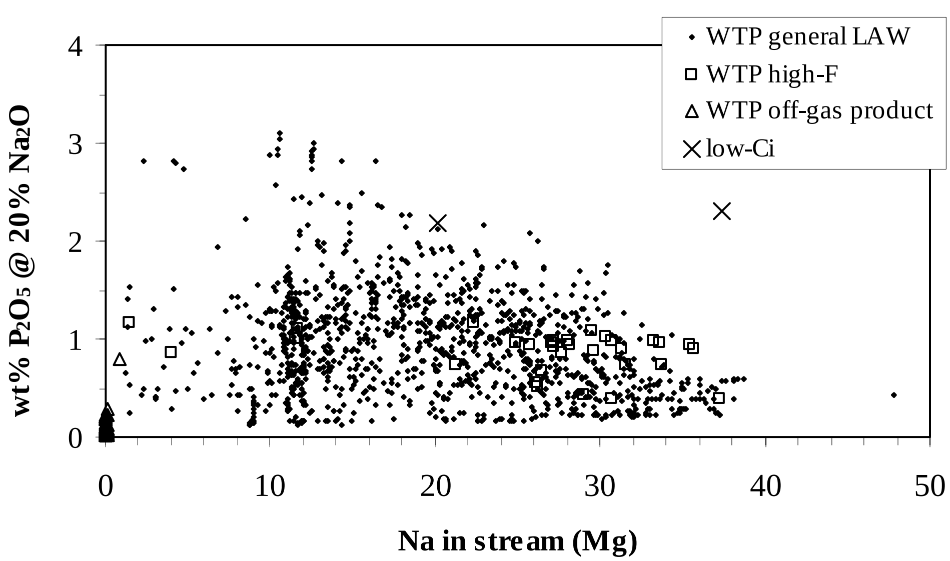

Figure 3.13b. Close-up of Nominal P_2O_5 Versus Na Mass by Stream

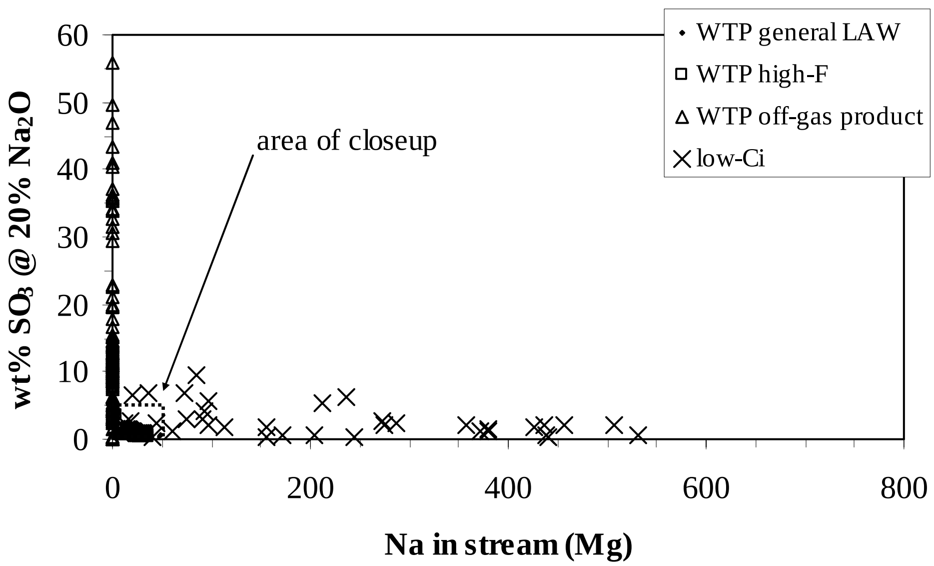

Figure 3.14a. Nominal SO_3 Concentration Versus Na Mass, by Stream

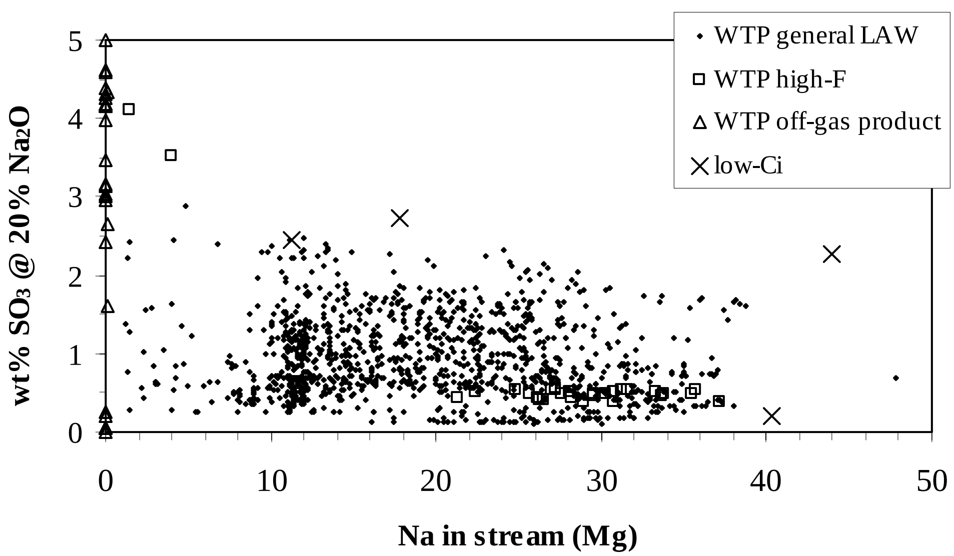

Figure 3.14b. Close-up of Nominal SO_3 Versus Na Mass, by Stream

4.0 Cluster Analysis

The WTP-pretreated and low-curie-waste feed streams formed a large population of compositions that, for practical purposes, had to be reduced to roughly 20 potential waste formulations. The first step in accomplishing this was to separate the clearly distinguishable sets. These were

- Streams from low-curie tank wastes
- Streams dominated by off-gas product (defined as containing less than 1000 kg Na)
- High-F WTP-pretreated LAW streams (defined as containing a nominal F concentration of 0.745 wt% or greater at 20 wt% Na_2O).[a] The fluoride breakpoint is low enough to have no significance to ICV. As was noted in Section 3 and shown in Figures 3.9 and 3.14, streams that contain more than this nominal F concentration, and streams that have less, tend to differ from each other in terms of some other constituent concentrations as well. This separation of populations was the reason for choosing the breakpoint.

The remaining majority of the WTP-derived streams were subjected to "cluster analysis," a statistical method for separating data points into groups. Each group contains the streams whose compositions are similar to the group's average composition and significantly different from the average compositions of the other groups. The computational tool used for this analysis was JMP™[b] (SAS 2004a, 2004b). The statistical method of analysis was *k*-means clustering, an iterative approach to assigning data points to the nearest cluster.

To perform a cluster analysis with the JMP program, the user inputs the variables to use as cluster-definition criteria and the desired number of clusters. The nominal concentrations of Al_2O_3, P_2O_5, and SO_3 (that is, the concentrations of those oxides at a nominal Na_2O concentration of 20 wt%) were chosen as cluster criteria. To prevent the higher concentration range of Al_2O_3 from overly influencing the cluster selection in its favor, the three concentrations were standardized by dividing them by their standard deviations before they were used to define clusters. Different numbers of clusters were tested and it was found that a minimum of 15 clusters were needed to produce distinct clusters with relatively narrow ranges of the criterion variables. Note that all of these 15 clusters are exactly the same as in the preceding Series-22 report.[c]

No close matches were found between the 36 low-curie tank waste streams and the 15 WTP-derived LAW clusters. By contrast, the Series-22 report found that the five BY tanks in the excluded low-curie waste set matched WTP-derived LAW clusters. Apparently the application of selective dissolution factors decreased the similarity between low-curie tank wastes and WTP-derived LAW.

(a) One borderline high-fluoride stream, the one predicted by G2 for the week of June 9, 2032, was placed in a low-fluoride cluster (number 14). This stream assignment did not significantly skew the composition of either of the clusters involved because the stream contained only 1% of the total cluster Na.
(b) JMP is a trademark of SAS Institute, Inc., Cary, North Carolina.
(c) Mahoney, L.A. November 12, 2004. *Waste Simulant Formulation for Series-22 Bulk Vitrification Tests*, letter report ST05.004, Pacific Northwest National Laboratory, Richland, Washington.

Because the current study found no matches between individual low-curie waste streams and WTP-derived clusters, the low-curie waste streams were put through cluster analysis separate from the one done for WTP-derived LAW. This approach also allowed the WTP-derived streams and the low-curie-waste streams to be maintained in separate categories, which is desirable because different blending and pretreatment assumptions were made for these groups. The low-curie cluster analysis separated the low-curie waste streams into 8 distinct clusters that were broader than the clusters for the WTP-derived LAW streams. These 8 clusters are replacements for the 4 low-curie clusters in the Series-22 report.

Table 4.1 gives the characteristics of the final 25 clusters in terms of the nominal concentrations of Al_2O_3, P_2O_5, and SO_3 (in 20 wt% Na_2O glass) and the mass of Na in each cluster. The “O,” “F,” and “Y*n*” clusters in Table 4.1 represent, respectively, off-gas product, high-F WTP-pretreated LAW, and low-curie tank wastes. This version of Table 4.1 should be used instead of Table 2 in the Series-22 report because it includes a larger set of low-curie wastes.. The current table has different low-curie waste clusters; in addition, the Na totals are different for some of the WTP-derived clusters because the Na contributed by the BY low-curie tanks has been removed.

Figures 4.1 through 4.3 depict the distributions of the nominal Al_2O_3, P_2O_5, and SO_3 concentrations in the clusters and in the total ST feed (labeled “ST”). The clusters are ranged along the x axis, and the nominal concentration is on the y axis. In the symbol used for each cluster, the box represents the range from the arithmetic average minus one standard deviation to the arithmetic average plus one standard deviation. The top line of the symbol ends at the maximum concentration, and the bottom line ends at the minimum. The diamonds represent the Na-weighted average nominal concentration, which is in most cases lower than the arithmetic average. Clusters that contain only one stream are shown by dashes, which in some cases are off scale and therefore marked with arrows.

Table 4.1. Cluster Definitions

Cluster	Mass of Na (Mg)	Nominal wt% [a]								
		Al_2O_3			P_2O_5			SO_3		
		Min.	Avg.	Max.	Min.	Avg.	Max.	Min.	Avg.	Max.
1	6059	3.6	4.5	5.9	0.16	0.51	0.93	0.11	0.42	0.78
2	1314	2.6	3.5	5.1	1.4	1.8	2.4	0.60	0.86	1.2
3	1715	3.5	4.4	5.8	0.89	1.2	1.6	0.97	1.3	1.7
4	273	4.7	5.9	6.6	2.2	2.7	3.1	0.45	0.66	1.0
5	14	4.6	4.8	5.8	1.4	1.6	1.6	1.9	2.0	2.4
6	2169	2.3	3.3	4.1	0.88	1.1	1.5	1.2	1.6	2.0
7	2571	2.0	3.2	4.4	0.58	0.98	1.4	0.41	0.83	1.2
8	1467	1.7	2.5	3.4	0.25	0.70	1.0	1.0	1.4	1.8
9	184	2.2	2.7	3.1	0.16	0.18	0.28	1.8	2.2	2.5
10	1019	6.0	7.1	8.5	0.16	0.44	1.0	0.13	0.38	0.88
11	1089	4.9	6.0	7.5	0.53	0.88	1.5	0.71	1.0	1.6
12	1478	1.5	2.4	3.3	1.2	1.5	2.0	0.82	1.2	1.7
13	958	1.2	2.0	3.2	0.86	1.2	1.5	1.8	2.0	2.9
14	740	3.9	4.9	6.9	0.89	1.4	1.9	0.33	0.70	1.1
15	2956	1.4	2.7	3.6	0.12	0.35	0.77	0.35	0.60	0.98
O	4.0	0.011	0.62	2.8	0.017	0.22	0.79	0.003	12	56
F	819	1.6	2.2	3.0	0.39	0.84	1.2	0.39	0.50	4.1
Y1[b]	40	0.067	0.067	0.067	16	16	16	0.22	0.22	0.22
Y2[c]	11	10	10	10	5.1	5.1	5.1	2.4	2.4	2.4
Y3[d]	1186	0.030	1.5	3.9	0.73	1.2	2.4	1.2	2.0	3.0
Y4[e]	212	1.3	1.3	1.3	3.0	3.0	3.0	5.4	5.4	5.4
Y5[f]	5691	0.031	0.61	1.7	0.16	1.1	4.4	0.17	1.4	4.1
Y6[g]	85	0.038	0.038	0.038	3.8	3.8	3.8	9.6	9.6	9.6
Y7[h]	204	0.2	0.2	0.2	8.5	8.5	8.5	0.48	0.48	0.48
Y8[i]	463	0	0.075	0.32	2.2	4.3	5.9	5.6	6.2	6.8
ST Feed[j]	27 998	0	3.4	10	0.017	0.96	5.9	0.003	1.1	56
Overall [k]	32 723	0	3.0	10	0.017	1.1	16	0.003	1.2	56

(a) "Nominal" indicates that concentrations are based on an assumed 20 wt% Na_2O, though some compositions would contain more or less than that amount of soda in practice.
(b) Cluster Y1 contains T-109 and is 100% double-counted.
(c) Cluster Y2 contains BX-103 and is 0% double-counted.
(d) Cluster Y3 contains BX-107, BY-102, BY-103, BY-108, and BY-111. The Na in the cluster is 32.0% double-counted (from BY-103).
(e) Cluster Y4 contains BY-109 and is 100% double-counted.
(f) Cluster Y5 contains B-101, B-106, BX-108, BX-109, BX-110, BX-111, BY-105, BY-112, S-105, S-109, TX-103, TX-105, TX-108, TX-110, TX-111, TX-112, TX-114, TX-115, TX-117, TY-102, and U-107. The Na in the cluster is 68.3% double-counted. It should be noted that S-109 waste is not conservatively representative of this cluster, being below average in all three criterion constituents (nominal Al_2O_3=0.48%, P_2O_5=0.51%, SO_3=0.52%).
(g) Cluster Y6 contains B-107 and is 0% double-counted.
(h) Cluster Y7 contains TX-118 and is 100% double-counted.
(i) Cluster Y8 contains B-102, B-103, B-105, B-108, and B-109. The cluster is 0% double-counted.
(j) The ST feed contains all WTP-derived streams plus the 20 excluded low-curie SST wastes. It does not include the 16 double-counted low-curie wastes.
(k) "Overall" contains all the streams, ST feed plus the 16 double-counted low-curie SST wastes.

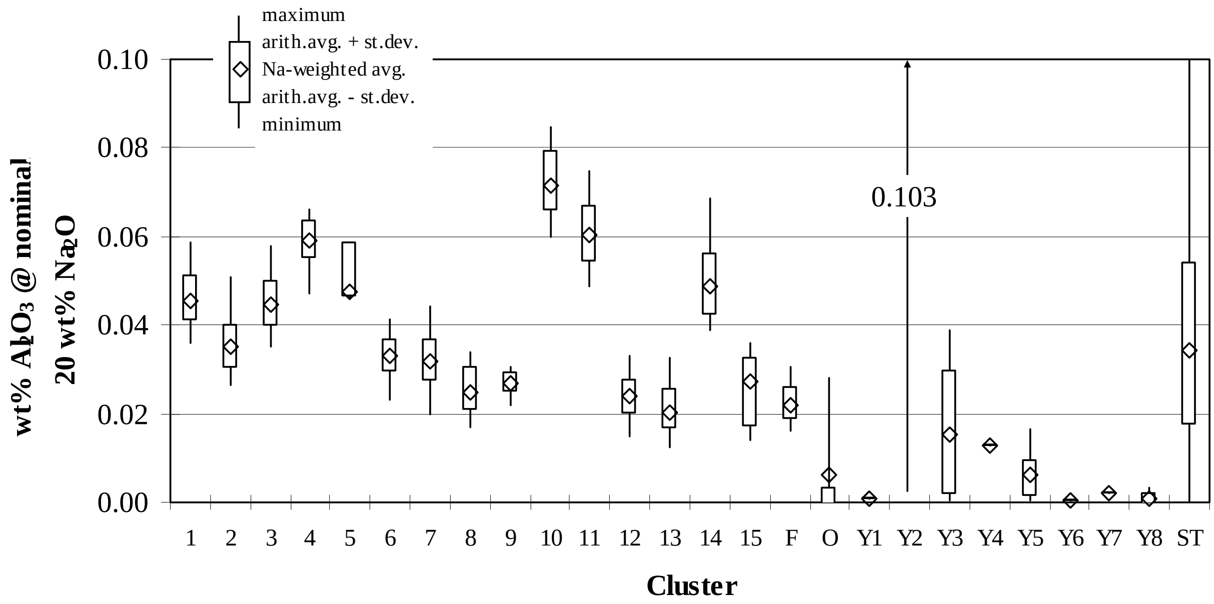

Figure 4.1. Distribution of Nominal Al_2O_3 Concentrations Among Clusters

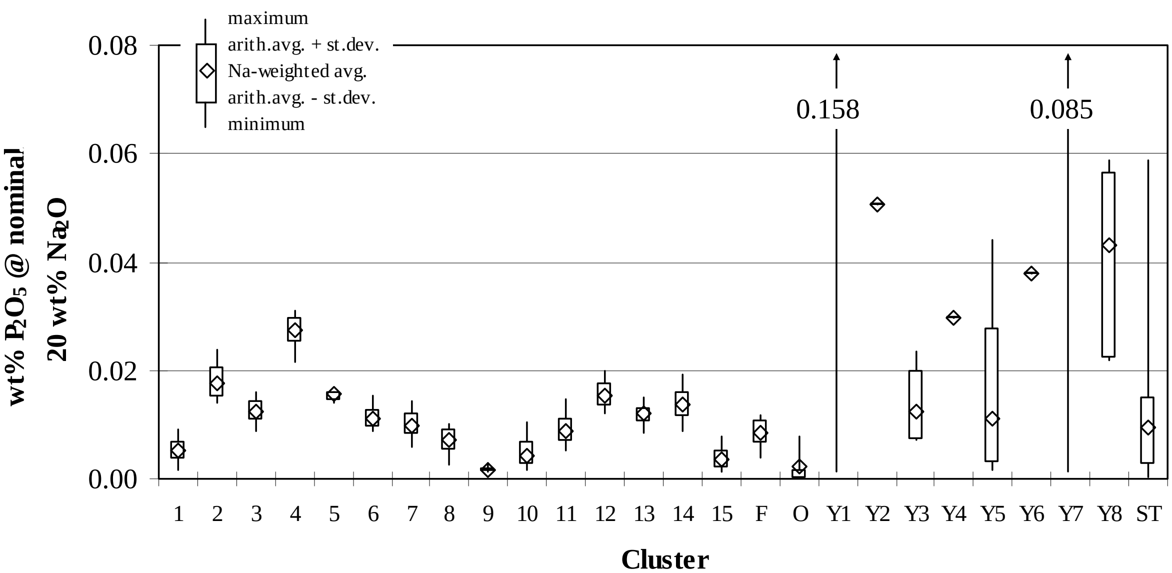

Figure 4.2. Distribution of Nominal P_2O_5 Concentrations Among Clusters

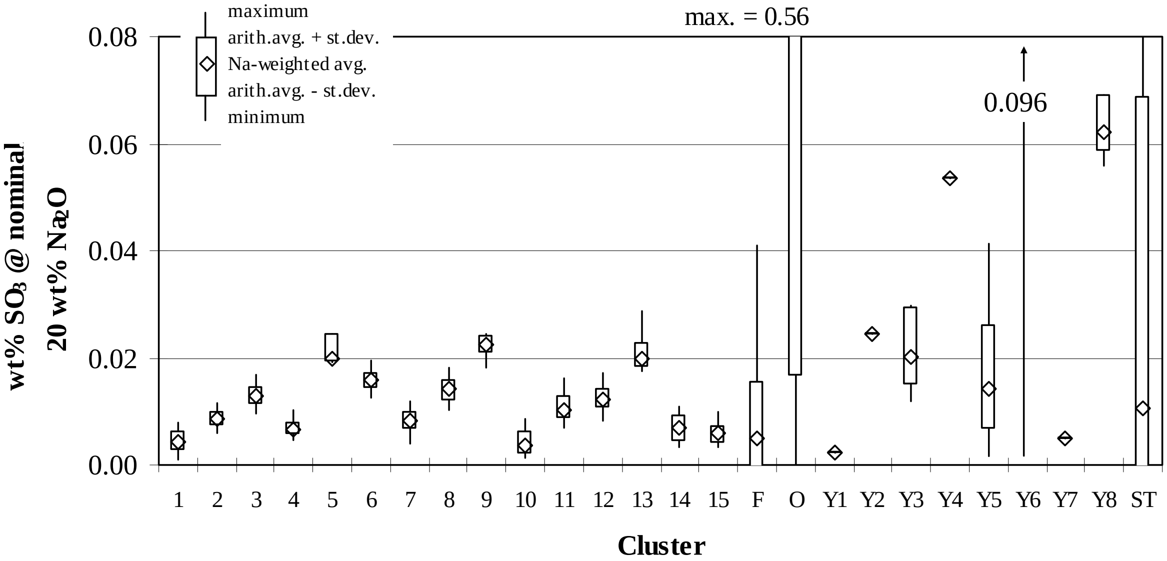

Figure 4.3. Distribution of Nominal SO_3 Concentrations Among Clusters

5.0 Cluster Compositions

The compositions of the 25 clusters already described were calculated in terms of the cluster-average waste oxide fraction of every constituent for which data were available. Equation (5.1) was used to find the waste-oxide fraction.

$$x_i = \frac{m_i f_i}{\sum_j m_j f_j} \tag{5.1}$$

where x_i = weight fraction of oxide *i* in waste-oxide mixture

m_i = mass of species *i* in stream

f_i = stoichiometric factor that converts species *i* to its oxide form; this factor is 0 for NO_2, NO_3, NH_3, OH, organic and inorganic carbon species, water, and other species with volatile products.

The resulting waste-oxide compositions, which are the compositions needed for glass formulation assessment, are given in Tables 5.1 through 5.25. Of these, Tables 5.1 through 5.17 are identical to Tables 3 through 19 in the Series-22 report. Tables 5.18 through 5.25 differ from Tables 20 through 23 in the Series 22 report and should be used instead of them.

A later report, supporting the Series 33 tests, will provide full recipes for the Series 33 simulants in terms of the sodium salts and other compounds found in the waste. Charge-balanced compositions will be provided as part of that task.

Table 5.1. Cluster 1 Waste Oxide Composition

Radioactive oxides	Wt. frac.	Supplemental Species Oxides	Wt. frac.	BBI Species Oxides	Wt. frac.
$^{106}RuO_2$	3.4E-18	Ag_2O	8.3E-06	Al_2O_3	0.169
^{113}CdO	1.2E-10	As_2O_5	3.9E-05	Bi_2O_3	6.4E-05
$^{12}5Sb_2O_3$	1.7E-12	B_2O_3	1.7E-04	CaO	0.00034
$^{126}SnO_2$	2.7E-07	BaO	8.8E-06	Cl	0.015
^{129}I	5.7E-06	BeO	3.7E-06	Cr_2O_3	0.0069
$^{134}Cs_2O$	4.9E-17	CdO	5.4E-06	F	0.0042
$^{137}Cs_2O$	9.9E-10	Ce_2O_3	8.1E-04	Fe_2O_3	0.00023
^{137}BaO	8.3E-13	Co_2O_3	6.6E-06	K_2O	0.018
$^{151}Sm_2O_3$	3.2E-07	Cs_2O	3.9E-09	La_2O_3	7.4E-06
$^{152}Eu_2O_3$	1.6E-11	CuO	5.9E-06	MnO	2.1E-05
$^{154}Eu_2O_3$	1.6E-10	Li_2O	1.3E-05	Na_2O	0.741
$^{15}5Eu_2O_3$	2.4E-11	MgO	6.1E-05	NiO	8.1E-05
^{226}RaO	5.5E-09	MoO_3	1.2E-04	PbO	0.00011
$^{227}Ac_2O_3$	2.9E-14	Nd_2O_3	4.2E-05	P_2O_5	0.0189
^{228}RaO	1.6E-12	PdO	7.6E-08	SiO_2	0.0079
$^{229}ThO_2$	2.3E-11	Pr_2O_3	1.7E-07	SO_3	0.0156
$^{231}Pa_2O_5$	9.8E-11	Rb_2O	1.1E-06	SrO	1.2E-05
$^{232}ThO_2$	1.0E-04	Rh_2O_3	2.4E-06	ZrO_2	6.1E-05
$^{232}UO_3$	5.6E-13	RuO_2	9.7E-06		
$^{233}UO_3$	6.4E-09	Sb_2O_3	4.3E-05		
$^{234}UO_3$	1.2E-08	SeO_2	3.7E-04		
$^{235}UO_3$	1.7E-06	Ta_2O_5	2.0E-07		
$^{236}UO_3$	4.7E-08	TeO_2	2.0E-07		
$^{237}NpO_2$	8.5E-07	ThO_2	1.2E-07		
$^{238}PuO_2$	1.4E-11	TiO_2	6.9E-06		
$^{238}UO_3$	2.6E-04	Tl_2O	7.0E-05		
$^{239}PuO_2$	1.1E-07	V_2O_5	2.9E-05		
$^{240}PuO_2$	5.4E-09	WO_3	3.2E-05		
$^{241}Am_2O_3$	2.2E-08	Y_2O_3	4.2E-06		
$^{241}PuO_2$	6.1E-11	ZnO	1.0E-05		
$^{242}Cm_2O_3$	3.7E-14				
$^{242}PuO_2$	2.5E-11				
$^{243}Am_2O_3$	1.6E-11				
$^{243}Cm_2O_3$	2.1E-13				
$^{244}Cm_2O_3$	1.6E-12				
^{59}NiO	1.4E-08				
^{60}CoO	2.5E-12				
^{63}NiO	1.7E-09				
$^{79}SeO_2$	3.3E-07				
^{90}SrO	5.5E-07				
$^{90}Y_2O_3$	1.7E-09				
$^{93}ZrO_2$	7.3E-06				
$^{93}Nb_2O_5$	7.9E-11				
$^{99}Tc_2O_7$	4.4E-05				

Note that the oxide weight fractions reported above and immediately to the left are for stable isotopes alone.