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7. Abstract

High-level waste (HLW) feed preparation flowsheet development was initiated in fiscal year (FY) 1994 to evaluate alternative flowsheets for preparing melter feed for high-temperature melter (HTM) vitrification testing. Three flowsheets were proposed that might lead to increased processing capacity relative to the Hanford Waste Vitrification Plant (HWVP) and that were flexible enough to use with other HLW melter technologies. This document describes the decision path that led to the selection of flowsheets to be tested in the FY 1994 small-scale HTM tests.

Feed preparation flowsheet development for the HLW HTM was based on the feed preparation flowsheet that was developed for the HWVP. This approach allowed the HLW program to build upon the extensive feed preparation flowsheet database developed under the HWVP Project. Primary adjustments to the HWVP flowsheet were to the acid adjustment and glass component additions.

Developmental background regarding the individual features of the HLW feed preparation flowsheets is provided. Applicability of the HWVP flowsheet features to the new HLW vitrification mission is discussed.

The proposed flowsheets were tested at the laboratory-scale at Pacific Northwest Laboratory. Based on the results of this testing and previously established criteria, a reductant-based flowsheet using glycolic acid and a nitric acid-based flowsheet were selected for the FY 1994 small-scale HTM testing.

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DEVELOPMENT OF THE HIGH-LEVEL WASTE HIGH-TEMPERATURE MELTER FEED PREPARATION FLOWSHEET FOR VITRIFICATION PROCESS TESTING

R. G. Seymour

ABSTRACT

High-level waste (HLW) feed preparation flowsheet development was initiated in fiscal year (FY) 1994 to evaluate alternative flowsheets for preparing melter feed for high-temperature melter (HTM) vitrification testing. Three flowsheets were proposed that might lead to increased processing capacity relative to the Hanford Waste Vitrification Plant (HWVP) and that were flexible enough to use with other HLW melter technologies. This document describes the decision path that led to the selection of flowsheets to be tested in the FY 1994 small-scale HTM tests.

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1.0 INTRODUCTION

High-level waste (HLW) feed preparation flowsheet development was initiated in fiscal year (FY) 1994 to evaluate alternative flowsheets for preparing melter feed for high-temperature melter (HTM) vitrification testing. Secondary to this objective was the desire to rectify problems encountered with the Hanford Waste Vitrification Plant (HWVP) flowsheet and to test modifications that might lead to increased processing capacity and flexibility (for use with other HLW melter technologies). This document describes the decision path that led to the selection of flowsheets to be tested in the FY 1994 small-scale HTM tests.

Feed preparation flowsheet development for the HLW HTM was based on the feed preparation flowsheet that was developed for the HWVP. This approach allowed the HLW program to build upon the extensive feed preparation flowsheet database developed under the HWVP Project. Primary adjustments to the HWVP flowsheet were to the acid adjustment and glass component additions. The HWVP feed preparation flowsheet[1] is depicted in Figure 1 (adapted from Kalia [1992]).

Three potential feed preparation flowsheets were considered as candidates for the HTM testing. The three flowsheets may be described as follows:

1. No acid adjustment flowsheet
2. No reductant flowsheet
3. Alternate reductant flowsheet.

All three flowsheets are described in more detail below. These three flowsheets were spawned from ideas discussed between Westinghouse Hanford Company (WHC) and Pacific Northwest Laboratory (PNL) personnel under the HWVP Project. However, because of the limitations placed on development work for the HWVP Project, schedule restrictions, and development priorities, WHC and PNL personnel were not able to adequately explore these flowsheets prior to FY 1994 testing activities.

Flowsheet selection for the HTM testing was based primarily on the following criteria (Wiemers and Smith 1994a).

- The flowsheet should reduce or eliminate the evolution of hydrogen (H_2) and ammonia (NH_3) from organic acid additions compared to the formic acid (HCOOH) HWVP flowsheet.

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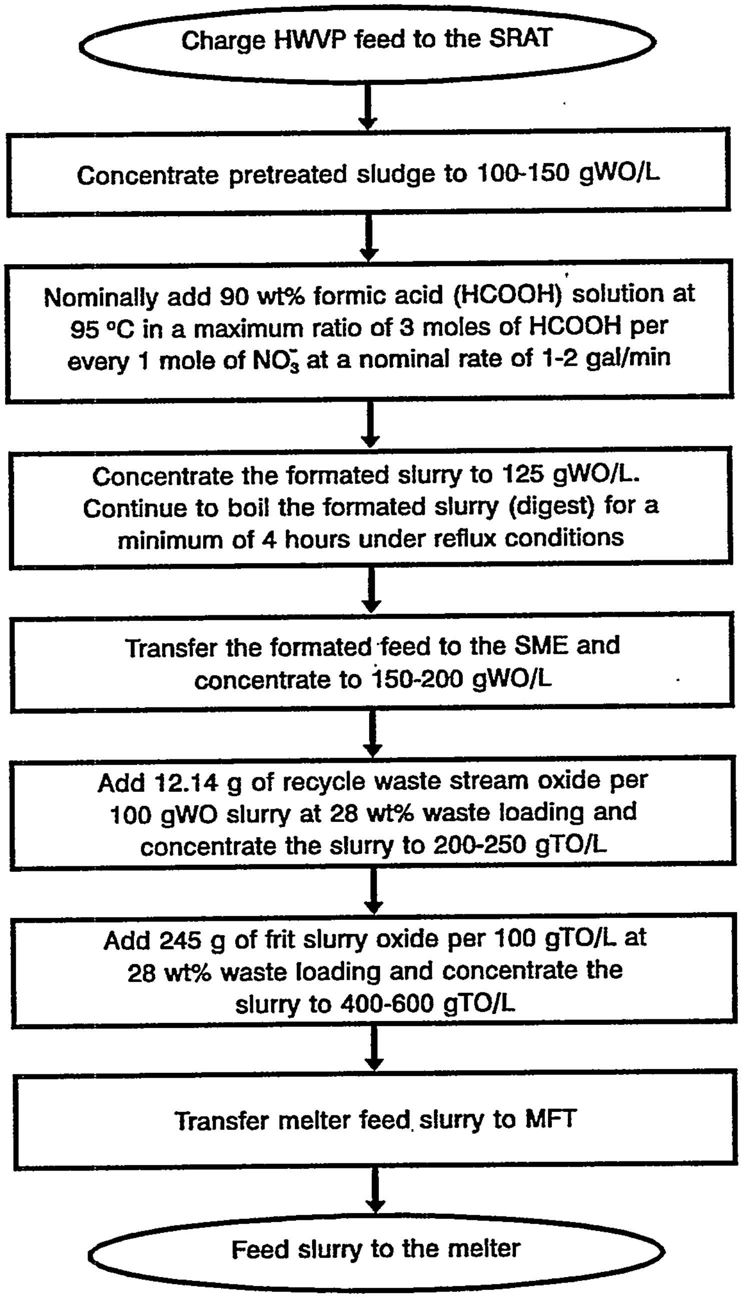
[1] Actual flowsheet used in laboratory-scale testing is slightly different than depicted in Figure 1. Transfers are not simulated in laboratory-scale testing. Thus, formated feed is concentrated to ≈200 gWO/L during digestion period.

Figure 1. Simplified Hanford Waste Vitrification Plant Feed Preparation Flowsheet.



HWVP = Hanford Waste Vitrification Plant
MFT = Melter feed tank
SME = Slurry mix evaporator
SRAT = Slurry receipt and adjustment tank
TO = Total oxide
WO = Waste oxide

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- During the flowsheet processing, slurry and melter feeds should retain acceptable rheological properties as defined by specifications in the *Hanford Waste Vitrification Plant Project Technical Data Package* (TDP) (Kalia 1992).
- The melter feed oxide concentration is similar to, or exceeds, the total oxide loading as specified in the HWVP TDP.
- Chemical additions and overall feed processing are relatively simple to control and provide overall flowsheet flexibility.
- The flowsheet is adaptable to compositional feed variability.

Downstream melter performance was also a consideration. However, at this time there are no economical methods available to assess how a melter feed will perform in the melter without actually conducting a melter test. Acceptability of a flowsheet in this regard was largely based on the judgement and experience of the PNL and WHC personnel.

Pacific Northwest Laboratory testing to support HTM flowsheet development is described in Wiemers and Smith 1994a and 1994b. However, because of the nature of this work, tests described in these references may become obsolete and new tests conducted in their place. In part, this document summarizes the tests which were conducted.

The strategy for the laboratory-scale testing was to initially focus on the ability of each of the flowsheets to mitigate H_2 and NH_3 because these gases were a considerable safety concern in the HLW vitrification plant. Testing subsequently focused on producing a feed with acceptable rheological properties and a melt with an acceptable cold-cap reactivity.

1.1 DISCUSSION OF THE SELECTION CRITERIA

The following sections further describe the criteria used to assess the alternative feed preparation flowsheets. Specifically, the rationale for the imposed limits is expressed.

1.1.1 Mitigation of H_2 and NH_3

Hydrogen and ammonia evolution during feed preparation processing has impacted designs of both the Defense Waste Processing Facility (DWPF) (at the Savannah River Site [SRS]) and the HWVP plants because of the potential safety problems associated with these gases. Because of the design and operational impacts, there is a strong incentive to eliminate the H_2 and NH_3 source terms during the feed preparation process.

It is recognized that eliminating H_2 and NH_3 sources from feed preparation processing in the HLW vitrification plant is probably not feasible because several organic species are likely to be present in the washed slurry feed. Organic acids such as HCOOH and citric acid are known to exist in the underground storage tanks (Reynolds et al. 1991; Babad et al. 1993) and may produce H_2 and/or NH_3 by catalytic decomposition in the presence of noble metals at elevated temperatures (70 to 100 °C). Moreover, H_2 is likely to be evolved from radiolytic decomposition of the organics and water during processing. However, it is prudent to reduce (as compared to the HCOOH flowsheet) or eliminate additional H_2/NH_3 source terms from the process when possible.

Operating limits for the HWVP for H_2 were 6 lb/h, while no operating limits had been established for NH_3 before cancellation of the project. Candidate flowsheets will be judged on their ability to reduce or eliminate H_2 and/or NH_3 evolution as compared with the HCOOH flowsheet that yields the <u>least</u> amount of these gases. Further discussion of H_2 and NH_3 evolution and related design and operational impacts are discussed in Section 2.1.2.2.

1.1.2 Acceptable Rheological Properties

It is recognized that in the impending redesign of the HLW vitrification plant, many of the rheological boundaries established for the HWVP can possibly be relaxed through a different design of the feed preparation system and associated sampling systems. However, in the absence of defined bounding rheological parameters, the criteria established under the HWVP Project are used as a basis for acceptable feed rheological properties. The rheological criteria are obtained from the HWVP TDP (Kalia 1992) and are shown in Table 1.

1.1.3 Solids Loading

While a similar solids loading used for the HWVP may not be necessary, depending on the melter technology selected for the HLW plant, it was believed that maximizing the solids content in the melter feed (without violating the other criteria) would benefit the plant in terms of heat-loading requirements and faster processing of the waste feed. The HWVP solids loading processing range is shown in Table 1.

1.1.4 Flowsheet Simplicity

It is also considered important that simplicity in the methods of control and the overall flowsheet processing be maintained in the new flowsheet. Simplicity was defined such that the selected flowsheets had the following attributes.

- The flowsheet did not have to be controlled too tightly, e.g., final pH of the melter feed must have a pH = 6 ±0.5, the temperature must be maintained at 90 °C ±0.1 °C, etc.
- The flowsheet control methods could be observed in real time (i.e., no laboratory analysis).
- The number of chemical additions and concentration cycling were minimized.

Table 1. Hanford Waste Vitrification Plant Technical Data Package Specifications for Selected Processing Parameters (Kalia 1992).[a]

Parameter	Formated slurry		Melter feed	
	Nominal	Design range	Nominal	Design range
Solids loading				
Total solids (wt%)	15	12-19	40	30-49
Total oxides (g/L)	125	100-150	500	400-600
Rheological[b]				
Apparent viscosity (cp at 25 °C) at 183 s^{-1}	25	3-50	70	5-170
Yield stress (dyne/cm^2)	25	4-100	100	5-260
Electrochemical				
pH	6	3.5-8	6	3.5-8

[a] Kalia, J., 1992, *Hanford Waste Vitrification Plant Project Technical Data Package*, WHC-SD-HWV-DP-001, Rev. 6, Westinghouse Hanford Company, Richland, Washington.

[b] Subsequent analysis performed by J. R. Baker, 1992, *Design Basis Slurry Rheological Properties* (internal memo 7F133-92-036 to L. D. Swenson, May 14), Westinghouse Hanford Company, Richland, Washington, indicates that these parameters for melter feeds should have maximum values of 150 dynes/cm^2 and 15 cp (at maximum shear) for yield stress and apparent viscosity, respectively.

In other words, it is desirable to maintain as much flexibility as possible to allow for potential restrictions imposed by future flowsheet problems and/or plant design.

1.1.5 Compositional Adaptability

It is important that the flowsheet handle the expected variety of feed types to be delivered to the HLW vitrification plant. To this end, a methodology was employed such that the flowsheets would avoid keying control of the flowsheet or chemical additions to any one waste feed component not known to be present in all feeds and/or in small quantities.

Moreover, the chemical additions to the flowsheet should be compatible with downstream processing criteria. For example, the addition of phosphoric acid (H_3PO_4) for rheological control may limit the waste loading due to limited solubility of phosphorus in the glass.

2.0 FLOWSHEET DEVELOPMENT AND SELECTION

Using the criteria stated above, two of the three versions of the HTM flowsheet were selected for use in the first phase of HTM testing (small-scale HTM-1 [SSHTM-1] test). A determination will be made after the SSHTM-1 test regarding which flowsheet to carry forward into the second phase of HTM testing (small-scale HTM-2 [SSHTM-2] test). The decision path that led to the development and selection of these HTM feed preparation flowsheets is described below.

To facilitate the discussion of the feed preparation flowsheet development in subsequent sections, the following questions are posed. These questions embody the fundamentals used for building the feed preparation flowsheets for HLW vitrification.

- Is a reductant needed for glass oxidation control?
- What type of reductants are acceptable for glass oxidation control?
- How much reductant is needed for glass oxidation control?
- What pH range is needed to obtain a rheologically acceptable melter feed?
- At what rate should pH adjustment chemicals be added?
- At what temperature should pH adjustment chemicals be added?
- Is a digestion period after pH adjustment necessary for Hanford Site's HLW-type feeds?
- What should be used for the internal HLW vitrification plant recycle stream addition?
- How should the glass components be added to process (i.e., physical form, dry, or slurry)?
- In what sequence should the chemical and glass component additions be made?

2.1 ALTERNATE REDUCTANT HTM FEED PREPARATION FLOWSHEET

This section describes the concept of the reductant-based HTM feed preparation flowsheet, background on the development of the flowsheet, and whether or not the flowsheet was selected for testing in the SSHTM-1 melter run.

2.1.1 Concept

Modify the HWVP feed preparation flowsheet using an organic acid other than HCOOH to obtain a melter feed with acceptable rheological properties and an acceptable cold-cap/melt reactivity based on the glass oxidation state.

2.1.2 Development Background

This section describes rationale for the features in this flowsheet and attempts to answer the questions posed above (see Section 2.0, bulleted items). The background of this flowsheet is discussed at length so that several aspects of the two other flowsheets do not have to be reiterated.

2.1.2.1 Reductant Requirements. Traditionally, organics have been added to the HLW feed to control the oxidation state of the melt pool in low-temperature (<1200 °C) melters to prevent volatilization of certain components in an over-oxidized melt pool and to prevent a phenomenon commonly called "foaming" or "reboil" (Wiemers et al. 1993; Bickford et al. 1990). The West Valley Demonstration Project (WVDP) has opted for sugar as its reductant source, while the DWPF (and the HWVP) have processed with an organic acid (HCOOH). The difference in the choice of reductant sources is primarily the result of differences in processing philosophy.

There are many metal species in the Hanford Site waste inventory (e.g., cadmium, lead, arsenic, cesium, and strontium) that are considered semi-volatile in the melter environment. However, the volatility of technetium and ruthenium are of particular interest because the volatility of these multivalent elements can be effectively controlled using reduction oxidation (redox) methods. Technetium and ruthenium, in their oxidized form (Tc_2O_7 and RuO_4), will readily volatilize at temperatures typically found in the melter cold-cap region (Bickford et al. 1986; Lammertz et al. 1985). Thus, to prevent this from occurring, a reductant is introduced into the feed to provide a reducing environment in the cold cap to maintain technetium and ruthenium in their less oxidized and less volatile forms (TcO_2 and RuO_2).

Of primary concern in the vitrification of HLW has been the foaming or reboil phenomenon in which a foam blanket forms an insulating layer between the cold cap and melt pool that prevents the heat from the glass pool from calcining and melting the incoming feed, decreasing the rate at which one can process the slurry feed. Excessive foam can increase the melt volume to the point that the melter offgas system is plugged. The foam can also affect the density of the melt pool which can interfere with the electrical distribution of the melter (Herborn and Smith 1993).

If such an incident should occur, processing must be terminated to let the foam recede. It has been theorized that excessive manganese reduction in the melt pool liberates enough oxygen to cause the foaming phenomenon (Bickford et al. 1990; Plodnic 1985). However, documentation that verifies this notion is minimal, and documented incidences of foaming in operating melters are elusive, especially with Hanford Site HLW feeds (Ryan 1994).

Thus, there is some question as to whether the reductant is actually needed to prevent this particular phenomenon with Hanford Site HLW feeds.

In HTM testing, the melter is expected to have a nominal operating temperature of 1350 °C with a potential to operate in temperature ranges up to 1550 °C (Smith et al. 1994). The behavior of redox equilibria in the HTM at these higher temperatures is unknown. The complex nature of the chemical interaction between multivalent species and other components in the cold cap and glass makes it extremely difficult to predict whether a reductant is required to control volatilization and/or foaming. Thus, a "no reductant" flowsheet was pursued as a possible flowsheet for the HTM and is described later. A reductant-based flowsheet development was maintained as a backup option in case the no reductant flowsheet did not meet expectations and for applications to other melter technologies.[1]

2.1.2.2 Type of Reductant. In the HWVP flowsheet, HCOOH was added as the reductant of choice for a number of reasons. Use of HCOOH in the HWVP can be traced directly to the DWPF at SRS where development of the organic acid melter feed preparation flowsheet had begun. Research at the Savannah River Technology Center (SRTC) had shown that several processing objectives with one chemical addition (HCOOH) could be accomplished (Ritter et al. 1990).

- Reduce the mercury in the feed slurry to its metallic state during feed preparation so the mercury could be subsequently removed by steam stripping.
- Lower the pH of the feed slurry to yield a slurry with acceptable rheological characteristics.
- Control the oxidation state of the glass in the melter to prevent excessive volatilization/foaming.

However, the flowsheet development at the SRTC had not shown that the evolution of H_2 and NH_3 via catalytic decomposition of HCOOH with noble metals (rhodium, ruthenium, palladium) in the feed could occur during feed preparation processing. The noble metals had been excluded from the Savannah River Laboratory simulant because of their exorbitant cost and minimal concentration in the feed.[2]

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[1] Currently, four melter technologies are under consideration for HLW vitrification: (1) HWVP liquid-fed ceramic reference melter, (2) high-temperature melter, (3) stirred melter, and (4) cold-crucible melter. (See Lambert 1994 for more information on these technologies.)

[2] It should be noted that cost and/or minimal concentration was the basis for omitting many of the other minor feed constituents. Interest in including noble metals in the simulant initially developed out of concern that testing programs should include as many of the minor constituents to simulate the actual waste as closely as possible. Coincidentally, concern was also growing with regards to precipitation and accumulation of the noble metals in the melter, as had been experienced in European melters (Elliott et al. 1994).

Tests with noble metals conducted later at PNL showed that although they are present in very small concentrations in the feed, noble metals play a significant role in feed preparation chemistry, including increasing the evolution of H_2 and NH_3 (Wiemers et al. 1987; Wiemers 1990). This phenomenon was later replicated on a larger scale at DWPF with both Hanford Site- and SRS-type melter feeds (Hutson 1993).

Discovery of the noble metals phenomenon precipitated nearly $10 million in redesign work to the HWVP to mitigate the potential explosion hazard from H_2 evolution alone. Definitive information on NH_3 generation became available after H_2 mitigation design changes were implemented. At the time design work on the HWVP was suspended, a final decision on NH_3 mitigation approach had not been made. Mitigation of the NH_3 was necessary because it can react with NO_x to form ammonium nitrate (NH_4NO_3), which will detonate under the right conditions.

A decision to incorporate significant design changes for H_2 and NH_3 mitigation was made at the DWPF. This decision was made as the DWPF was nearing completion of construction. A hardware fix and flowsheet modifications were approved at the cost in excess of $10 million to mitigate the H_2 and NH_3/NH_4NO_3 problems.

With these cost incentives in mind, the HWVP Project began research to mitigate H_2 and NH_3 generation during processing of Hanford Site HLW in the vitrification plants. Two approaches were initiated simultaneously. The first was to modify the HCOOH flowsheet by controlling pH, temperature, and chemical addition timing. The other approach was to begin investigating other organic acids that could possibly be substituted for HCOOH.

Modification of the HCOOH flowsheet was met with limited success. The H_2 and NH_3 source terms were reduced to less than one-fourth of the amount previously observed (Smith et al. 1994). However, this variation of the flowsheet yielded a melter feed that had the potential for considerable gas evolution because a significant amount of the carbonate (CO_3^{2-}) and NO_x producing species were still present in the melter feed. A scenario was postulated: if the melter feed was inadvertently and uncontrollably heated, gases could evolve at a rate that could possibly over-pressurize the feed preparation system and/or cause the melter feed to foam and carry over solids into the offgas train. The risk from this kind of an event is minimal and could be easily mitigated. Thus, this flowsheet is generally regarded as a backup should the alternative flowsheets perform inadequately.

Substitution of other organic acids for HCOOH in the feed preparation process has shown considerable promise in preliminary testing--not only was the NH_3 considerably reduced or eliminated, but the H_2 evolution was almost totally eliminated in every case (King et al. 1993).[1] Because of this success, much of the FY 1994 feed preparation flowsheet efforts were then

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[1] No hydrogen was observed within R. B. King's analytical tolerance, i.e., >500 ppm.

focused on this approach to solving the NH_3 (and H_2) generation problems. An account of the alternative reductant investigation is the subject of a subsequent FY 1994 WHC milestone (Seymour 1995).

A number of similar organic acids (carboxylic) to HCOOH based on acid dissociation constant and potential reducing capacity relative to HCOOH were selected in the alternative reductant investigation. These acids (glycolic, glyoxylic, glycine, lactic, pyruvic, butyric, levulinic, oxalic, malonic, tartaric, and citric) were screened in a limited component neutralized current acid waste (NCAW) system at the University of Georgia under conditions known to produce H_2 and NH_3 with HCOOH (King et al. 1993).

Several organic acids were then eliminated based on a set of previously established criteria (Seymour 1993) and the remaining organic acids (glycolic, lactic, oxalic, citric) were then tested at PNL with an NCAW simulant under conditions known to evolve H_2 and NH_3 with HCOOH (Wiemers and Smith 1994a and 1994b). All but two of these organic acids (glycolic acid and oxalic acid) were eliminated because some NH_3 was observed during processing.

Further PNL laboratory-scale tests were conducted with glycolic and oxalic acids. Although tests conducted with oxalic acid eliminated H_2 and NH_3 evolution, subsequent rheological measurements indicated that acceptable rheological properties were not obtainable at reasonable solids loadings. This result was attributed to the precipitation of insoluble oxalates. Glycolic acid, on the other hand, did not completely eliminate the H_2 and NH_3 evolution but did yield melter feeds with acceptable feed properties. Although glycolic acid exhibited some H_2 and NH_3 (less than one one-hundredth of that observed in a comparable HCOOH test[1]), the decision was made to proceed with the glycolic acid as a substitute for HCOOH during the HTM tests.

2.1.2.3 Reductant Addition Amount. A rough estimate of the amount of the reductant (glycolic acid) needed for glass oxidation control in the melt pool may be obtained by determining the amount of HCOOH present in the melter feed in previous feed preparation tests. Then, on a comparable carbon basis, the amount of glycolic acid required can be calculated. However, such an estimate may be flawed in that the acids may be lost by thermal decomposition, evaporation, or other mechanisms that are not easily accounted for. To obtain an empirical basis for determining how much glycolic acid is required, a series of tests needed to be conducted to obtain the necessary information.

Because an organic acid was selected as the additive, two factors figure into determining the amount of organic acid added to the feed slurry: (1) how much is needed to reduce the pH to a level to obtain acceptable rheological properties of the melter feed, and (2) how much is needed to obtain an acceptable glass oxidation state in the glass as measured by the $Fe^{2+}/\Sigma Fe$ method. The amounts of organic acid needed to account for these two factors may not necessarily be the same, particularly if the organic acid is a weak

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[1] Based on preliminary data. Final data are to be published in an FY 1995 PNL report summarizing FY 1994 alternative flowsheet activities.

acid with a long carbon chain (i.e., more carbon for reducing purposes with very little acid benefit). To obtain the necessary data, a strategy was developed using tests already scheduled to be conducted for other flowsheet development purposes.

Spiking the final melter feed to obtain multiple redox data points was not an option because it is unknown how much of the glycolic acid would remain at the end of the feed preparation for redox control and how important the processing of the feed was to the final redox state of the glass. The test sequence and strategy are described below. Test 4 was devised to specifically address whether the melter feed could be spiked with reductant. The primary objective of the other tests was to resolve other flowsheet development issues, but the tests were also used to obtain the bounding glass oxidation data.

Test 1: Conduct a test containing no reductant to obtain a baseline redox measurement with HTM glass components. This test was conducted to support the no reductant flowsheet.

Test 2: Obtain redox data from a glass made from melter feed prepared in a test to investigate whether glycolic acid would produce H_2 or NH_3 under conditions that produce H_2 and NH_3 with HCOOH. This involves intentionally adding more than the amount of glycolic acid needed to only reach a pH of 6 (see Section 2.1.2.4) and/or obtain an acceptable redox state in the glass (as estimated from a carbon basis compared with HCOOH). It is expected that this test would yield a glass whose oxidation state is fairly reduced ($Fe^{2+}/\Sigma Fe>0.333$).

Test 3: Obtain redox data from glass made from melter feed prepared in a test devised to use glycolic acid for rheological control (i.e., use the HWVP flowsheet and substitute glycolic acid for HCOOH and the HTM glass components for low-temperature melter glass components at the appropriate steps).

Test 4: Conduct a test such that the feed slurry is cooled before glycolic acid is added. This test was designed to determine whether the thermal treatment after the organic acid addition (digestion) has any obvious effect on the redox state of the glass made from Hanford Site-type feeds. If the results of this test were negative, then one could both eliminate the digestion period from the flowsheet and confidently add additional (spike) glycolic acid to the melter feed after a feed preparation test had been completed without having to process the feed and glycolic acid through the entire feed preparation flowsheet to obtain each glass redox data point.

Test 5: Conduct a test with a small amount of glycolic acid and subsequently add glycolic acid to the melter feed in increments to obtain multiple redox data points.

Glass is made from the melter feeds produced in the tests described above by melting the feed in a closed-crucible procedure developed for the HWVP Project (PNL Technical Procedure WTC-006-29 [Olson 1991]). The glass is then analyzed for Fe^{+2} and ΣFe (PNL Technical Procedure 7-40.20 [Burt 1991]).

An acceptable oxidation state of the glass was defined as a glass whose $Fe^{2+}/\Sigma Fe$ ratio falls within 0.005 to 0.33 (Kalia 1992). This range was developed for the operation of the HWVP melter. Iron (Fe) was chosen as the indicator because of its abundance in the HLW feed and because the Fe^{+2} valence state is measurable in the glass.

The lower $Fe^{2+}/\Sigma Fe$ bound represents the lowest oxygen potential a glass can possess without the possibility of provoking a foaming episode.[1] The upper bound represents the maximum reduced state a glass can possess without risking significant precipitation of metals and metal sulfides (Bickford et al. 1990). This upper $Fe^{2+}/\Sigma Fe$ bound was particularly important because a settled metallic layer on the bottom of the melter provides a conductive layer through which the electrodes can short circuit. Short circuiting can lead to corrosion of the electrodes and surrounding refractory (Cooper et al. 1994).

It is unknown whether this oxidation range remains valid for the higher melt temperatures expected in the HTM. In the absence of another way to gauge the amount of reductant to add for reducing purposes, it was decided that the flowsheet development would continue to use the $Fe^{2+}/\Sigma Fe$ oxidation range as a target for reductant additions until other information is available.

Tests 1-3 above were completed. Test 3 was somewhat modified because sodium bicarbonate ($NaHCO_3$) was used to trim the sodium glass component in the HTM glass. The buffering capacity of $NaHCO_3$ elevated the pH out of the processing range for rheological control. A decision was then made to rerun Test 3 with a different sodium glass component (see Section 2.1.2.9 for glass component changes). However, because of the temporary shutdown of Building 325, access to the feed process chemistry laboratory was often interrupted; thus, Test 3 was conducted without offgas analysis because the monitoring equipment was inaccessible.[2] An acceptable redox state ($Fe^{2+}/\Sigma Fe \approx 0.12$) was ultimately obtained for this test.

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[1] This lower limit is near the detection limit of Fe^{2+} in glass ($Fe^{2+}/Fe^{3+} \approx 0.001$) as measured by the calorimetric method (Goldman 1985). Allegedly, no foaming has been observed when there was a measurable quantity of Fe^{2+}. However, the scientific justification for the correlation between foaming and $Fe^{2+}/\Sigma Fe$ is far from perfect, as discussed by Ryan (1994).

[2] Offgas analysis was not really a concern because adequate offgas measurements had been obtained in the previous experiment with glycolic acid to sufficiently estimate offgas emissions for safety and stack emission concerns for HTM testing.

Moreover, the 325 Building shutdown caused a severe scheduling impact to these testing activities, resulting in the postponement of Tests 4 and 5 to meet higher priority needs for the SSHTM-1 test.

From Tests 1-3 (including Test 3 rerun), the appropriate amount of glycolic acid required in the feed preparation flowsheet could be gauged (albeit minimal data) subject to pH adjustment requirements.

2.1.2.4 pH Adjustment Addition - Type and Amount. As received, the Hanford Site feeds cannot be sufficiently concentrated to meet the melter feed solids loading requirements (see Section 1.1.3) and maintain acceptable rheological properties (see Section 1.1.2) for pumping and agitation purposes. As previously stated, acid is needed to modify the rheological properties of the alkaline Hanford Site HLW vitrification feeds through neutralization/solubilization. An acceptable pH range for melter feeds was established under the HWVP Project and is specified in the HWVP TDP (Kalia 1992). These specifications are shown in Table 1.

This pH range was based on recommendations from the DWPF flowsheet development and additional vitrification testing conducted at PNL. There is some speculation that the feed preparation flowsheet could be operated with slurries possessing a pH up to around nine. However, because of time and resource limitations, this option could not be fully explored. Thus, it was decided to maintain the HWVP TDP specifications in the development of these flowsheets, i.e., nominally decrease the slurry pH to around six.[1]

Preliminary feed preparation testing revealed that the glycolic acid had sufficient acid power to adjust the pH of the slurry to around six without over-reducing the glass.

2.1.2.5 pH Adjustment Addition - Rate. The operating range for the delivery of HCOOH to the HWVP feed preparation system was nominally 1 gal/min and not to exceed 2 gal/min of 90 wt% HCOOH (Kalia 1992). Tests conducted at the Integrated DWPF Melter System (IDMS) facility at the SRTC indicated that the upper rate may be too fast because the IDMS feed preparation system over-pressurized due to the excessive rate of feed preparation offgases that were emitted (Hutson 1993). However, because the offgas system design in the IDMS facility was significantly different from the HWVP in its ability to handle the offgas volume, it was determined that the upper-addition rate probably was still a valid limit. The upper-addition rate was scheduled to be retested in the prototypic feed preparation system at PNL, but mission changes have eliminated that test. The nominal HCOOH rate has processed smoothly at both the IDMS and PNL vitrification system testing facilities. Thus, it was decided that this rate would be used to estimate a comparable rate with glycolic acid in development of the HTM flowsheet.

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[1] Because Hanford Site feeds tend to exhibit some buffering capacity, a pH specification shown in subsequent flowsheets is an <u>initial</u> target pH and the slurry pH is expected to drift upwards to the desired slurry pH.

A comparable acid delivery rate was estimated from the delivery of the H+ as a function of time, i.e., mole H^+/min using HCOOH = mole H^+/min using glycolic acid.

2.1.2.6 pH Adjustment Addition - Temperature. The HCOOH was nominally added to the HWVP feed preparation flowsheet at 95 °C. Like many steps in the HWVP flowsheet, this parameter was a carryover from the DWPF flowsheet. The HCOOH was added at this temperature primarily to accelerate the kinetics of the reactions occurring in the formated slurry (e.g., reduction of mercury and manganese, solubilization of some slurry components, and destruction of carbonates, nitrites, and nitrates [Larson 1989]). Processing at this temperature also facilitated the liberation of the gases as they were formed in the aqueous solution, i.e., minimal potential in the feed for gas evolution.

Because the bases for this temperature specification still applies to Hanford Site HLW feeds, it was decided that the glycolic acid would be added at 95 °C. Future testing will determine whether the mercury, expected to be in the feeds to the new HLW vitrification plant (Orme 1994), will be reduced under these conditions with glycolic acid.

2.1.2.7 Digestion Cycle. This step in the feed preparation flowsheet is also carryover from the DWPF flowsheet. Its function was primarily to steam strip the reduced mercury to the offgas condensate and reduce the manganese from a +4 valence state to a +2 valence state by boiling the feed slurry for several hours after the acid addition. Reduction of the manganese has been reported as necessary to avoid foaming of the melt pool caused by oxygen release from the reduction of MnO_4 to MnO_2 (Plodnic 1985). Relative to Hanford Site feeds (NCAW), this phenomenon has been unsubstantiated. In a first attempt to evaluate the necessity of this step,[1] Test 4 (Section 2.1.2.3) was proposed. However, because Test 4 could not be conducted, it was decided that this feature would be maintained in the feed preparation flowsheet for the time being.

2.1.2.8 Recycle Addition. Because the HWVP was going to be a self-contained facility, it was to be responsible for treating its waste streams, i.e., little or no radioactive waste would be sent back to tank farms. Thus, the various waste streams within the HWVP were combined, concentrated, and sent back to the feed preparation system (Kalia 1992). However, because the new HLW facility is yet undefined with respect to the destination and composition of its internal waste streams, it was decided that this addition would be eliminated from the feed preparation flowsheet until the stream is defined.

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[1] The digestion step needs to be further clarified as it really consists of two parts. In the first part, the feed is concentrated and mercury is stripped from the feed. In the second step, the feed is maintained for a period of time at boiling temperatures under total recycle conditions to complete the manganese reduction. The intent is to eliminate the second part of the digestion period.

2.1.2.9 Glass Component Additions. The HTM glass formulation for NCAW, shown in Table 2, was developed by PNL's glass formulation task (Smith and Wiemers 1994). Additional glass components required for the low-temperature melter (NCAW formulation) were silica, boron, and lithium for NCAW, which was added as a glass frit (Kalia 1992). Lithium and boron were added as fluxing agents that sufficiently lowered the yield temperature of the glass to be processed in an Inconel[1] electrode melter (i.e., 1150 °C).

Table 2. High-Temperature Melter Glass Formulation for Neutralized Current Acid Waste (Smith and Wiemers 1994).*

Glass component	Concentration in glass (wt%)	Glass component	Concentration in glass (wt%)
Al_2O_3	4.51	Na_2O	16.66
B_2O_3	0.00	Nd_2O_3	2.37
BaO	0.19	NiO	1.10
CaO	0.39	P_2O_5	0.19
CdO	1.44	PdO	0.10
CeO_2	0.29	Pr_6O_{11}	0.19
Cr_2O_3	0.24	Rb_2O	0.10
Cs_2O	0.29	Rh_2O_3	0.10
CuO	0.29	RuO_2	0.29
F	0.58	SO_3	0.53
Fe_2O_3	14.07	SiO_2	46.03
La_2O_3	1.20	Sm_2O_3	0.10
Li_2O	0.00	SrO	0.19
MgO	0.10	Y_2O_3	0.10
MoO_3	0.58	ZrO_2	7.54
MnO_2	0.29	Total =	100.0

NOTE: Total minors (Ba, Cd, Ce, Cr, Cs, Cu, F, La, Mn, Mo, Nd, Ni, P, Pd, Pr, Rb, Rh, Ru, S, Sm, Sr, Y) = 10.71 wt% of the glass.

*Smith, G. L., and K. D. Wiemers, 1994, *Small-Scale High Temperature Melter - 1 (SSHTM-1) Test Plan*, Milestone PHTD-C94-03.02J, Rev. 0, Pacific Northwest Laboratory, Richland, Washington.

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[1] Inconel is a trademark of Inco Alloys International, Inc.

However, these fluxing agents are (apparently) no longer needed at the temperatures to be experienced in the HTM. Silica and aluminum will be used as the primary building blocks for the high-temperature glass and sodium will be used as a fluxing agent. To this end, additional silica and sodium are needed to complete the glass formulation with NCAW. Thus, the physical form and delivery of these glass components needed to be determined.

2.1.2.9.1 Chemical Form - Silica. Initial feed preparation testing used was what was thought to be a TAMSCO[1] silica source. However, it was subsequently determined that the silica was not the TAMSCO product and contained a large amount of impurities (>20 wt% sodium) that facilitated devitrification of the glass. The TAMSCO silica was then replaced with a silica source referred to as F-110 (sand). The F-110 particle size distribution, which is reasonably consistent with HWVP TDP frit criteria (-80 to 200 mesh) (Kalia 1992), is shown in Table 3. However, it has been recommended that the acceptable particle size range be modified to -60 to 200 mesh because this is expected to give the melter feed slurry much better rheological characteristics. Melting rate and cold-cap characteristics could be affected by use of a courser silica source.

Table 3. Particle Size Distribution for the F-110 Silica Source (Whittington and Lamar 1994).*

Mesh size	Percentage of F-110
40	--
50	<1
70	4
100	20
140	43
200	26
270	6
>270	<1

*Whittington, K. F., and D. A. Lamar, 1994, *Small-Scale High Temperature Melter - 2 (SSHTM-2) Test Plan*, Milestone PVTD-C94.04-19C, Rev. 0, Pacific Northwest Laboratory, Richland, Washington.

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[1] TAMSCO is a trademark of TAM Ceramics, Inc.

2.1.2.9.2 Chemical Form - Sodium. Initial feed preparation testing used $NaHCO_3$ as the sodium source. However, it was determined that $NaHCO_3$ caused a substantial pH rebound out of the acceptable processing range (pH $\approx$ 6-8). The forms of sodium that were considered as candidates are shown in Table 4.

Of the candidates listed in Table 4, the organic salt, specifically sodium glycolate ($NaC_2H_2O_4$), was initially selected because both ions of the salt were beneficial to the process and it was believed that the initial glycolic acid addition amount could be decreased to counter possible over-reduction in the melt pool. However, it was soon discovered that the glass oxidation state would still be too reduced by using this form of sodium. Moreover, minimizing the initial glycolic acid addition decreased the flexibility of the flowsheet to handle process pH upsets without possibly over-reducing the melt pool.

Sodium nitrate was then selected as a source for sodium glass component additions because it does not affect the pH of the slurry and minimizes the deleterious effects on the vitrification system as a whole. Obviously, the volume of NO_x evolution from the melter and the oxidation state of the melt pool may be affected by the additional NO_3^-, but this problem was considered minor in comparison to the detrimental effects from other possible sodium sources.

2.1.2.9.3 Delivery Form. In the HWVP flowsheet, the additional glass components were delivered as frit slurry. Despite the ease in delivery (metering to the feed preparation system), this method had several problems:

- Added a significant amount of water, which subsequently had to be boiled off in the feed preparation system or in the melter
- The frit slurry is not easy to keep homogenous because of fast settling rates
- It was also found that the frit must be resistant to acidic and basic environments because these conditions facilitated gel formation with certain frits in the frit and melter feed slurries (Smith 1994)
- Minor upsets, operating errors, or equipment malfunctions can cause piping to be rapidly and extensively plugged with settled frit.

For these reasons, alternative approaches such as a pneumatic transfer system for dry glass components should be considered. Based on these considerations, a decision was made to feed the silica and sodium in the HTM tests as dry additions to the feed preparation process. It should be noted that the deliquescent nature of solid sodium nitrate ($NaNO_3$) could pose a problem in the vitrification plant. Nonetheless, the ease of adding solid $NaNO_3$ during testing temporarily superseded this concern until a more formal determination of the handling problems associated with $NaNO_3$ could be made.

Table 4. Sodium Glass Component Candidates for the Alternate Reductant Feed Preparation Flowsheet.

Sodium form	Possible processing detriments
Na_2CO_3	Will probably buffer the pH of melter feed out of acceptable processing range.
Na_2SO_4	Sulfate forms an immiscible scum at the melt pool cold-cap interface; many of the metals form insoluble sulfides in the melt pool; increases SO_x emissions from the melter.
Na_3PO_4	Phosphate forms an immiscible scum at the melt pool cold-cap interface.
Na_2O	Sodium oxide is deliquescent and would present a considerable handling problem in an aqueous environment.
Organic salt	Additional carbon source in the melter feed may over-reduce the melt pool; puts additional constraint on reductant addition.
$NaNO_3$	Will increase NO_x emissions; may require additional reductant to compensate for additional nitrate (self defeating).
$NaNO_2$	Will increase NO_x emissions; may require additional reductant to compensate for additional nitrate created by HNO_2^- disproportionation (self defeating); buffers pH of the slurry.
Na_2O-SiO_2	Sodium silicate (water glass) would likely dissolve/polymerize under feed preparation conditions resulting in a detrimental effect to melter feed rheological properties.

2.1.2.10 Flowsheet Sequence. Because the flowsheet development is based on the HWVP flowsheet, the natural tendency was to operate the alternative flowsheet in the same sequence of chemical additions and concentrations. Moreover, this approach capitalized upon the forethought implicit in the HWVP flowsheet design.

Two of the more important considerations in the design of the feed preparation flowsheet are the timing of the concentration cycles and chemical additions. In the HWVP flowsheet, the majority of feed concentration is performed when the slurries have low solids loadings. Concentration cycles are conducted in this manner because heat transfer is more efficient to remove water when heat adsorbing solids are not present. This property of the feeds, in turn, influences the timing of the glass component additions, which make up the majority of the solids loading in a melter feed.

The acid is added in the beginning of the feed processing so that the slurries possess acceptable rheological properties as they become concentrated. Without the acid, the slurries would be extremely hard to pump, agitate, or maintain homogeneity.

Because throughput capacity is such an important consideration in the design of the new HLW vitrification plant, every attempt was made to concentrate the feeds as much as possible before glass component additions so that minimal concentration of the melter feed would be required, if at all. Moreover, extended boiling periods tend to exacerbate drying of feed on the steam coils and dissolution of glass components that can lead to gel formation. These considerations are reflected in the alternate reductant flowsheet shown in Figure 2.

2.1.3 Selection

From the decisions indicated in the previous sections, an alternate reductant flowsheet was assembled and tested on the laboratory-scale. Preliminary laboratory-scale processing results indicate that all parameters are within the operating ranges discussed above.[1] The flowsheet depicted in Figure 2 was selected to be tested in the SSHTM-1 test.

2.2 NO ACID ADJUSTMENT FEED PREPARATION FLOWSHEET

This section describes the concept, background, and selection status of the no acid adjustment feed preparation flowsheet.

2.2.1 Concept

Process the HLW feed slurry through the vitrification feed preparation process without any acid (or reductant) adjustment to the feed slurry. The necessary pH adjustment would be supplied through buffering of the feed slurry by the glass component additions.

2.2.2 Development Background

A no acid adjustment flowsheet was considered a candidate for preparing melter feed for the HTM testing as alluded to in Section 2.1. Principally, the decision to investigate this type of flowsheet was made based not only on the desire to "baseline" the oxidation potential of the HTM, but to determine if this flowsheet could be operated by eliminating the acid/reductant addition and judiciously selecting a glass component that could achieve the necessary pH adjustment.

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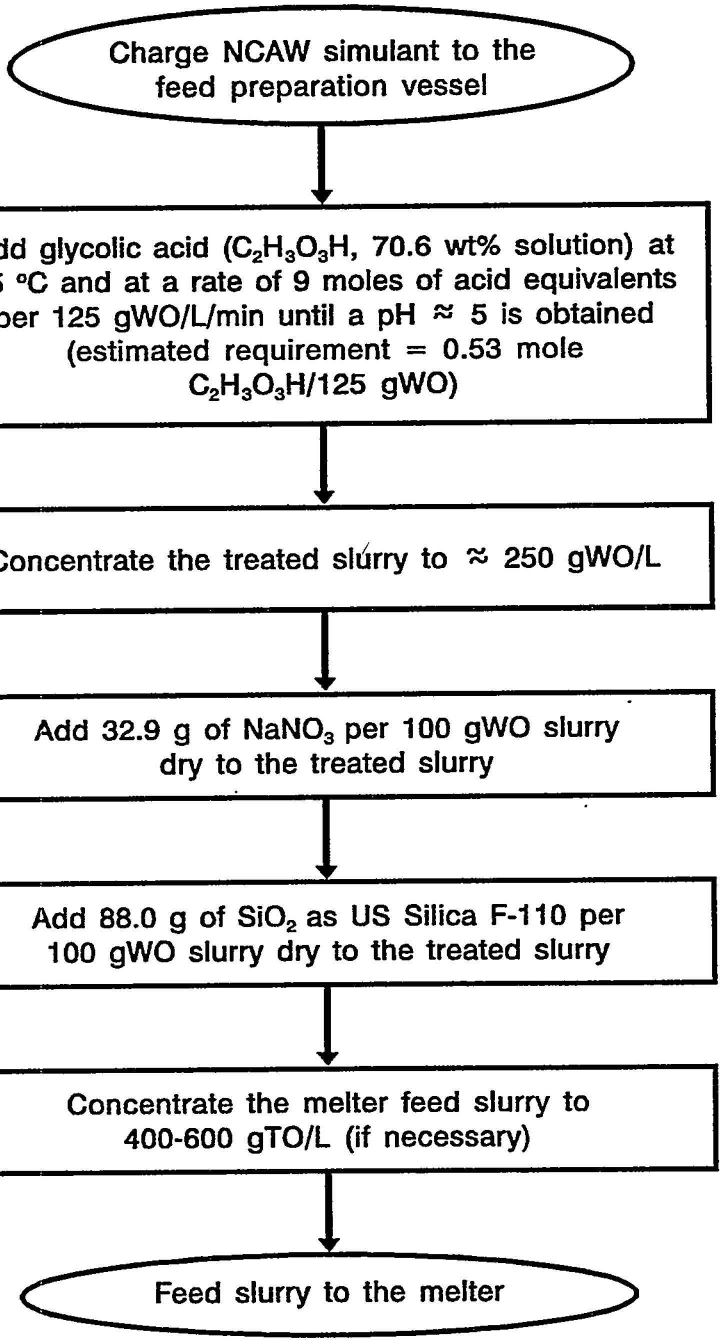
[1] Data will be published in an FY 1995 PNL report summarizing FY 1994 alternative flowsheet activities.

Figure 2. Alternate Reductant Feed Preparation Flowsheet.



NCAW = Neutralized current acid waste
TO = Total oxide
WO = Waste oxide

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As discussed in Section 2.1, HLW feed preparation flowsheets have been primarily developed around organic acids in conjunction with low-temperature (<1050 to 1150 °C) melters. However, it is not known how the redox equilibria will behave at the higher temperatures (1350 to 1500 °C) expected in the HTM. Therefore, because the HTM has not been tested with HLW feeds, proper redox control of the melt pool during melter operation has not been established, and a "baselining" (no reductant) of melt pool behavior is prudent. Thus, a no reductant option was pursued as a flowsheet for initial HTM testing.

Because the reductant source was also an acid source in the reference HLW flowsheet, a replacement for the acid was required. It was then suggested that one of the glass component additives be used as an acid source instead of replacing the acid/reductant addition with another acidic chemical addition, thereby combining two chemical additions. The no acid adjustment flowsheet greatly simplifies the feed preparation flowsheet by reducing the necessary process steps to a glass component addition step and concentration step.

Comparing this flowsheet to the alternate reductant flowsheet, the following features have been eliminated:

Eliminated feature	Reason for elimination
Reductant addition	Reductant may not be required for control of HTM
Digestion	Reductant not added.

Thus, the remaining features that need to be addressed are the pH adjustment (type and amount, rate, temperature); glass component additions; and flowsheet sequence.

2.2.2.1 pH Adjustment Addition - Type and Amount. Because the same feed slurry will be processed by this flowsheet, sodium and silica will still be needed as glass components. Thus, the sources for silica or sodium had to be able to modify the pH of the slurry downward to produce acceptable rheological properties. Sodium bicarbonate was selected as the sodium source because of its capability to buffer solutions to <pH = 9. Although this slurry pH will be outside of the HWVP feed specification, the potential benefit from such a simplified flowsheet temporarily superseded this concern.

2.2.2.2 pH Adjustment Addition - Rate. Because the initial gas evolution from the feed slurry is predominately pH dependent, a similar rate of addition was used in this flowsheet as discussed in the alternate reductant flowsheet.

2.2.2.3 pH Adjustment Addition - Temperature. Because the potential for gas evolution during an initial pH adjustment to the feed is temperature dependent, the same temperature (95 °C) was maintained when adding the $NaHCO_3$ as in the alternate reductant flowsheet.

2.2.2.4 Glass Component Additions. This section describes the chemical and delivery forms of the glass component additions for the no acid adjustment feed preparation flowsheet.

2.2.2.4.1 Chemical Form - Silica. Because the pH adjustment additive was available from the sodium source, the F-110 silica source selected in the alternate reductant flowsheet was also used in this flowsheet.

2.2.2.4.2 Chemical Form - Sodium. Sodium bicarbonate was selected as the sodium chemical form based on the need for pH adjustment.

2.2.2.4.3 Delivery Form. For similar reasons in the alternate reductant flowsheet, the silica source will be added dry. Moreover, because $NaHCO_3$ is relatively stable and easy to handle in a solid form, it was decided that it would also be added dry to the feed slurry.

2.2.2.5 Flowsheet Sequence. Although the general HWVP flowsheet sequence was followed in this flowsheet, one of the glass component additions was moved up in the sequence of the flowsheet due to the fact that the $NaHCO_3$ was also being used as a rheological modifier. The no acid adjustment flowsheet is shown in Figure 3.

2.2.3 Selection

From the decisions indicated in the sections above, the no acid addition flowsheet was assembled and tested on the laboratory-scale.

Preliminary results from laboratory-scale process testing of this flowsheet indicate that it is not feasible, within the criteria established earlier, to operate the feed preparation flowsheet in this way. Unfortunately, after the $NaHCO_3$ had been added, the feed could not be concentrated beyond 228 gTO/L (pH $\approx$ 9.5) without exceeding the rheological specifications (at 228 gTO/L, viscosity = 28.5 Pa·s, yield stress = 14.2 Pa). A final concentration of 382 gTO/L was obtained for the melter feed after the silica addition.[1] This solids loading was deemed to be undesirable, and because there was limited time available to try to find ways to increase solids content, this flowsheet was abandoned as a possibility for initial HTM testing.

2.3 NO REDUCTANT FEED PREPARATION FLOWSHEET

This section describes the concept, background, and selection status of the no reductant feed preparation flowsheet.

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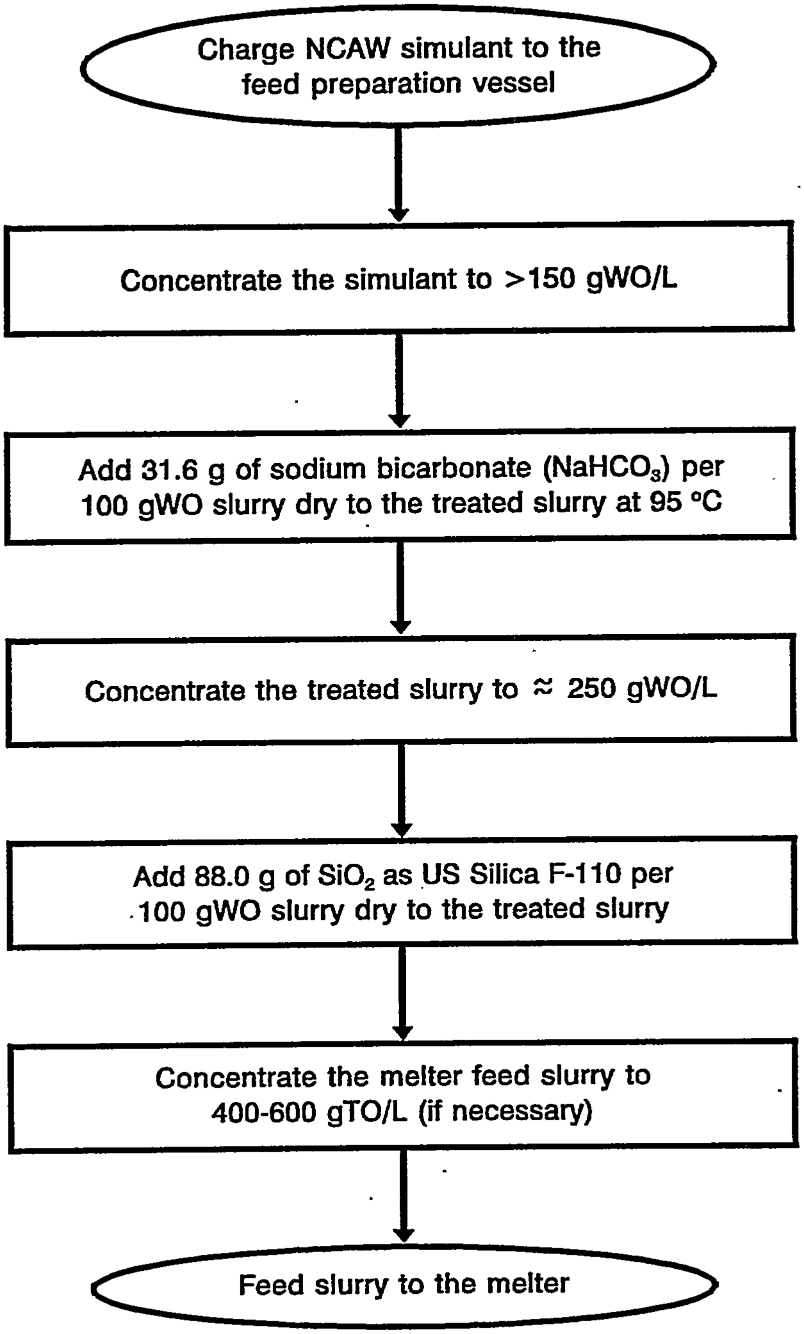
[1] Final data will be published in an FY 1995 PNL report summarizing FY 1994 alternative flowsheet activities.

Figure 3. No Acid Adjustment Feed Preparation Flowsheet.



NCAW = Neutralized current acid waste
TO = Total oxide
WO = Waste oxide

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2.3.1 Concept

Process HLW feed through the vitrification feed preparation process with acid adjustment to the slurry but without a reductant addition. Acid would be added to provide the pH adjustment needed to rheologically modify the melter feed.

2.3.2 Development Background

This flowsheet is very similar to the no acid adjustment flowsheet, but now the pH adjustment will be supplied by nitric acid (HNO_3). The motivation for running this flowsheet in this manner is the same as that stated for the no acid addition flowsheet. This flowsheet also provided an opportunity to test the sensitivity of the glass oxidation state/foaming to an oxidized feed under HTM conditions. The fundamental differences from the no acid addition flowsheet are subsequently described.

2.3.2.1 pH Adjustment Addition - Type and Amount. Because the $NaHCO_3$ addition was insufficient to provide the necessary pH adjustment, another nonreducing acid had to be selected for the pH adjustment step. Table 5 contains the list of readily available acids considered and their detrimental effect to the vitrification process.

Of the nonreducing acids listed in Table 5, nitric acid was considered the most compatible with the vitrification process. Thus, the decision was made to use HNO_3 for the pH adjustment additive. Similar to the alternate reductant flowsheet, the HNO_3 will be added until a pH ≈ 6 is reached.

Table 5. Acid Candidates for the No Reductant Feed Preparation Flowsheet.

Acid	Possible processing detriments
H_3PO_4	Phosphate forms an immiscible scum at the melt pool cold-cap interface.
H_2SO_4	Sulfate forms an immiscible scum at the melt pool cold-cap interface; many of the metals form insoluble sulfides in the melt pool; increases SO_x emissions from the melter.
HBr	Bromine will not dissolve very well in glass; bromine is corrosive to the processing system.
HCl	Chlorine will not dissolve very well in glass; chlorine is corrosive to the processing system.
HF	Fluorine is corrosive to the processing system.
HNO_3	Will increase NO_x emissions; may over-oxidize the melt pool from the additional nitrate (self defeating).

2.3.2.2 pH Adjustment Addition - Rate. Because the initial gas evolution from the feed slurry is predominately pH dependent, a similar rate of addition was used in this flowsheet as discussed in the alternate reductant flowsheet.

2.3.2.3 pH Adjustment Addition - Temperature. Because the potential for gas evolution during an initial pH adjustment to the feed is temperature dependent, the same temperature (95 °C) was maintained when adding the HNO_3 as in the alternate reductant flowsheet.

2.3.2.4 Glass Component Additions. This section describes the chemical and delivery forms of the glass component additions for the no reductant feed preparation flowsheet.

2.3.2.4.1 Chemical Form - Silica. Unfortunately, testing with this flowsheet was initially conducted with the contaminated TAMSCO silica. The flowsheet testing was then repeated with the F-110 silica source selected for the alternate reductant flowsheet.

2.3.2.4.2 Chemical Form - Sodium. Initial testing of this flowsheet was conducted with $NaHCO_3$ as the sodium source. Although the upward rebound of the pH caused by the $NaHCO_3$ addition was not as profound as in the initial alternate reductant flowsheet tests, the sodium source was changed to $NaNO_3$ to be consistent with the alternate reductant flowsheet so that the two flowsheets could be compared on a relatively equivalent basis.

Preliminary calculations of the amount of expected NO_x in both the feed preparation and melter offgas from the no reductant flowsheet (without HWVP recycle stream contribution) indicate that NO_x levels will be approximately three times more than experienced in nominal operation of the HWVP flowsheet. However, this will probably not significantly affect the design of the new HLW vitrification plant because the expected plant throughput will already require extensive NO_x treatment systems.

2.3.2.4.3 Delivery Form. For similar reasons in the alternate reductant flowsheet, the silica and sodium sources will be added dry.

2.3.2.5 Flowsheet Sequence. Again, for similar reasons stated in Section 2.1.2.10, the general HWVP flowsheet sequence was maintained in this flowsheet. The no reductant flowsheet is shown in Figure 4.

2.3.3 Selection

Two tests were needed to adequately characterize the flowsheet. In the first test, HNO_3 was added for pH adjustment and TAMSCO silica and $NaHCO_3$ were added as glass component additions. Nitric acid was added until the feed simulant pH was adjusted to approximately 5.5. All parameters (pH, temperature, viscosity, yield stress, offgas evolution [no H_2 or NH_3]) were within acceptable limits. However, before this melter feed could be melted, the problem with the TAMSCO silica was discovered and the feed was scrapped.

A second test was conducted under the same conditions as the first test except silica was added as the F-110 sand and sodium was added as $NaNO_3$. Although offgas data were not taken, all other parameters were acceptable including the melt behavior and oxidation state of the glass ($Fe^{2+}/\Sigma Fe \approx 0.06$).[1] Thus, the decision was made to also carry the no reductant flowsheet into SSHTM-1 testing. The final no reductant flowsheet that will be used in the SSHTM-1 test is shown in Figure 4.

3.0 SUMMARY

This document described the decision path that led to the selection of flowsheets to be tested in the FY 1994 small-scale HTM tests. Development of HLW feed preparation flowsheets was initiated in FY 1994 to evaluate alternative flowsheets for preparing melter feed for HLW vitrification other than that used in the HWVP.

Three flowsheets that might lead to increased processing capacity relative to the HWVP and that were flexible enough to use with other HLW melter technologies were proposed. The flowsheets under consideration were:

1. No acid adjustment feed preparation flowsheet
2. No reductant feed preparation flowsheet
3. Alternate reductant feed preparation flowsheet.

The development for these HLW HTM feed preparation flowsheets was based on the flowsheet that was developed for the HWVP. This approach allowed the HLW program to build upon the extensive feed preparation flowsheet database developed under the HWVP Project. The primary differences among the proposed flowsheets and the HWVP flowsheet were the acid adjustment and glass component additions.

The proposed flowsheets were tested at the laboratory-scale at PNL. The performance of the alternative flowsheets was evaluated against a set of established criteria, including the following.

- The flowsheet should reduce or eliminate the evolution of H_2 and NH_3 from organic acid additions compared to the HCOOH HWVP flowsheet.
- Slurry and melter feeds during the flowsheet processing should retain acceptable rheological properties as defined by specifications in the HWVP TDP.
- The melter feed oxide concentration is similar or exceeds the total oxide loading as specified in the HWVP TDP.

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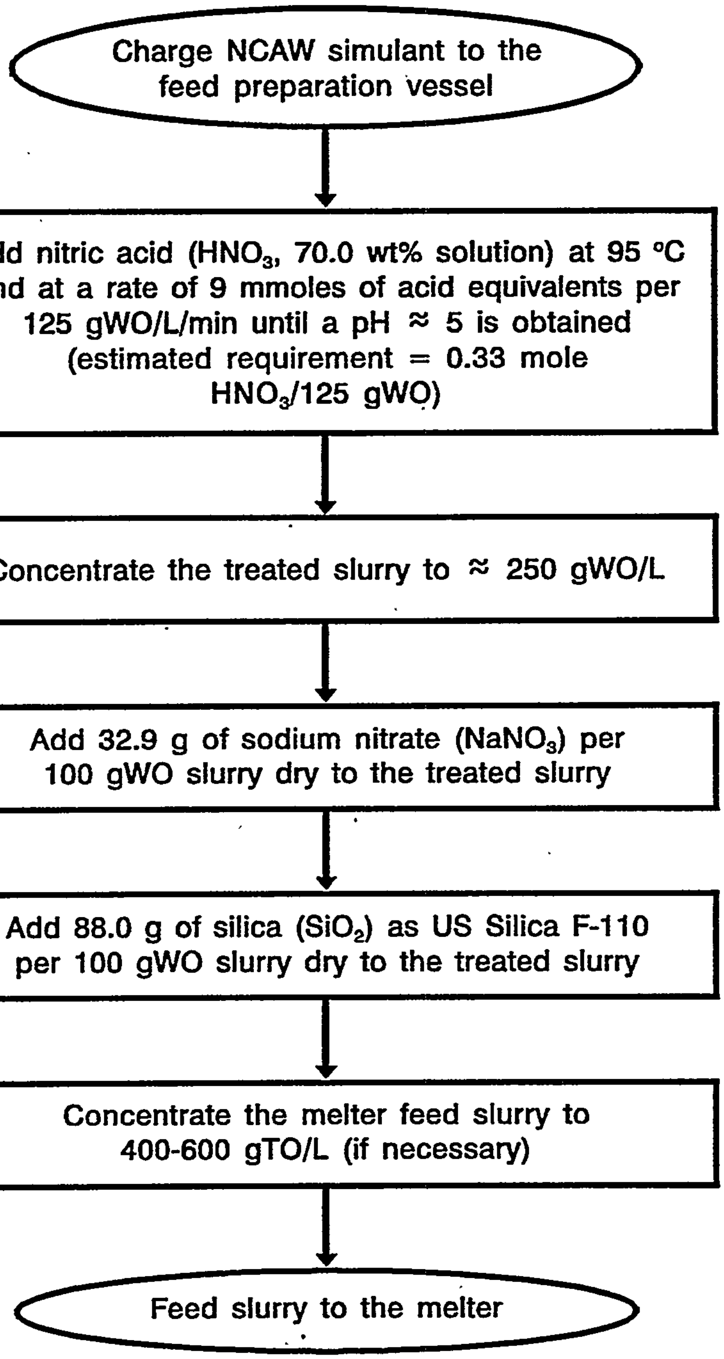
[1] Based on preliminary data. Final data to be published in an FY 1995 PNL report summarizing FY 1994 alternative flowsheet activities.

Figure 4. No Reductant Feed Preparation Flowsheet.



NCAW = Neutralized current acid waste
TO = Total oxide
WO = Waste oxide

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- Chemical additions and overall feed processing are relatively simple to control and provide overall flowsheet flexibility.
- The flowsheet is adaptable to compositional feed variability.

Testing initially focused on the ability of each of the flowsheets to mitigate H_2 and NH_3, followed by the ability of each flowsheet to yield a feed with acceptable rheological properties and a melt with an acceptable cold-cap reactivity. Based on the results of this testing and the established criteria, a reductant-based flowsheet using glycolic acid and an HNO_3 acid-based flowsheet were selected for the FY 1994 small-scale HTM testing.

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5.0 GLOSSARY

ABBREVIATIONS AND ACRONYMS

DWPF	Defense Waste Processing Facility
FY	fiscal year
HLW	high-level waste
HTM	high-temperature melter
HWVP	Hanford Waste Vitrification Plant
IDMS	integrated DWPF melter system
MFT	melter feed tank
NCAW	neutralized current acid waste
PNL	Pacific Northwest Laboratory
redox	reduction oxidation
SRS	Savannah River Site
SRTC	Savannah River Technology Center
SSHTM-1	small-scale HTM-1 test
SSHTM-2	small-scale HTM-2 test
TDP	Technical Data Package
WHC	Westinghouse Hanford Company
WVDP	West Valley Demonstration Project

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