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Small-Scale High Temperature Melter - 1 (SSHTM-1) Data Package

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February 1996

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
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Pacific Northwest National Laboratory
Richland, Washington 99352

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SMALL-SCALE HIGH TEMPERATURE MELTER - 1 (SSHTM-1) DATA PACKAGE

February 1994

Prepared by: GL Smith, HD Smith, EM Tracey, RL Myers, JA Sills,
DL Fisher, and KD Wiemers

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QA LEVEL

This work was performed to satisfy PNL FY 1995 milestone number PVTD-C95-02.02Y and was conducted in accordance with Impact Level II quality assurance requirements as defined by the PVTD QA Plan ETC-001 and the PNL QA Manual PNL-MA-70.

FIGURES

TABLES

EXECUTIVE SUMMARY

This data package, milestone C95-02.02Y, provides a brief observation and operation report on available data for the Small-Scale High Temperature Melter-1 (SSHTM-1) feed preparation activities. The test was conducted in two melter feed batch segments prepared from two different feed preparation flowsheets. Testing primarily addressed feed preparation alternate flowsheet options tested in the laboratory to mitigate potential safety issues related to generation of hydrogen and ammonia, to produce acceptable melter feed rheological properties, to maximize total waste oxide loading in the glass, to simplify the vitrification flowsheet, and to increase vitrification flowsheet processing rate. The two flowsheets selected for testing were 1) no reductant addition and titration with HNO_3 to provide an acceptable melter feed rheology near the target oxide loading (Alternate HTM Flowsheet 1), and 2) titration with glycolic acid, an alternate reductant to HCOOH (Alternate HTM Flowsheet 2).

Specific findings at this time include:

Off-Gas and Slurry Chemistry

- Preliminary data analyses show a direct correlation between the laboratory-scale and the small-scale tests. The reliability of laboratory-scale tests to predict processing activity on the small-scale is very good.
    - Off-gas total production and peak generation rates were similar within a factor of two for the laboratory- and small-scale system. Those numbers for CO_2 were predictable within 10 to 20%; within the estimated reproducibility for these tests.
    - No H_2 was observed during Alternate HTM Flowsheet 1 tests on either the laboratory- or small-scale.
    - Hydrogen production was observed during Alternate HTM Flowsheet 2 processing, a non-noble metal containing slurry simulant, on both processing scales in similar quantities (on the order of 1% of amounts observed with formic acid processing of noble metal containing slurry simulants).
    - Ammonia did not appear to be a reaction product for either flowsheet on either scale.

  - Laboratory- and small-scale nitrite and nitrate amounts essentially paralleled one another.

  - Similar amounts of organic carbon were found in both laboratory- and small-scale glycolic acid prepared feeds and indicated that little glycolate had been consumed on either scale.

  - Laboratory- and small-scale condensates were generally consistent in their compositions containing mainly nitrate, with the small-scale a little more acidic than their laboratory equivalent (as expected since the small-scale tests employed air as a sweep gas which would have oxidized NO to NO_2 producing more nitrate in the condensate).

- Comparison of Alternate HTM Flowsheets 1 and 2 suggests that more nitrite is destroyed during melter feed preparation steps when glycolic acid is used than when nitric acid is used in treating the waste simulant for the same equivalents of acid added.

Rheology

Due to the sampling procedure described in section 3.2, some caution must be taken with the application of the rheological and physical property data.

- Both the laboratory- and small-scale feed preparation systems exhibited difficulty in mixing the high total oxide loaded melter feeds prepared from Alternate HTM Flowsheets 1 and 2. This could be overcome in the laboratory by increasing the stirring rate.

- Due to the poor mixing characteristics of the melter feed treated with nitric acid in the small-scale feed preparation system, the melter feed was only concentrated to 191 gWO/L. The target concentration was 240 gWO/L.

- At a gTO/L of 354, the high temperature melter feed prepared using Alternate HTM Flowsheet 1 in the small-scale tanks, has plastic viscosities and yield stresses (determined by fitting the Bingham model to shear rate sweep data) within the specifications of 25 mPa•s and 15 Pa.

- At a gTO/L of 422, the high temperature melter feed prepared using Alternate HTM Flowsheet 2 in the small-scale tanks, has plastic viscosities within the specification of 25 mPa•s and yield stresses of 16 to 22 Pa, which is above the specification of 15 Pa.

- From a rheological performance perspective, the glycolic acid treated melter feed had higher oxide loadings relative to the nitric acid treated melter feed, for similar rheological properties.

- The nitric acid treated melter feed is slightly rheopectic (increases in viscosity under constant shearing conditions).

- The glycolic acid treated melter feed gels (i.e. the rheological properties greatly increase) when allowed to sit without continual stirring.

- Although the gTO/L, pH, wt% solids, and viscosities were similar for both Alternate HTM Flowsheets 1 and 2, the yield stresses of the melter feeds and the waste simulants prepared in the laboratory-scale processing runs were 35% lower than the yield stresses of the melter feeds prepared in the small-scale processing runs.

- For both Alternate Flowsheets 1 and 2, the plastic viscosities (determined by fitting the Bingham model to shear rate sweep data) remained below the specification of 25 mPa•s for the feed aged in the laboratory as well as for the feed aged in the small-scale system (except for the Alternate Flowsheet 2 feed aged in the laboratory).

- For both Alternate Flowsheets 1 and 2, the yield stresses were higher for the feed aged in the laboratory and in the tanks (except for the Alternate Flowsheet 1 feed aged in the small-scale system) than the specification of 15 Pa.

The laboratory aging procedure is currently under development therefore the significance of the variations in the rheological measurements is not known.

Glass Redox / Cold Cap Chemistry

- Insufficient data and analyses are available at this time to provide an accurate assessment of the redox chemistry and scaling factors. Further analyses of the cold cap, high temperature redox chemistries, and potential scaling factors will be addressed in the SSHTM-1 letter report, milestone T3C-95-129.

Small-Scale Feed Preparation Equipment Operation

- The small-scale feed preparation system was used to prepare two batches of feed simulant for the SSHTM-1 test, one with nitric acid addition and one with glycolic acid addition. This test was the first time this equipment was used for a feed preparation test, and, accordingly, there were a number of start up problems encountered. The use of this equipment for this application was also somewhat different than originally intended, which also resulted in some problems. These problems were satisfactorily addressed and the feed preparation equipment was used to successfully achieve all test objectives.

1.0 INTRODUCTION

This data package, milestone C95-02.02Y, provides a brief observation and operation report on available data for the Small-Scale High Temperature Melter-1 (SSHTM-1) feed preparation activities. The test was conducted in two melter feed batch segments prepared from two different feed preparation flowsheets. Testing primarily addressed feed preparation alternate flowsheet options tested in the laboratory to mitigate potential safety issues related to generation of hydrogen and ammonia, to produce acceptable melter feed rheological properties, to maximize total waste oxide loading in the glass, to simplify the vitrification flowsheet, and to increase vitrification flowsheet processing rate. The two flowsheets selected for testing include 1) no reductant addition and titration with HNO_3 to provide an acceptable melter feed rheology near the target oxide loading (Alternate HTM Flowsheet 1), and 2) titration with glycolic acid, an alternate reductant to HCOOH (Alternate HTM Flowsheet 2)[a]. The glycolic acid process flowsheet, Alternate HTM Flowsheet 2, was fed to the melter first followed by the nitric acid process flowsheet, Alternate HTM Flowsheet 1. Refer to the Small-Scale High Temperature Melter-1 (SSHTM-1) Test Plan and Test Plan, Addendum 1, milestones C94-03.02J, Rev. 0 and C94-03.02J, Rev. 0, Addendum 1, for further details. A complete letter report will be prepared and issued in July 1995 to fulfill milestone number T3C-95-129. This letter report will include a summary of this data package and small-scale high temperature melter operation and glass pool melt/glass product data and analysis. Preliminary small-scale high temperature melter operation data is provided in another data package, milestone PVTD-T3C-95-138, covering run information from both SSHTM-1 and SSHTM-2.

This data package describes the alternate flowsheet selection criteria used for SSHTM-1 testing, small-scale system equipment operation, and a comparison of laboratory- and small-scale melter feed preparation. Two appendices provide both the laboratory- and small-scale melter feed preparation data for Alternate HTM Flowsheet 1 and 2, Appendix A and B respectively.

2.0 ALTERNATE HTM FLOWSHEET SELECTION CRITERION

2.1 Introduction

High-level radioactive waste stored in tanks at the U.S. Department of Energy's Hanford Site will be pretreated to concentrate radioactive constituents and then fed to the vitrification plant. A flowsheet for melter feed preparation within the vitrification plant (based on Hanford Waste

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[a] Seymour, R.G., 1995. "Development of the High-Level Waste High-Temperature Melter Feed Preparation Flowsheet for Vitrification Process Testing," WHC-SD-WM-SP-008, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Vitrification Plant design (HWVP)), calls for formic acid (HCOOH) addition during the feed preparation step in order to adjust melter feed rheology and melt redox conditions. However, the potential for generating hydrogen (H_2, Wiemers 1989[1]) and ammonia[b] (NH_3) during treatment of high-level waste (HLW) with HCOOH was identified in laboratory-scale testing at the Pacific Northwest Laboratory. Work performed at PNL during FY 1991[c], FY 1992[d], and FY 1993[e2] further documented the generation of H_2 and NH_3 in neutralized current acid waste (NCAW) slurries treated with HCOOH. Studies at the University of Georgia under contract with Savannah River Technology Center (SRTC)[3] and PNL have verified the catalytic role of noble metals in the generation of H_2 and NH_3. Both laboratory-scale and pilot-scale studies at SRTC have documented the H_2 and NH_3 generation phenomena[4].

The reference process flowsheet has been typified by a sequence of approximately 2-4 hours for the acid addition at 95°C, followed by digestion for 4-5 hours at 99 to 102°C, addition of a recycle waste stream, and then completion with glass former addition at a lower temperature, ranging from ambient to 50°C. Release of H_2 is observed immediately subsequent to NO_2^- destruction, with increasing amounts generated in proportion to the amount of HCOOH added. Ammonia generation appears to follow a similar trend.

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[b] Wiemers, K.D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate on Glass Redox Adjustment*. Technical Report HWVP-90-1.2.2.03.03A. Pacific Northwest Laboratory, Richland, Washington.

[c] Wiemers, K.D., M.H. Langowski, M.R. Powell, and D.E. Larson. 1993. *Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant-Fiscal Year 1991: Evaluation of Offgas Generation, Reductant Requirements, and Thermal Stability of an HWVP NCAW Feed Simulant*, Technical Report to Westinghouse Hanford Company, PHTD-C91.03.02C, Pacific Northwest Laboratory, Richland, Washington.

[d] Smith, H.D., K.D. Wiemers, M.H. Langowski, M.R. Powell, and D.E. Larson. 1993. *Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant-Fiscal Year 1992: Evaluation of Offgas Generation and Ammonia Formation*. Technical Report PHTD-C93-03.02. Pacific Northwest Laboratory, Richland, Washington.

[e] Patello, G.K., H.D. Smith, K.D. Wiemers, R.E. Williford, R.D. Bell, and R.G. Clemmer. 1994. *Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant-Fiscal Year 1993: Effect of Noble Metals Concentration on Offgas Generation and Ammonia Formation*. Technical Report PVTD-TDE-94-439. Pacific Northwest Laboratory, Richland, Washington.

Nitrate is believed to be the source of NH_3. The reactions for H_2 and NH_3 generation are:

$$HCOOH \rightarrow CO_2\uparrow + H_2\uparrow \qquad (catalyzed)$$

$$NO_3^- + 5HCOOH \rightarrow NH_3\uparrow + 4CO_2\uparrow + COOH^- + 3H_2O \quad (catalyzed).$$

Since H_2 and NH_3 (as NH_4NO_3) may create hazardous conditions in a vitrification plant, it is important to reduce the H_2 generation rate and the amount of NH_3 to the lowest levels possible, consistent with desired melter feed characteristics.

The next two sections describe the alternate flowsheet selection criteria.

2.2 Selection Criteria

The selection of the melter feed process flowsheets for the SSHTM-1 run are based on: 1) mitigation of H_2 and NH_3 generation during feed preparation, 2) acceptable feed rheological properties, 3) maximum total oxide loading, 4) flowsheet simplicity, and 5) adaptability to feed compositional variability.

The first down selection criteria for chemical additives employed to adjust glass redox and melter feed rheology was mitigation of H_2 and NH_3 generation. Mitigation ideally means elimination of H_2 and NH_3 generation; however, realistically alternate sources of H_2 and NH_3 may be present in the waste itself[5]. The peak H_2 generation rate and total amount of NH_3 produced were compared with results observed during HCOOH reference flowsheet tests. The reference flowsheet baseline data used for comparison with the alternate HTM flowsheets is provided in Table 4.5.1.

The values of 15 Pa and 25 mPa•s for the yield stress and plastic viscosity, respectively, were chosen as the laboratory and small-scale feed preparation system rheological screening data[f] based upon communication with PVTD cost account 1.2.2.04.14[g] and the Hanford Waste Vitrification Technical Data Package[h].

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[f] The rheological screening data is taken from a PNL Don't Say It--Write It (DSI) memo: Laboratory Rheological Screening Data to distribution from P. A. Smith dated May 23, 1994.

[g] Beckette, M. R. and L. K. Jagoda (1994). Detailed Design Data Package; NCAW Waste Simulant Properties (SIPT 2/LFCM 8 Campaign), PHTD-K1017, Rev. 0, U. S. Department Energy Report, Pacific Northwest Laboratory, Richland, Washington.

[h] Hanford Waste Vitrification Technical Data Package, WHC-SD-HWV-DP-001.

Discussions with PVTD cost account 1.2.2.04.14 personnel regarding the SIPT 2/LFCM 8 campaign revealed that a solids loading of approximately 485 g TO/L for the FY 91 NCAW reference melter feed met the above conditions and was satisfactorily pumped into the melter. The grams of total oxide per liter of melter feed (gTO/L) for the SSHTM-1 tests were the maximum values achievable while meeting the rheology requirements.

Simplicity and adaptability to compositional variability are considered long-term assessment goals. For this study, the simplicity of the tested process flowsheets will be compared with previous reference HCOOH flowsheet test experience, primarily in a qualitative manner. The description may include such issues as number of process steps and a subjective evaluation of ease of operation. Additional testing will be required to evaluate sensitivity to operation control parameters and feed composition, and process predictability and reliability.

2.3 Selected Alternate HTM Flowsheets

The two flowsheets chosen are no reductant addition and titration with HNO_3 to provide acceptable melter feed rheology near the target oxide loading, (Alternate HTM Flowsheet 1), and titration with glycolic acid, an alternate reductant to HCOOH (Alternate HTM Flowsheet 2).

Alternate HTM Flowsheet 1 was chosen based on a no reductant scenario to mitigate hydrogen and ammonia production. However, untreated waste slurry (pH ≈ 11) could not be concentrated to 240 gWO/L. Nitric acid was added to allow a higher total oxide loading in the slurry and meet the rheological requirements. This change to the flowsheet provided an additional benefit in that it was an opportunity to test an oxidized melter feed and to simplify the baseline flowsheet. The nitric acid flowsheet met the hydrogen and ammonia, rheology, and maximum total oxide loading criteria. Since pH is correlated with the amount of acid added it was used as the control parameter for acid addition based on previous laboratory experience. In addition, laboratory testing showed that it had simple processing characteristics and that the $Fe^{+2}/\Sigma Fe$ value (0.06, provided from laboratory standard crucible redox testing) was in an acceptable range (0.005-0.23)[g] for laboratory melts made from this feed.

The glycolic acid flowsheet, Alternate HTM Flowsheet 2, was chosen from a number of potential candidates for replacement of HCOOH which were considered based on criteria related to acidity, oxidation potential, and plant operations issues.[i] Thirteen alternate reductant candidates were screened in a series of laboratory tests by Dr. R. B. King and his associates

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[i] Seymour, R.G., 1995. "Evaluation of Alternate Chemical Additives for High-Level Waste Vitrification Feed Preparation Processing," WHC-SD-WM-SP-009, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

at the University of Georgia to evaluate the potential for H_2 and NH_3 generation during treatment of a simplified NCAW simulant.[j] Three reductants, oxalic, glycolic, and lactic acidified the NCAW simulant without detectable H_2 or NH_3 generation. Additional laboratory-scale tests were conducted at PNL to evaluate alternate flowsheets for mitigation of H_2 and NH_3, while maintaining acceptable melter feed properties.[k]

When an organic acid is used to control both pH (for acceptable rheology) and redox conditions, it is necessary to take into account the reducing potential of the acid per acid equivalent. In these PNL tests, glycolic acid was chosen as the best of the three reductants based on reduced carbon contribution over lactic acid (lactic acid contributes 50% more carbon per unit of acidity) and based on acceptable rheological properties (oxalic acid treatment produced a melter feed with unacceptable rheological properties in the target total oxide loading range).

3.0 LABORATORY- AND SMALL-SCALE SYSTEM EQUIPMENT DESCRIPTION AND OPERATION

Details on target waste slurry simulant, melter feed, and glass compositions, processing steps, test matrix, etc. processed through both the laboratory- and small-scale systems may be found in the Small-Scale High Temperature Melter-1 (SSHTM-1) Test Plan and Test Plan, Addendum 1, milestones C94-03.02J, Rev. 0 and C94-03.02J, Rev. 0, Addendum 1, respectively.

3.1 Laboratory-Scale System Equipment Description and Operation

Introduction/Overview

Several preliminary laboratory-scale slurry processing runs were made prior to the small-scale slurry processing runs to estimate the amounts and rates of off-gas production for initial safety or other engineering calculations. These laboratory tests were presented in the test plan addendum. On the basis of these laboratory tests, the basic test procedures

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[j] R.B. King, N.K. Bhattacharyya, and V. Kumar. December 1993, Monthly Technical Report, "Hanford Waste Vitrification Plant Hydrogen Study: Preliminary Evaluation of Alternatives to Formic Acid." Prepared for Pacific Northwest Laboratory under contract number 125770-A-A2.

[k] PHTD-C94-03.02B, Rev. 0 Investigation Plan. "FY 1994 Feed Preparation Chemistry Laboratory-Scale Tests, Evaluation of Alternate Flowsheets and Measurement of Properties Related to Slurry Transport." February 14, 1994.

PHTD-C94-03.02B, Rev. 0 Investigation Plan Addendum. "FY 1994 Feed Preparation Chemistry Laboratory-Scale Tests, Evaluation of Alternate Flowsheets and Measurement of Properties Related to Slurry Transport." March 22, 1994.

given in Section 4.2 were developed. When the processing tests were performed on the small-scale, the newness of the system and some related engineering difficulties caused the processing tests to deviate from the original processing test parameters such as initial waste oxide loading, acid addition rate and digestion/concentration time resulting in a modified procedure. Therefore, laboratory versions of the modified small-scale processing tests were made, so that the basis of comparison of the two scales would be as close as possible. The laboratory reproductions of the small-scale processing tests are identified as T95-SSHTMGLYC-1 and T95-SSHTMHNO3-1, -2, -3. The reasons for doing three nitric acid laboratory processing tests are discussed in the next paragraph.

The primary reason for doing three nitric acid processing tests were testing difficulties that were identified with the laboratory system. During the first processing test (T95-SSHTMHNO3-1) there was a problem controlling the temperature within ± 2°C of the target acid addition temperature. This was subsequently identified as a mixing problem resulting from too low a stirring rate. (When this simulant has an elevated gWO loading it tends to form a weak gel when heated to temperatures near boiling. If the stirring action is not vigorous enough, it will not mix properly allowing temperature gradients to develop in the slurry simulant. By increasing the stirring rate, causing the slurry to mix more vigorously, this problem is not observed.) Processing test T95-SSHTMHNO3-2 was performed using exactly the same slurry simulant starting material, but with increased stirring rates. This processing test went well for the first 3-4 hours. Then a sweep gas inlet tube began to crack (noticed first on the GC as an increase in the O_2 and N_2 content of the sweep gas) and failed completely a few hours later. This processing test does provide some good reproducibility data for the first few hours of this test. Laboratory processing test T95-SSHTMHNO3-3 was a complete test with all systems operating properly, acceptable temperature control, and no gas leaks. The third test was used for comparison of laboratory- versus small-scale feed preparation data.

Equipment

Equipment and test methods employed are shown in Figure 3.1.1 which is a schematic of the instrumented reaction vessel. An overall schematic of the off-gas measurement system is given in Figure 3.1.2.

The instrumented reaction vessel shown in Figure 3.1.1 consisted of a 2-L Pyrex kettle placed in a temperature controlled heating mantle. The Pyrex® kettle lid was modified to accept a thermocouple, acid addition tube, pH electrode, pH automatic temperature compensator, agitator shaft, condenser, sweep gas inlet, slurry sampling port, and baffle to enhance vertical mixing. A second condenser was added in series to the first condenser connected to the vessel lid. Acid was introduced below the surface of the simulant through a Teflon® tube using a peristaltic pump to control the addition rate. The sweep gas, argon with a helium tracer, carried off-gases from the reaction vessel plenum, through the condensers to the off-gas measuring system (Figure 3.1.2).

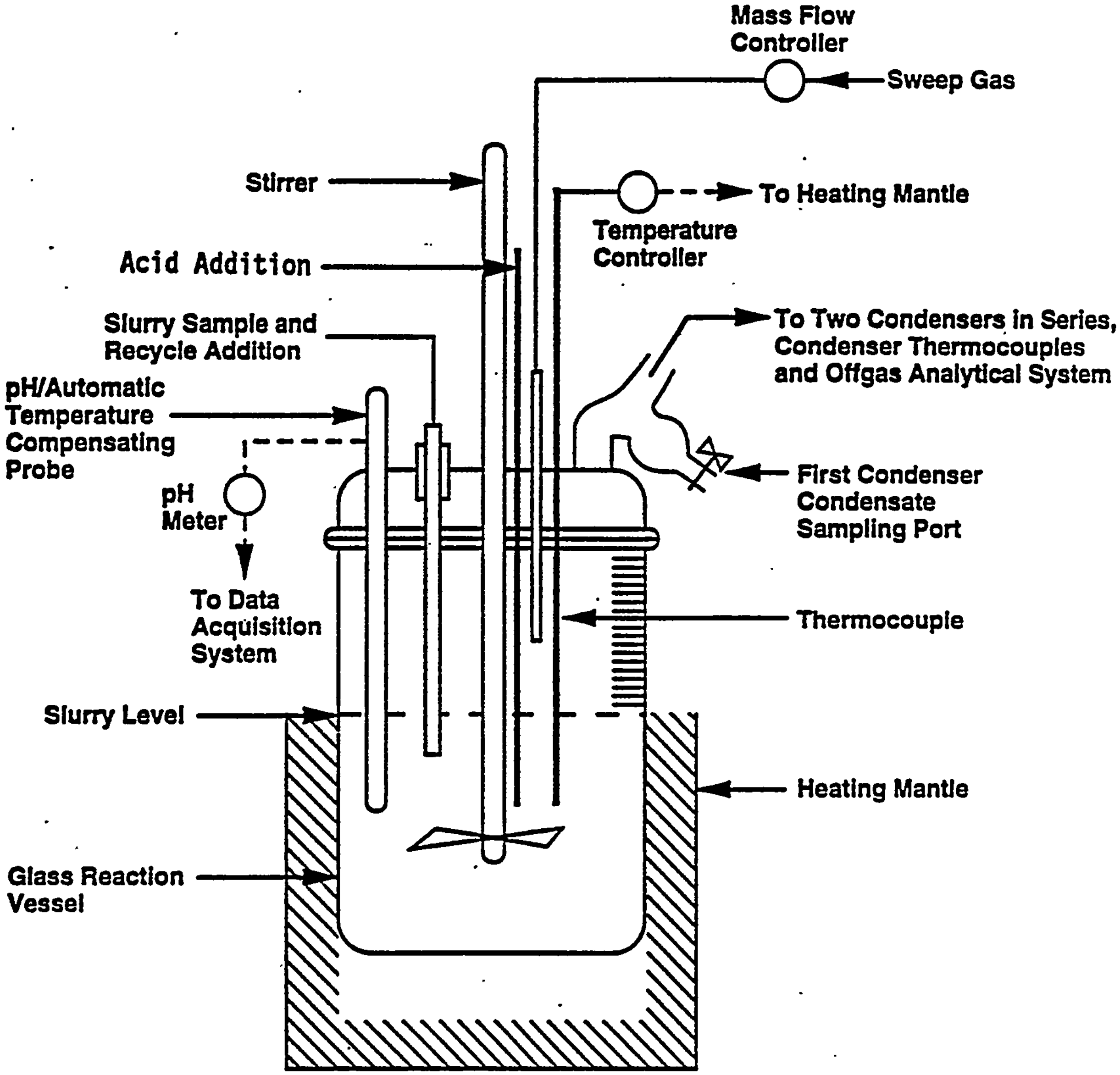

Figure 3.1.1 Schematic of the Laboratory-Scale Reaction Vessel Used for Feed Preparation Process Testing.

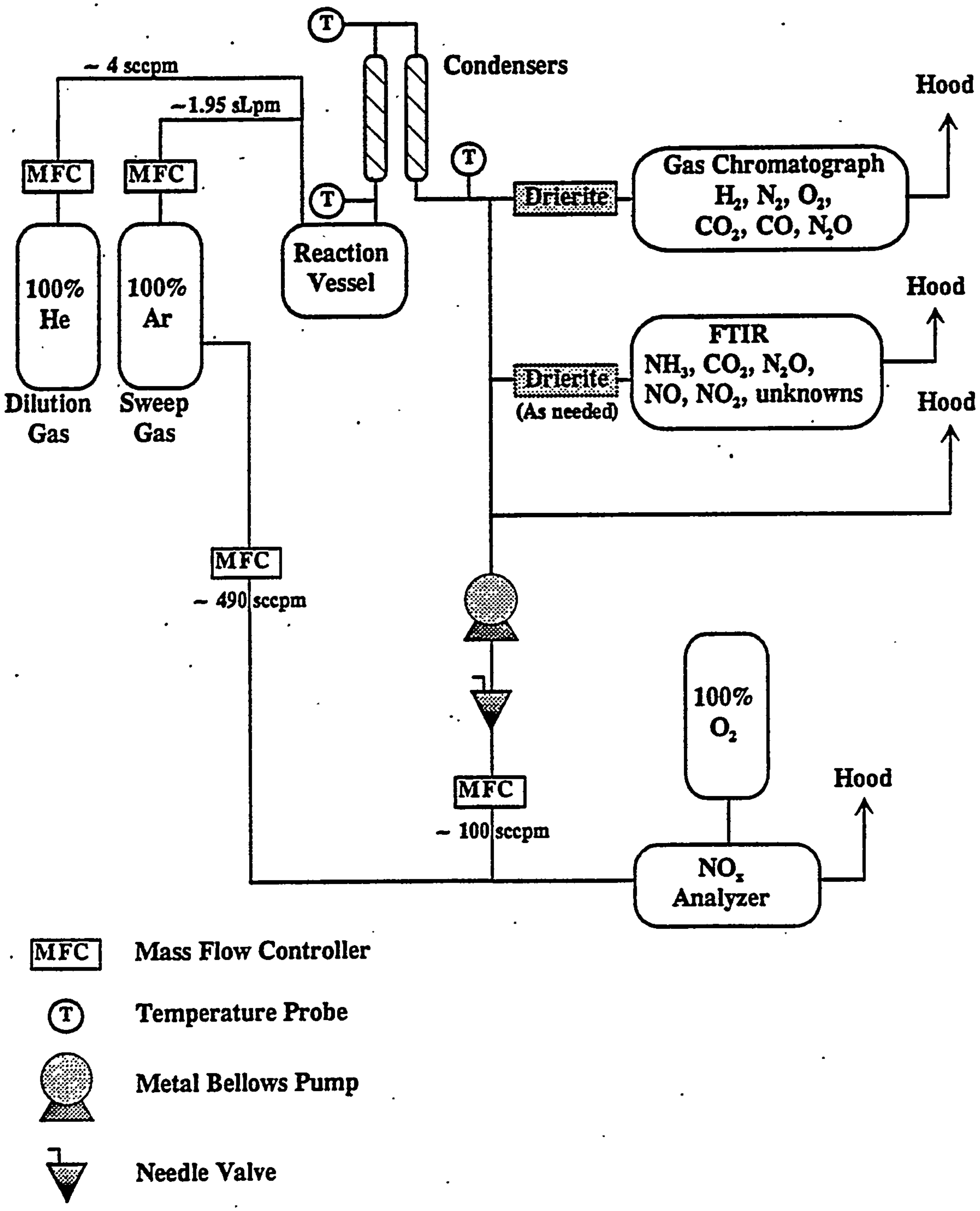

Figure 3.1.2 Schematic of the Laboratory-Scale Off-Gas Equipment Configuration for Feed Preparation Process Testing.

Figure 3.1.2 includes a schematic of the off-gas measuring equipment configuration. Because of the dynamic nature of the feed process chemistry and resultant gas generation, real-time monitoring capabilities were employed to characterize the generation rates of the major gaseous reaction products. The emission rate behaviors of H_2, CO_2, and N_2O were monitored using a gas chromatograph (GC). A chemiluminescent NO/NO_x analyzer was used to measure primarily NO_x. The nominal sample rate of the GC was approximately 80 s, while the nominal sample rate of the NO_x analyzer was 60 s. A Fourier transform infrared (FTIR) spectrometer analyzed gas samples on an approximately 3 minute cycle time providing a backup analysis for each of the above gases plus NH_3, except for H_2, and detection of other unknown, IR sensitive, gaseous species.

Operation

Tests steps specific to SSHTM-1 laboratory testing are described in the following sections.

a. Preparations for Acid Addition:

1. A given weight of waste slurry simulant with known gram oxide waste loading and specific gravity was placed into the precleaned reaction vessel (for modified small-scale laboratory test, a preconcentrate waste simulant was used). If needed, $NaNO_2$ and Na_2CO_3 are added to bring the slurry concentrations of nitrite and carbonate to target levels.

2. The reaction vessel lid which had been modified for the instrumentation, agitation, sampling, and off-gas collection was clamped in place.

3. Antifoam was added. The antifoam agent used was Dow Corning 544 (see the data logs in the appendices for actual amounts used).

4. Initial slurry sample was collected.

b. Acid Addition: The temperature, pH, and off-gas generation rate were measured as a function of process time. The temperature was maintained within 93 ± 2°C. The following steps were taken to add acid.

1. The sweep gas (1.946 L/min Ar + 0.004 L/min He) flow rate was established.

2. Acid was added at a predetermined rate (on the order of 9 mmole H^+ equivalents per 125 gWO/L - min, see the data logs in the appendices for actual amounts) until the addition was complete.

3. Slurry was sampled. Final condensate samples for this period were collected.

c. Digestion/Concentration: Temperature, pH, and off-gas measurements were continued. The following steps were followed during the digestion/ concentration period.

1. The slurry temperature was raised to boiling.
2. The slurry was heated to a specified temperature, usually between 90-95°C.
3. Waste slurry simulant concentrated to a target of approximately 240 gWO/L.
4. Slurry was sampled. Final condensate samples for this period were collected.

d. Glass Component Addition: Glass components batched into waste slurry to complete melter feed.

During the tests, both condensate and slurry samples were taken. Primary condensate was collected from the first condenser while secondary condensate was collected from the second condenser. There was always 100 to 1,000 times more primary condensate volume than secondary. The condensate samples were collected over a period of time. Slurry samples, on the other hand, were collected at specific times, generally before and after acid addition and after digestion.

Following each test, the remaining treated melter feed simulant was placed in a tightly capped, labeled container. This material was held in reserve for future melting, rheology, or chemical studies.

A technical activity log was maintained during the tests. The primary function of the log was to record observations of slurry color and slurry behavior. The log was also used to record slurry temperature and pH as a backup to the data acquisition system and to record the beginning and ending of the various test stages. Most slurry observations were about the degree of foaming and the actions taken to control the foam. Other observations were predominantly about the appearance of secondary phases in the form of films or scum on the slurry surface or about the slurry color.

3.2 Small-Scale System Equipment Description and Operation

Introduction/Overview

The small-scale feed preparation system was used to prepare two batches of feed for the SSHTM-1 test. This feed preparation test was the first use of the feed preparation system, except for some Slurry Test Loop pressure drop/flow testing which used part of the equipment. The first preparation (Alternate HTM Flowsheet 2) using glycolic acid was started with the addition of NCAW waste simulant to Tank HB-32 on August 8,1994 and was completed with the addition of $NaNO_3$ and SiO_2 glass making components to the treated waste slurry that was in Tank HB-33 on August 14, 1994. The treatment of the simulated waste slurry with glycolic acid occurred on August 10, 1994. The second preparation (Alternate HTM Flowsheet 1) using nitric acid was started on August 12, 1994 with the placement of waste slurry simulant in Tank HB-32. Treatment with nitric acid occurred on August 14, 1994 and addition of $NaNO_3$ and SiO_2 components to this slurry occurred on August 19, 1994. Approximately 1514 liters (400 gallons) of melter feed was made for each alternate HTM flowsheet.

Equipment

The equipment is described in detail in the "SMALL-SCALE HIGH TEMPERATURE MELTER - 1 (SSHTM-1) TEST PLAN", C94-03.02J, Rev. 0, and will be summarized here. A number of problems were encountered with the start-up of the SSHTM feed preparation test system, as would be expected for the first use of similar equipment. These problems and the resolutions are summarized in the sections that follow. Also, several equipment recommendations based on SSHTM-1 experience are made to facilitate testing and ease of operations for future feed preparation tests.

The SSHTM Feed Preparation equipment is located on the third floor High Bay in 324 Building and consists of three 500 gallon tanks with various equipment as outlined below:

a. Feed Preparation Tank, HB-32: The feed preparation tank (refer to Figure 3.2.1) is designed primarily for feed preparation, including chemical addition, concentration, and reaction. The tank is equipped with a two-impeller agitator, a heating/cooling coil, a steam condenser, and a drain diaphragm pump. The instrumentation includes a bubbler fluid level monitoring system, a capacitance level probe, steam flow rate, condenser off-gas flow rate, condenser cooling water flow rate, temperature readouts (condenser off-gas, condenser cooling water, condenser seal pot, and three in-tank locations), tank pressure, and agitator power and speed. There were no provisions for automatically recording data. In addition, there was an off-gas cart, a schematic of this equipment is shown in Figure 3.2.2, with various equipment for analyzing off-gas during acid addition and digestion/concentration.

b. Melter Feed Tank, HB-33: The melter feed tank is a 500 gallon tank equipped with an internal cooling coil, a two-impeller agitator, and a diaphragm pump that feeds a recirculating loop, one branch of which feeds the small-scale melter. Instrumentation in this tank is limited to one temperature of tank contents, an ultrasonic level detector, and load cells to determine weight.

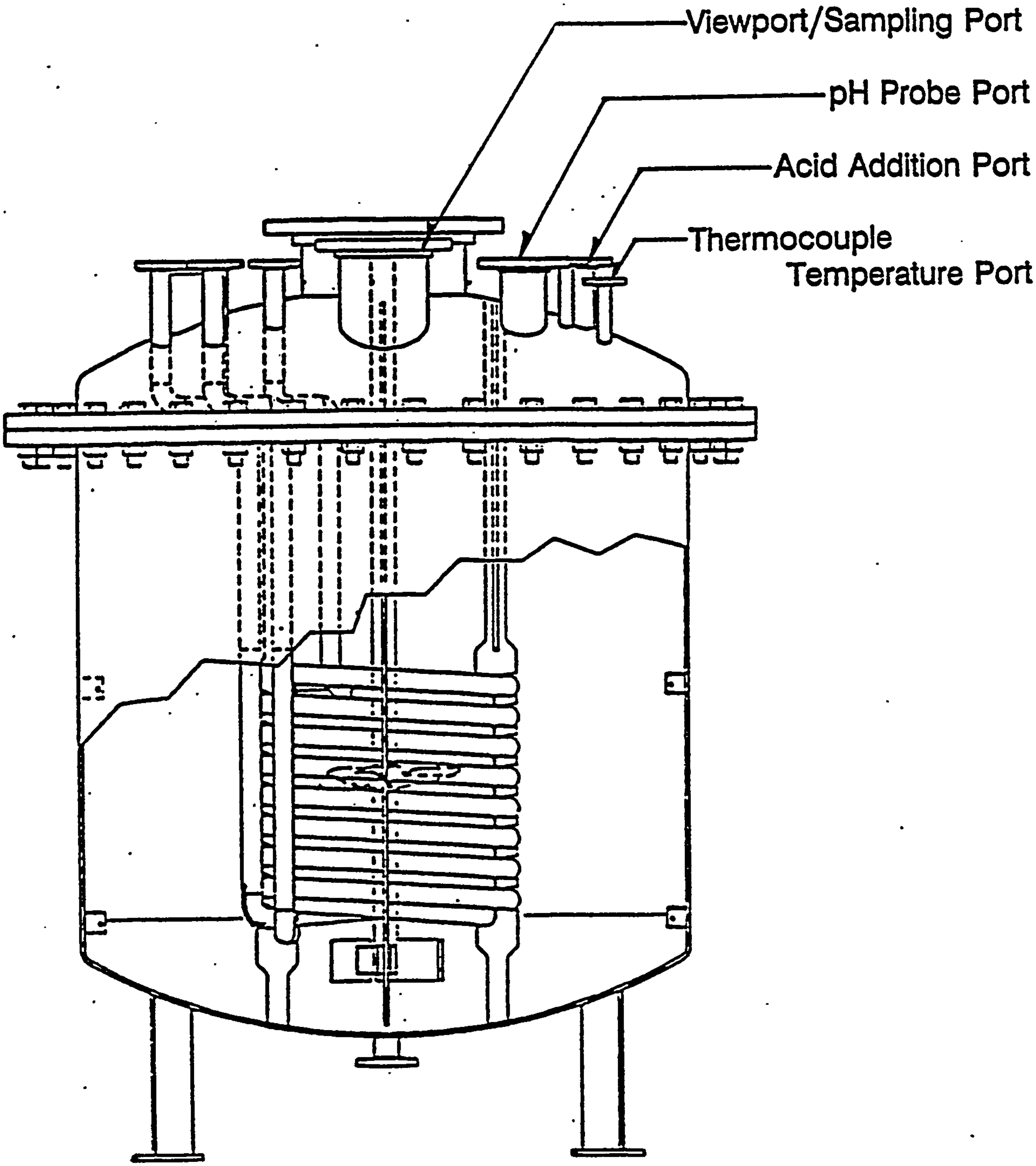

Figure 3.2.1 Schematic of Tank HB-32 Used for Small-Scale Feed Preparation Process Testing.

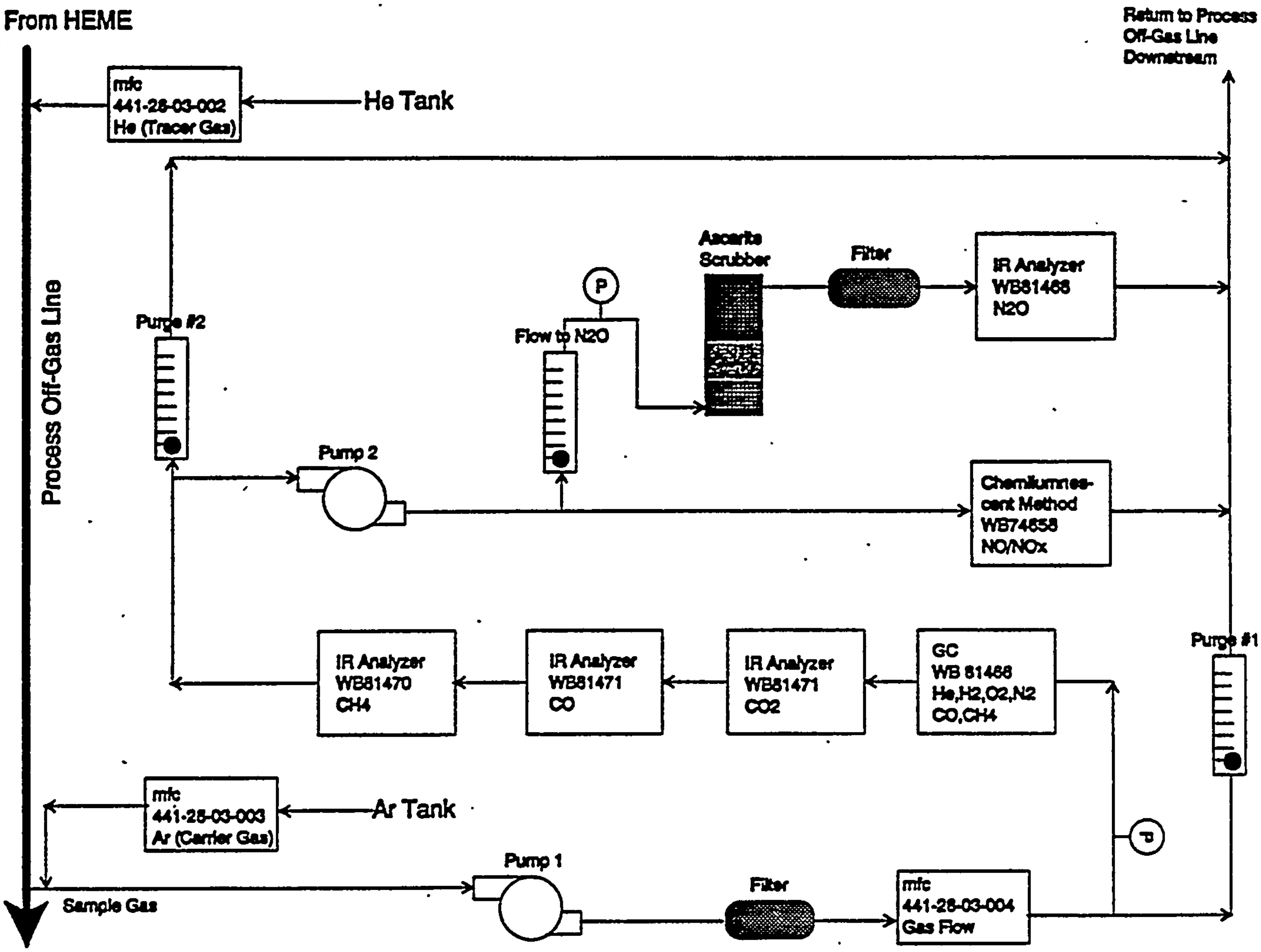

Figure 3.2.2 Schematic of the Small-Scale Off-Gas Equipment Configuration for Feed Preparation Process Testing.

c. Frit Slurry Tank, HB-34: The frit slurry tank is a 500 gallon tank equipped with an internal cooling coil, a two-impeller agitator, and a centrifugal pump for fluid transfers. Instrumentation includes a capacitance level probe and one temperature sensor for tank contents. This tank was used for the slurry test loop work.

Operation

The SSHTM-1 melter feed preparation was performed by loading Tank HB-32 (capacity ≈550 gallons) with about ten drums (50-55 gallons each) of waste slurry simulant with an oxide loading of about 110 gWO/L. This slurry was agitated, heated to boiling via steam heating coils in the tank, and concentrated. Additional drums of waste slurry were added to obtain a final total waste oxides loading in the tank of approximately 338 Kg. The total oxide loading included quantities of Na_2O added as the nitrite and the nitrate needed to shim the nitrite and nitrate to levels consistent with the FY 1991 Reference NCAW waste composition. The waste slurry oxide loading prior to treatment with either glycolic or nitric acid was around 180 gWO/L.

Titration of the slurry with nitric acid (Alternate HTM Flowsheet 1) or glycolic acid (Alternate HTM Flowsheet 2) began once Tank HB-32 was loaded with the required amount of waste oxides and enough condensate removed to allow acid addition without overfilling the tank. Nitric acid at 70 wt% (Alternate HTM Flowsheet 1) or 70.6 wt% glycolic acid (Alternate HTM Flowsheet 2) were both added to a target pH of 4.8 ± 0.1 (temperature 93 ± 2°C) as measured with an on-line pH measurement probe. The addition rate for HNO_3 was 109.8 kg (241.8 lbs) in 55 minutes and for glycolic acid was 162 kg (356.8 lbs) in 80 minutes (for specific addition rate data concerning Alternate HTM Flowsheet 1 and 2, see Log A4.1 and Log B4.1, respectively, in the attached appendices). The temperature of the waste slurry during acid addition was approximately 95°C and the rate of acid addition was at or below the scale-up rate based on laboratory tests. Off-gas, amounts and composition, were measured beginning with the start of acid addition and continued through the end of the digestion/concentration period (about 8-9 hours total). The off-gas system measured NO_x, N_2O, CO_2, CO (although CO was not detected), and H_2 (see Figure 3.2.2). Slurry and condensate samples were removed periodically during the acid addition and digestion periods for analyses which included determination of NH_3 by selective ion electrode.

The acid treated waste slurry was concentrated to about 240 gWO/L in preparation for addition of silica (SiO_2 sand) and Na_2O ($NaNO_3$). The nitric acid treated waste slurry began to show poorer flow properties and cling to the heating coils as the waste slurry concentration approached 220 gWO/L, so concentration was stopped and between 46 to 68 liters of water were added back in an attempt to restore good flow properties. Good flow properties were not restored and an additional 38 liters of water were added to tank HB-32. This did improved the mixing some but there was still a stagnant area approximately 10 cm wide along the inside tank wall. At this point the feed was transferred to tank HB-34, which provided better mixing capabilities. A rheology sample taken from tank HB-34, after the transfer, showed that the added water, 84 to 106 liters, lowered the oxide loading to 191 gWO/L. Figure 3.2.3 provides comparative schematics of tanks HB-32 and HB-33 (tank HB-33 is almost identical to tank HB-34). For similar waste oxide loadings, melter feed treated with glycolic acid has lower rheological property values than melter feed treated with nitric acid. Therefore, similar mixing problems were not encountered when processing the glycolic acid treated melter feed.

Observations/Problems

Problems experienced with the SSHTM feed preparation equipment during the SSHTM-1 feed preparation test were typical of a first-time use or start-up of a large system. Also, various provisions were implemented to obtain some of the data or information required by the test plan. This sections describes in detail the major problems and how they were resolved to satisfy test requirements.

It should also be noted that the equipment overall worked well and was successfully used in the preparation of melter feed simulant for the SSHTM test and obtaining data in support of the feed preparation process.

a. Agitator: The location of the top agitator blade in HB-32 was higher than shown on the manufacturer's drawings and too high to achieve good mixing.

A second problem with the agitation in HB-32 is that is was much less efficient than in HB-33, as evidenced by a visual comparison with the mixing in HB-32 and HB-33 of the same melter feed. Figure 3.2.3 provides comparative schematics of tanks HB-32 and HB-33 showing differences of impeller types and coil configurations. The melter feed (with glycolic acid) was agitating very poorly in HB-32 with caking building up on the coils and an approximate 6-inch dead area around the tank periphery. After its transfer to HB-33, which was done to allow the second batch with nitric acid to be made up in HB-32, the mixing improved dramatically. Mixing characteristics of the feed was a limiting factor in acid addition and percent oxide concentration.

b. Data Recording: The MICON control system was to be used for data recording, but it was not available because of hardware problems.

c. Tank Volume: There is no good provision for measuring tank volume or weight in the SSHTM feed preparation system, feed preparation tank, HB-32. Although there is a dip tube bubbler system in HB-32, those measurements are often inaccurate, particularly during boiling and agitation. The capacitance level probes require calibration with the particular fluid in use. This device was not calibrated since the waste simulant changes throughout the feed preparation process as different chemicals are added and the simulant is concentrated/diluted. An ultrasonic level probe located in HB-33 proved to be the most accurate of the three types.

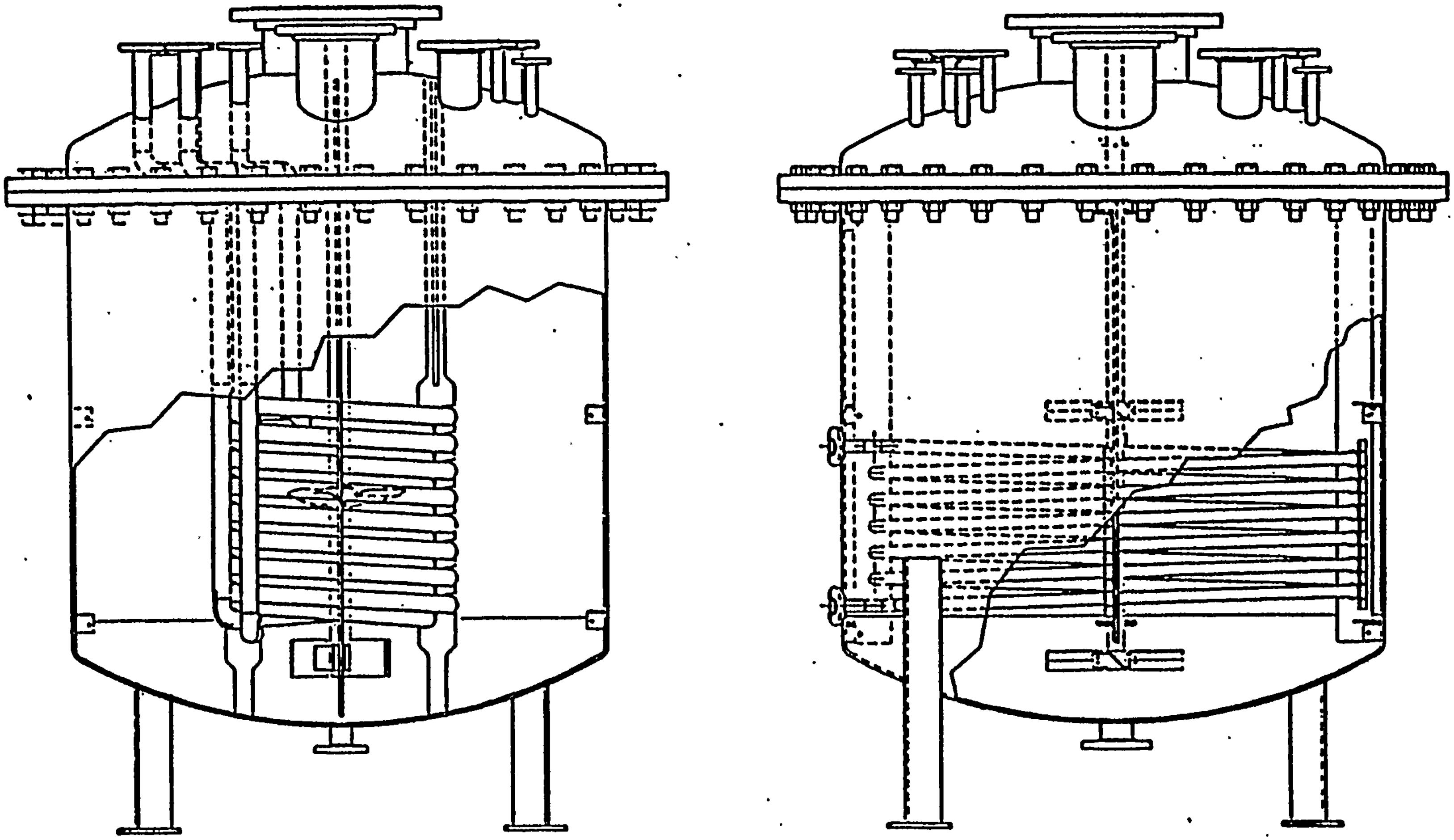

Figure 3.2.3 Comparative Schematics of Tank HB-32 (left schematic) and HB-33 (right schematic) Showing Differences of Impeller Types and Coil Configurations.

d. Condensate Flow: There is no flow meter on the condensate line and, therefore, no on-line method to determine amount of condensate removed.

e. Sampling: There is a provision for taking samples from the 2 inch drain line on Tank HB-32. Slurry feed can be recirculated back into the tank through the drain line and sampled from the appropriate port. However, this method was not used as the drain line and pump used to recirculate the slurry move a large volume of slurry. This would add a large amount of flush water to the feed simulant every time a sample was taken.

f. pH Measurement: There is no provision for pH measurement in any of the SSHTM feed preparation tanks as found in the full scale prototypic tank (HB-15).

g. HB-32 Temperature Control: A single coil is used for both heating and cooling, one or the other but not simultaneously, in HB-32 . The steam supply and cooling water are controlled manually and some difficulty was experienced achieving and maintaining a desired temperature. Excessively long slurry concentration times during melter feed preparation are likely due to inefficient heat transfer from the coils. Inefficient heat transfer could be due to caking on the coils or characteristics of the melter feed slurry simulant. As there was significant caking on the coils and the caking was easily washed off when the tank was rinsed, it appears that poor mixing was the cause of the caking. Observed improvement of mixing in the melter feed tank with the same slurry may be attributed to the lack of heating/cooling coils in the center of tanks HB-33 and HB-34 as opposed to tank HB-32 and different impeller design.

h. SSHTM not Fed Directly from HB-33: The pinch valve that was to be used to feed the melter directly from the HB-33 feed line failed during SSHTM-3 testing.

<u>Problem Resolution</u>

a. Agitator: The location of the top agitator blade in HB-32 was higher than shown on the manufacturer's drawings and too high to achieve good mixing. The agitator was removed and the top blade relocated in accordance with manufacturer's drawings. The position of the agitator blades on the other two tanks, HB-33 and HB-34, were checked and found to be okay.

Mixing characteristics of the feed prevented further concentration and/or acid addition. Although the glycolic acid feed was concentrated as required, it was right at the limit of the capability of the equipment to keep it mixed. In the second melter feed batch, the nitric acid addition was stopped just short of the amount required because it became too thick to keep it mixing properly. Even though the melter feed tank agitator, in Tank HB-33, was doing a better job of mixing, both melter feed batches experienced stagnant areas.

b. Data Recording: Manual readings were taken at periodic intervals during the course of feed preparation test activities. The pH meter and one temperature probe were wired into a visual display monitor in the test area, making the observation of these values easier. Seven temperatures were monitored on a borrowed computer with data recording software set up for that purpose. These temperatures were read-out real time on a screen and recorded electronically and converted to MS Excel format.

c. Tank Volume: As a check, data from a calibration run with a known volume of water as correlated with vertical location of tank components was used with visual observations of liquid level. In addition, a rod with tabs welded onto it in set increments was made to provide an indication of the level of simulant in HB-32 by visual observation. This device, however, was never calibrated with a known volume of liquid due to time constraints on the beginning of testing and was not used during the test. This rod is available for future testing. Throughout the test tank volume was determined by accurately measuring and recording amounts of materials added and removed. During the concentration steps, for example, the amount of condensate removed was determined by weighing the condensate (see section below). Slurry density and weight percent total solids were calculated based on these volumes and the known amounts of chemicals added and compared with analytical data. The analysis and calculated data compared favorably.

d. Condensate Flow: The amount of condensate removed during concentration and digestion activities was determined by using a drum scale and weighing the drum used to collect the condensate. The weight was then converted to a volume. During the digestion the drum was located on the second floor of the high bay in a fume hood to protect against toxic fumes. The distance between the condenser, located on the third floor, and the drum required a long tube.

e. Sampling: Several slurry samples were obtained by dipping a bottle taped to the end of a stick or metal tube into the feed from the top port. Although this method provided valuable data, it is messy and only obtains samples from the top of the waste simulant. A small peristaltic pump was borrowed and set up with tubing to pull a sample from the simulant through a flange in the top of the feed preparation tank. Although this was a simple solution, it required borrowing hardware and improvising the set-up. A much preferred solution would be to purchase and permanently install a dedicated system for sampling, especially when a significant amount of data depends on sample analysis.

f. pH Measurement: A pH meter and several probes were borrowed and the probe was mounted in a stainless steel tube and sealed to isolate the electrical connections from the slurry and provide protection to the probe. This probe was then inserted into the simulant from one of the top flange penetrations.

g. HB-32 Temperature Control: The temperature in HB-32 was controlled by manually setting either the steam supply flow or cooling water flow. Because it was manually controlled and the delay in system response, there was some overshoot and temperature fluctuations around the desired set point. These fluctuations were minimized by good operator judgement.

h. SSHTM not Fed Directly from HB-33: Melter feed was pumped into a 55 gallon day tank near the SSHTM and then peristalticly pumped to the melter.

i. Vacuum Feed System: A vacuum feed system procured for the addition of dry chemicals was used for the first time during SSHTM-1 feed preparation. This system worked very well, saving a considerable amount of time and effort during the addition of dry glass forming chemicals.

j. Rinse Water Volume: A flow meter on the water line was used to determine the amount of rinse water added when rinsing tank internals, sampling equipment, empty drums, etc. During previous testing rinse water volume was estimated by operator judgement.

Recommendations for Future Testing

The small-scale feed preparation system equipment was successfully used to prepare feed for the SSHTM-1 test and obtain valuable feed preparation process information. There are several improvements that can be made to the equipment that would greatly facilitate the monitoring and acquisition of data during the feed preparation process. Since the primary purpose of feed preparation tests is to document the feed preparation process and obtain feed physical and chemical properties data, it is strongly recommended that these equipment improvements be made to support any future feed preparation testing. These recommended improvements are given below, and not in any particular order of priority.

a. Access Stand: Design an access stand for use with the small-scale feed preparation equipment providing safe access for observation, sampling, chemical addition, and future equipment modification or changes.

b. Tank Volume: Use a simple, inexpensive visual gage that can be calibrated with any liquid, as a backup verification volume check.

Add capability for total tank weight (load cells) measurement, to confirm amounts of chemicals added or removed; use in combination with specific gravity analysis to check direct volume measurements.

c. Temperature Indication: Provide real-time temperature indication on same level (third floor) as feed preparation equipment.

d. Sampling: Include small sample pump and sample lines. Sampling and analysis is a major source of data for feed preparation tests.

e. Acid Addition: Include peristaltic or metering pump for acid addition, a critical activity of feed preparation.

f. Off-gas Equipment: Provide dedicated equipment for off-gas analysis and indication. Sharing off-gas equipment with melter operation results in extra overtime and risk to equipment, data, and schedule. Off-gas sampling and analysis is a major source of data for feed preparation and melter tests.

g. Heating/Cooling Control: Provide electronic control of HB-32 heating and cooling to achieve a more stable system response. Separate heating and cooling coils may be required.

h. Data Recording: Provide automatic electronic recording of data.

i. Agitation System: Redesign of the agitation system to allow for a wider range of processing conditions, i.e. higher agitation speed.

3.3 Differences Between the Laboratory and SSHTM Equipment and Procedures

The reaction vessel materials are borosilicate glass (laboratory-scale) versus stainless steel (small-scale). If the transition elements have any catalytic activity, then those reactions might be enhanced in the small-scale system. The sweep gas in the laboratory-scale system is pushed through the reaction vessel resulting in a slight over pressure in the reaction vessel whereas the sweep gas is pulled through the small-scale processing tanks resulting in a slight negative pressure in that system. The slight negative pressure might result in a greater tendency to foam in the small-scale system. Also, the sweep gas is argon in the laboratory system and air in the small-scale system, hence there should be a tendency for the NO to oxidize to NO_2 in the small-scale system as compared to the laboratory-scale system resulting in more acid and higher nitrate containing condensate produced by the small-scale system.

4.0 PROCESSING WASTE SLURRY to MELTER FEED: LABORATORY- versus SMALL-SCALE

4.1 Introduction

The SSHTM-1 Test provided an unique opportunity to compare laboratory-scale slurry processing to that on a small-scale. The scale factor between the two levels of testing based on processing volume was about 1200, so the size difference was very significant. In this section, the two scales of processing are compared on the basis of slurry chemistry and off-gas production. Rheology and glass redox data for a very limited number of laboratory- and small-scale samples are also discussed. Revisions to the rheological characterization procedure will be addressed in a subsequent deliverable, T3C-95-130. Evaluation of the cold cap redox reactions will be provided in the SSHTM-1 letter report, milestone T3C-95-129.

Preliminary conclusions are drawn as to the reliability of laboratory-scale tests in predicting processing activity on the small-scale.

4.2 Alternate HTM Flowsheet Procedures

Alternate HTM Flowsheet 1 - To obtain acceptable rheological properties in concentrated slurries, once the rheology limit is reached, it is necessary to lower the pH with an acid addition. This has been shown to be the case in a number of tests where rheology properties have been investigated as a function of acid concentration, see the "Slurry Characterization Data Package, milestone C94-03.02W, for more detail. In Alternate HTM Flowsheet 1, HNO_3 is added to reduce the pH to 4.8 ± 0.1, then the slurry is concentrated to about 240 gWO/L. The processed slurry is turned into melter feed by adding Na_2O as $NaNO_3$ and the SiO_2 as sand (such as glass makers sand F-110 from U.S. Silica). This flowsheet is diagrammed as follows:

Titrate to pH 4.8 ± 0.1 ---> Conc. to 240 gWO/L ----> Add $NaNO_3$ ---> Add SiO_2

Alternate HTM Flowsheet 2 - Alternate HTM Flowsheet 2 parallels Alternate HTM Flowsheet 1 in a number of aspects with the principle difference being the substitution of a reducing weak organic acid for an oxidizing strong inorganic acid. Again the acid is added until the pH has been reduced to 4.8 ± 0.1. Then the slurry is concentrated to about 240 gWO/L, and Na_2O is added as $NaNO_3$ and the SiO_2 is added as sand. This flowsheet is diagrammed as follows:

Titrate to pH 4.8 ± 0.1 ---> Conc. to 240 gWO/L ----> Add $NaNO_3$ ---> Add SiO_2

These flowsheets were implemented in the same way, as closely as possible, on both the laboratory- and small-scale.

4.3 Test Materials

The laboratory- and small-scale SSHTM melter feeds were prepared from the same stock NCAW slurry simulant[1] with a target composition given in Table 7.1 of the "SMALL-SCALE HIGH TEMPERATURE MELTER - 1 (SSHTM-1) TEST PLAN". The waste simulant for all feed preparation batches did not contain noble metals. Please refer to section 7.0 of the test plan for detailed information on the NCAW slurry composition. Compare the analyses for small-scale samples 6.4.12-5 (Alternate HTM Flowsheet 1) and 6.4.12-1,2,3 (Alternate HTM Flowsheet 2) in Tables A4.2.2 and B4.2.2 in Appendix A and B, respectively with the target composition. In general the analyses compare reasonably well for the major elements and most of the minor elements. Potassium cannot be determined accurately and other elements such as calcium tend to be low when analyzed by ICP-AES.

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[1] The waste slurry simulant was prepared by Optima using the following test instructions: Test Instructions for Slurry-Integrated Performance Testing-Weigh Out of Chemicals and Preparation of NCAW Simulant, TI92-SIPT-100, Rev. 0, October 15, 1992.

4.4 Melter Feed and Condensate Composition and Chemistry

Introduction

The composition of the waste slurry simulant as it was processed into melter feed was followed by analyzing slurry samples and related condensate samples taken after each processing step. The complete summary of the analytical data that was gathered is given in Appendices A and B. A preliminary discussion of these data are given in the following paragraphs. A mass balance will be compiled in the subsequent letter report (milestone number T3C-95-129) to compare actual amounts of nitrate produced and other components consumed.

Discussion

Waste Simulant Chemistry (Alternate HTM Flowsheet 1)

The initial waste simulant composition, after necessary additions of nitrite and nitrate, was identical for both the laboratory- and small-scale processing runs since the same stock simulant was used for both. See Tables A4.2.2 and A3.2 in Appendices A for the slurry analyses of samples SSHTM1-6.4.12-5 (small-scale) and T95-SSHTMHNO3-3-1-1 (laboratory-scale).

Based on off-gas analysis and waste simulant chemical analyses, the laboratory- and small-scale process chemistry appeared to be similar. After addition of HNO_3 (0.64 mole/L for slurry with a gWO/L of approximately 174), nitrite decreased by 20 to 25% primarily due to disproportionation and nitrate increased significantly, by 0.64 moles, primarily due to HNO_3 addition; compare sample analyses SSHTM1-8.0.10-3 AND T95-SSHTMHNO3-3-1-2 in Tables A4.2.2 and A3.2, respectively. The observed increase in nitrate is close to a corrected estimate based on 0.63 moles nitrate (refer to Figure A6.2.1) per liter for a slurry with the same waste oxide loading treated with nitric acid to a pH of 4.8 ± 0.1. The small decrease in nitrite shown for both laboratory- and small-scale appears to be consistent with the amounts of NO and N_2O generated (refer to Table 4.5.2). A slight increase in slurry pH was observed. This may be attributed to concentration of the slurry or possibly chemical reactions. Little additional compositional change occurs during the digestion period, consistent with the observed off-gas activity.

Waste Simulant Chemistry (Alternate HTM Flowsheet 2)

As for the Alternate HTM Flowsheet 1, the initial analytical values for the starting waste simulant should be the same since the same starting material was used for both laboratory- and small-scale processing runs (see Appendix B (Alternate HTM Flowsheet 2) slurry analyses for sample SSHTM1-6.4.12-1,2,3 and T95-SSHTMGLYC-1-1-1).

Based on off-gas analysis and waste simulant chemical analyses, the laboratory- and small-scale process chemistry appeared to be similar. After addition of glycolic acid (0.65 mole/L for slurry with a gWO/L of approximately 180), a 10 to 15% decrease in nitrite was observed at the completion of acid addition. During the digestion period there was an additional 25% decrease in nitrite and a small increase in amount of nitrate. The 0.65 moles of glycolic acid per liter is equal to 1.35 wt% organic carbon. About 1.50 wt % organic carbon was measured in the treated slurry, suggesting that little of the glycolate is lost during slurry processing; compare slurry samples SSHTM1-8.0.10-3 and T95-SSHTMGLYC-1-1-2 in Tables B4.2.2 and B3.2. This suggests that the nitrite destruction has occurred via nitrite disproportionation which would form nitrate and increase the pH of the solution as was also observed (compare SSHTM1-9.0.7-5 with T95-SSHTMGLYC-1-1-3). The amount of nitrite destruction appears to be consistent with the off-gas totals for NO_x and N_2O given in Table 4.5.2.

Condensate Chemistry

The condensate produced during the feed preparation runs on both the laboratory- and small-scale were weak nitric acid solutions with acid concentrations proportional to the amount of NO_x generated during the period the condensate was collected.

For Alternate HTM Flowsheet 1 (nitric), the most acid condensate was produced during the acid addition period on both laboratory- and small-scales. For Alternate HTM Flowsheet 2 (glycolic), most of the NO_x was observed after the glycolic acid addition was complete (during digestion). The small-scale nitrate concentration was higher than the laboratory-scale for condensate generated during the digestion period (refer to Section 3.3).

It was noted that a small contamination of the condensate with slurry components occurred during the small-scale procedure because of foaming even though anti-foam agent had been added.

NH_3 Generation

Ammonia analysis was completed for initial waste simulant materials, waste after acid addition, waste after digestion/concentration, and condensate samples. The small amounts of NH_3 observed (at most a few ppm) may be ascribed to tramp NH_3 from batch materials. Ammonia generation is not believed to have occurred during melter feed processing on either scale for either flowsheet. The measured ammonia values are given in the chemical analyses tables in Appendices A and B.

Summary

Overall the waste and condensate process chemistry results observed during the small-scale melter feed preparation runs could be predicted from the laboratory-scale processing runs on the same material. Specific findings at this time include: 1) Laboratory- and small-scale nitrite and nitrate levels essentially paralleled one another; 2) Similar amounts of organic carbon were found in both laboratory- and small-scale glycolic acid prepared feeds and indicated that little glycolate had been consumed on either scale; 3) Condensates were also generally consistent in their compositions containing mainly nitrate, with the small-scale a little more acidic than their laboratory equivalent (as expected since the small-scale tests employed air as a sweep gas which would have oxidized NO to NO_2 producing more nitrate in the condensate). The small-scale test condensates were contaminated in varying amounts with slurry due to foaming making detailed comparisons inappropriate; 4) Ammonia did not appear to be a reaction product for either flowsheet on either scale; 5) Comparison of Alternate HTM Flowsheets 1 and 2 suggests that more nitrite is destroyed when glycolic acid is used than when nitric acid is used in treating the waste simulant for the same equivalents of acid added.

4.5 Melter Feed Preparation Off-Gas Profiles

Introduction

Off-gas data were collected during Alternate HTM Flowsheet 1 and Alternate HTM Flowsheet 2 during the acid addition and digestion/concentration periods, for both the laboratory- and small-scale, using the gas detector arrays shown in Figures 3.1.2 and 3.2.2, respectively. The principle gases measured were CO_2, N_2O, NO_x, and H_2. Ammonia was not measured with these gases as it tends to remain in solution (unless the pH is alkaline) or collected in acid solution (condensates) and is best measured in those materials using a selective ion electrode (SIE) method. Alternate HTM Flowsheet 1 and Alternate HTM Flowsheet 2 data are discussed together in the following paragraphs as the issues are not as flowsheet dependent.

Discussion

Off-gas profiles with CO_2, N_2O, NO_x, and H_2 (if present) plotted as a function of time are shown in Figures A3.3.1 to A3.3.5 and A4.3.1 to A4.3.2, for Alternate HTM Flowsheet 1 and Figures B3.3.1 to B3.3.2 and B4.3.1 to B4.3.2, for Alternate HTM Flowsheet 2 in Appendices A and B, respectively. Comparing laboratory- and small-scale off-gas profiles, CO_2 is similar for both scales for both flowsheets (see Table 4.5.1 for comparison). No H_2 was observed during the HNO_3 feed preparation and a small amount was observed during the glycolic acid feed preparation. Observed values of NO_x are of the same order of magnitude (within a factor of two) respectively for both preparations on both scales. The N_2O generation was essentially zero for all feed preparations (see Table 4.5.1).

The most interesting observation is the similarity in the shape of the H_2 profile for the laboratory- and small-scale glycolic acid runs. The principle profile in both cases rises to a maximum, falls, and then begins to rise monotonically until the temperature is decreased at the end of the processing run. The profile features are observed to develop more rapidly for the small-scale run but those features appear to be identical for both processing runs. One speculation about the observed shift in time scale is

Table 4.5.1 Peak Off-Gas Generation Rates and Total Off-Gas Generated for the Formic Acid Reference Flowsheets and for Both the Laboratory- and Small-Scale Alternate HTM Flowsheet 1 and Alternate HTM Flowsheet 2 Tests.

	Off-Gas Generated During Processing				
	CO_2	N_2O	H_2	NO_x	NH_3[a]
HCOOH Reference Flowsheet 1[c], (NCAW without noble metals)					
Peak Generation Rate (mmole/125 gWO/min)	3.6	0.105	0.0007	2.6	b
Total Off-Gas Generated (mmole/125 gWO)	162	5.4	0.12	193	0.058
HCOOH Reference Flowsheet 3[d], (NCAW with 30% NO_2^-, 300% NO_3^-, excess HCOOH)					
Peak Generation Rate (mmole/125 gWO/min)	4.4	0.35	0.86	2.55	b
Total Off-Gas Generated (mmole/125 gWO)	378	13.6	54.7	73.6	18.3
Laboratory Alternate HTM Flowsheet 1[e]					
Peak Generation Rate (mmole/125 gWO/min)	3.303	0.005	BDL[g]	1.191	b
Total Off-Gas Generated (mmole/125 gWO)	123.9	0.119	BDL[g]	37.26	< 0.08
Laboratory Alternate HTM Flowsheet 2[f]					
Peak Generation Rate (mmole/125 gWO/min)	3.64	0.027	0.0014	0.44	b
Total Off-Gas Generated (mmole/125 gWO)	153	3.82	0.219	82.98	0.030
Small-Scale Alternate HTM Flowsheet 1					
Peak Generation Rate (mmole/125 gWO/min)	3.65	A/BDL[h]	BDL[g]	0.80	b
Total Off-Gas Generated (mmole/125 gWO)	141	A/BDL[h]	BDL[g]	29.26	0.01
Small-Scale Alternate HTM Flowsheet 2					
Peak Generation Rate (mmole/125 gWO/min)	3.87	A/BDL[h]	0.0018	0.28	b
Total Off-Gas Generated (mmole/125 gWO)	180	A/BDL[h]	0.483	76.75	0.07

(a) Measured amounts in condensate + maximum amount in slurry normalized to 125 gWO.
(b) Not measured but usually equal to or less than the H_2 generation rate.
(c) HCOOH Reference Flowsheet 1 is equivalent to test 1.16-2 (SIPT).
(d) HCOOH Reference Flowsheet 3 is equivalent to test T94-HCOOH Base-1 (SIPT).
(e) Laboratory Alternate HTM Flowsheet 1 is the no reductant flowsheet, data from test T95-SSHTMHNO3-3. H_2 and NH_3 data should be compared to HCOOH Reference Flowsheet 3.
(f) Laboratory Alternate HTM Flowsheet 2 is the glycolic flowsheet, data from test T95-SSHTMGLYC-1. H_2 and NH_3 data should be compared to HCOOH Reference Flowsheet 3.
(g) BDL: Below Detection Limit of 0.0001 mmole/125 gWO/min for the laboratory-scale and small-scale sytems.
(h) N_2O was generated At or Below the Detection Limit (detection limit is 0.03 mmole/125 gWO/min for Alternate HTM Flowsheet 1 and 0.014 mmole/125 gWO/min for Alternate HTM Flowsheet 2).

that it is related to a catalytic effect based on the presence of transition metal element oxides which are present in both the slurry simulant and the stainless steel components. Since the small-scale feed preparation tank, HB-32, is stainless steel and the laboratory reaction vessel is borosilicate glass with a stainless steel agitator, the relative amount of stainless steel in contact with the slurry during processing is larger in the small-scale system by about an order of magnitude. The acid addition factor discussed below is another possible reason for the observed difference.

Other small differences were observed in the H_2 profiles which were possible scale effects, such as the early H_2 pulse observed during the small-scale run. It was also observed that the small-scale system has an "early" shoulder on the CO_2 profiles for both flowsheets. This suggests that there was a portion of the slurry reacting at a lower pH (about 7 or less) from the beginning of acid addition. The volume of the small-scale acid stream entering the slurry simulant was 1200 times larger than the laboratory-scale hence the slurry concentration differences in the small-scale system may be expected to take longer to remove. It has been observed in other laboratory tests that the rate of acid homogenization can significantly alter the reaction path during processing with an acid. (Note that this "effect" has not been systematically studied. However, it was observed during an NCAW processing run in which a defect in the tubing used with the peristaltic pump caused the formic acid to be added about three times the nominal rate. The off-gas response was the first sign that something was "wrong" in that the relative amounts of NO_x and CO_2 were very different from what was expected based on similar tests.)

Table 4.5.1 gives the off-gas production totals and peak generation rates for the laboratory- and small-scale runs. The totals are calculated from the off-gas profiles,shown in Figures A3.3.1 to A3.3.5 and A4.3.1 to A4.3.2, for Alternate HTM Flowsheet 1 and Figures B3.3.1 to B3.3.2 and B4.3.1 to B4.3.2, for Alternate HTM Flowsheet 2 in Appendices A and B,by numerical integration using the trapezoidal rule. The peak rate values were read directly from the figures. These results are compared quantitatively in Table 4.5.2. For this table the values being compared were normalized using the scale factor of 1200. In this table the ratio of the normalized laboratory-scale to the small-scale values are presented.

As shown in Table 4.5.2, the quantities of CO_2 observed all agree within 20% and the peak generation rates agree within ±10% or less. These values are probably within the accuracy with which the two systems can be compared. The greatest differences between the laboratory- and small-scale systems are for NO_x. For this gas the difference may be due to scale effects (i.e. acid addition stream diameter) as alluded to above. The observed differences are less than a factor of two and in some cases much less than that.

The peak H_2 generation rate differed by 22%. The comparison of amounts of H_2 generated are biased by the fact that with respect to H_2 generation the runs were not completed. The small-scale run, which began to generate H_2

Table 4.5.2 Comparison of Off-Gas Generation Rates and Total Off-Gas Generated for the Laboratory- and Small-Scale Alternate HTM Flowsheet 1 and Alternate HTM Flowsheet 2 Tests. The comparison is made by a ratio of the normalized laboratory- to small-scale values provided in Table 4.5.1. The values used for the calculation of this data were normalized using the scale factor of 1200 (scale between the laboratory- and small-scale systems).

	Ratio[a] of Normalized Laboratory- to Small-Scale Off-Gas Generation Values				
	CO_2	N_2O[b]	H_2	NO_x	NH_3
Alternate HTM Flowsheet 1[c]					
Peak Generation Rate	0.90	N/A	d	1.49	N/A
Total Off-Gas Generated	0.88	N/A	d	1.27	0.6
Alternate HTM Flowsheet 2[e]					
Peak Generation Rate	0.94	N/A	0.78	1.57	N/A
Total Off-Gas Generated	0.85	N/A	0.45	1.08	0.43

(a) Ratio calculation:(Normalized Laboratory-Scale Value)/(Normalized Small-Scale Value)=(Table value).

(b) N_2O was not measured during the small-scale Alternate HTM Flowsheet 1 run due to an equipment malfunction. The N_2O peak generation rate for both the Laboratory- and small-scale Alternate HTM Flowsheet 2 runs were at or below the detection limit, therefore, ratios were not calculated.

(c) Alternate HTM Flowsheet 1 is the no reductant, nitric acid process flowsheet; data from test T95-SSHTMHNO3-3.

(d) No hydrogen produced.

(e) Alternate HTM Flowsheet 2 is the alternate reductant, glycolic acid process flowsheet.

earlier in greater quantities, is observed to have generated 55% more than the laboratory-scale run. However, the rate of increase of H_2 generation for the laboratory-scale run is greater at the end of the run than that measured for the small-scale run (compare Figures B3.3.2 and B4.3.2). A longer run time may be required to compare total amounts of H_2 equivalently.

Though the H_2 generated during both glycolic acid feed preparation runs was very small (less than a factor of 100 for both peak rate and total amount) relative to that observed in the reference formic acid flowsheet, the fact that H_2 was being produced in a non-noble metal containing system and that it was still increasing at the completion of the run indicates that additional testing may need to be performed. The investigation should include parameters such as time factor and other potential sources of H_2.

Summary

Off-gas total production and peak generation rates were similar within a factor of two. Those numbers for CO_2 were predictable within 10 to 20%; within the estimated order of reproducibility for these tests. The other components which displayed less consistency were also present in significantly smaller quantities, near detection limits.

Hydrogen production was observed during Alternate HTM Flowsheet 2 processing, a non-noble metal containing slurry simulant, on both processing scales in similar quantities (on the order of 1% of amounts observed with formic acid processing of noble metal containing slurry simulants). The release pattern was the same on both processing scales but the small-scale pattern developed over a shorter time span (about half the time). No H_2 was observed during Alternate HTM Flowsheet 1 tests on either the laboratory- or small-scale.

The small amount of NH_3 measured cannot be distinguished from tramp ammonia by addition from batch chemicals.

4.6 Rheology and Gram Waste Oxide Loading

Introduction

For both Alternate HTM Flowsheet 1 and Alternate HTM Flowsheet 2, a preliminary melter feed was prepared in the laboratory (500 ml) to predict the off-gases, rheology, and redox potential of the melter feed. These laboratory tests were presented in the addendum and on the basis of these laboratory tests, the basic test procedures given in section 4.2 were developed. Next, both feeds were prepared in a small-scale system (1514 liters). Due to the newness of the system and some related engineering difficulties, the processing test parameters deviated from the original processing test parameters. A third feed for both Alternate HTM Flowsheets was prepared in the laboratory in which the processing test parameters performed during SSHTM-1 testing were duplicated. This third feed preparation procedure was completed so that laboratory- and small-scale data could be more easily compared and in this section is called the "modified feed procedure." The rheological and physical property data for Alternate HTM Flowsheet 1 is contained in Appendix A while the data for Alternate HTM Flowsheet 2 is contained in Appendix B. The appendices consist of the experimental and results sections, tables summarizing the rheology and physical property data, and the rheograms and modeling results. This section provides a general discussion of the results.

Discussions

Alternate HTM Flowsheet 1

As the nitric acid treated waste simulant was concentrated to 240 gWO/L in the small-scale system, mixing became poor and solids began to accumulate on the heating coils. It was approximated that this occurred at an oxide loading of 220 gWO/L. The plastic viscosity, determined by fitting the Bingham model to shear rate sweep data, at this oxide loading was 31 mPa•s while the yield stress was 20 Pa. An attempt was made to improve mixing by diluting the feed with water but this did not improve the problem so the feed was transfer to tank HB-34. Once the feed was transferred to tank HB-34, mixing improved and the feed preparation procedure continued.

The final melter feed, at an oxide loading of 354 gTO/L, had a viscosity of 19 mPa•s and a yield stress of 15 Pa. During the aging in the small-scale system, the plastic viscosities and yield stresses remained at or below the specifications of 25 mPa•s and 15 Pa, respectively.

Alternate HTM Flowsheet 1 slurry was fed into the small-scale high temperature melter from a day tank from which rheology samples were taken during SSHTM-1 testing. During the initial first few hours of the Alternate HTM Flowsheet 1 (nitric acid) segment the average processing rate of this feed at a temperature of 1350°C was about 6 L/hr. As indicated by the low processing rate, the nitric feed did not process well. The feed mounded under the feed nozzle, and did not spread out over the cold cap surface. This behavior of the feed resulted in small, localized, elevated slurry pools, rather than more typical slurry pools that spread out over the cold cap surface encompassing about 50% of the cold cap surface area. After about 36 hours into this segment, an attempt to increase the spreading of the feed on the cold cap surface was implemented by adding glycerine to the feed in an attempt to reduce the feed viscosity. The glycerine addition had no marked effect on the processing rate of the nitric feed. Boric acid was shimmed into the day tank in a second attempt to increase the processibility of the nitric feed. Within a few hours, the feed was spreading over the cold cap surface, and the previously rigid, crusty cold cap became flexible with active venting throughout the cold cap surface. Testing of both melter feeds retrieved from the day tank showed that neither of these additions appeared to affect the rheological properties of the feed. Because the melter feed rheological properties were unaffected by the glycerine or boric acid additions, the problem with cold cap spreading and melting is likely not the result of poor melter feed preparation but the result of compositional inadequacies in the glass and cold cap (refer to Table A4.4.1).

The melter feeds' rheological properties typify rheology for a concentrated colloidal suspension. The melter feeds exhibit shear thinning behavior (decreasing viscosity with increasing shear rate) and slight rheopexy (increasing viscosity under steady shear conditions). The rheopectic behavior of this suspension needs to be further examined because it may cause significant increases in viscosity under shearing conditions. Also, the plastic viscosity decreased with increasing temperature while no significant changes in the yield stress were detected with increasing temperature.

The melter feeds prepared in the laboratory have different rheological properties than the melter feeds prepared in the small-scale system even when the weight percent solids, gTO/L and pH values are similar. The melter feed prepared in the laboratory using the modified feed preparation procedure, has the same physical properties as the melter feed prepared during the small-scale run. The plastic viscosities of the two samples are also similar but the yield stress of the feed prepared in the laboratory is much lower than the yield stress of the feed prepared in the small-scale system. These results indicate that feed preparation, as well as solids loading and pH, affect the rheology of the slurries (see Table 4.6.1).

Figure 4.6.1 shows the aging behavior of the feed prepared in the small-scale system and aged in the small-scale system and the feed prepared in the small-scale system and aged in the laboratory. Over the 12 day period, the plastic viscosity remained below the specification of 25 mPa•s for both feeds. The Bingham yield stress was higher than the specification of 15 Pa for the feed aged in the laboratory and 15 ± 1 Pa for the feed aged in the tanks. The laboratory aging procedure is currently under development therefore the significance of the variations in the rheological measurements are not known.

Alternate HTM Flowsheet 2

As the glycolic acid treated waste simulant was concentrated to 240 gWO/L in the small-scale system, the plastic viscosity, determined by fitting the Bingham model to shear rate sweep data, increased from 8 mPa•s to 19 mPa•s and the yield stress increased from 11 Pa to 16 Pa. No problems with mixing were observed.

The final melter feed, at an oxide loading of 422 gTO/L, had a plastic viscosity of 19 mPa•s and a yield stress of 16 Pa. During the aging in the small-scale system, the plastic viscosity never increased beyond 25 mPa•s, but the yield stress was consistently higher than the specification of 15 Pa.

Alternate HTM Flowsheet 2 slurry was fed into the small-scale high temperature melter from a day tank from which rheology samples were taken

Table 4.6.1 Physical Property and Rheology Data for Alternate HTM Flowsheet 1.

Alternate HTM Flowsheet 1[d]	g TO/L	pH (@ ≈22°C)	wt % solids	Density (g/ml)	Yield Stress (Pa[a])	Plastic Viscosity (mPa·s[b])	Correlation Coeff. (R^2)[c]
Preliminary Laboratory-Scale[e]:							
Before silica addition	253	7.2	35.9	1.22	13.8	28.1	0.91
After silica add. & dilution[f]	425	7.2	42.2	1.33	11.2	27.8	0.93
Modified Laboratory-Scale:							
Before silica addition	190	7.4	24.8	1.11	11.1	15.4	0.82
After silica addition	339	7.4	36.6	1.23	9.9	17.1	0.87
Small-Scale:							
Before silica addition	191	----	25.3	1.15	11.7	16.2	0.81
After silica addition	354	----	36.6	1.29	15.1	18.6	0.75

(a) Laboratory rheological screening data value for the yield stress is 15 Pa. The yield stress was calculated by fitting the shear rate sweep data to the Bingham model.
(b) Laboratory rheological screening data value for the plastic viscosity is 25 mPa·s. The plastic viscosity was calculated by fitting the shear rate sweep data to the Bingham model.
(c) Least squares correlation coefficient of shear rheology data fit to the Bingham equation.
(d) Alternate HTM Flowsheet 1 is the no reductant, nitric acid processed flowsheet.
(e) Rheology measurements were taken at 25°C for the preliminary laboratory-scale feeds and at 50°C for the modified laboratory-scale feeds and the small-scale feeds.
(f) Preliminary laboratory-scale melter feed samples were diluted after the silica addition was made and before the rheological measurements were taken.

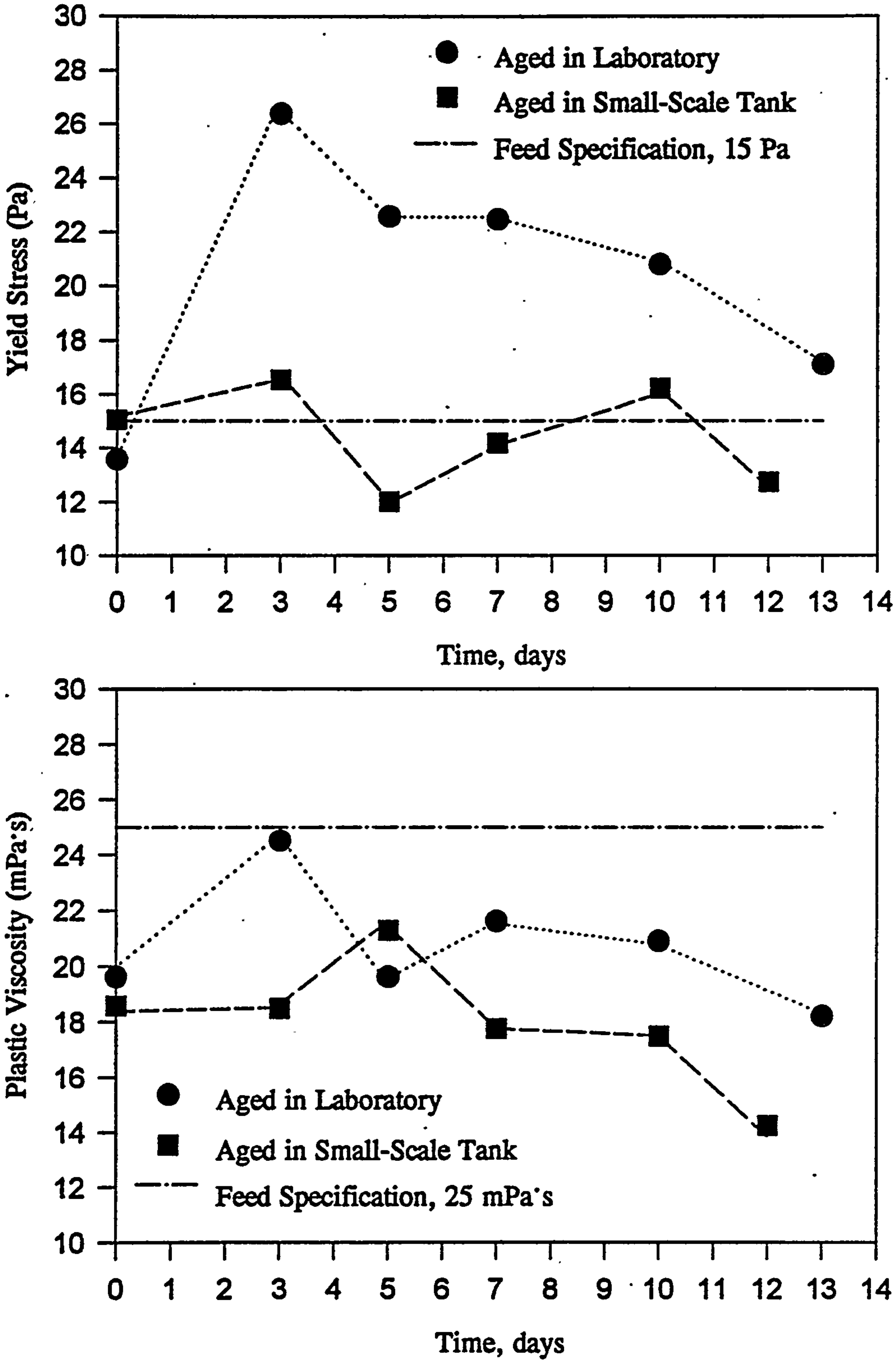

Figure 4.6.1 Plastic Viscosity and Yield Stress as a Function of Aging Time for Alternate HTM Flowsheet 1 Feed Prepared in the Small-Scale System.

during SSHTM-1 testing. The oxide loading of the glycolic feed batch was approximately 422 gTO/L. This feed was fed throughout the test segment with one exception. Due to problems with plugging of the feed line approximately 100 liters of slightly diluted feed, 400 gTO/L, was fed to the melter in an attempt to alleviate clogging of the feed line. This problem was resolved by a slight modification to the feed system. During the rest of the glycolic feed test segment 440 gTO/L feed was processed. The initial operating temperature of the melter was 1350°C, but to increase the processing rate and thus decrease the time required for the melter composition to reach steady state, glycolic feed was processed at temperatures ranging from 1350°C to 1450°C. Processing rates ranged from a low of about 10 L/hr (at 422 gTO/L) to a high of about 24 L/hr (at 400 gTO/L).

The melter feeds' rheological properties typify rheology for a concentrated colloidal suspension. The melter feeds exhibit shear thinning behavior (decreasing viscosity with increasing shear rate) and thixotropy (decreasing viscosity under conditions of steady shear). Also, the plastic viscosity decreased with increasing temperature while no significant changes in the yield stress were detected with increasing temperature.

The melter feeds prepared in the laboratory have different rheological properties than the melter feeds prepared in the small-scale system even when the weight percent solids, gTO/L and pH values are similar. The melter feed prepared in the laboratory following the modified feed preparation procedure, has the same physical properties as the melter feed prepared during the small-scale run. The plastic viscosities of the two samples are also similar (± 4 mPa•s) but the yield stress of the feed prepared in the laboratory is approximately 50% lower than the yield stress of the feed prepared in the small-scale system. These results indicate that the feed preparation procedure, as well as solids loading and pH, affect the rheology of the slurries (see Table 4.6.2).

Figure 4.6.2 shows the aging behavior of the feed prepared in the small-scale system and aged in the small-scale system and the feed prepared in the small-scale system and aged in the laboratory. Over the 5 day period, the plastic viscosity remained below the specification of 25 mPa•s for the feed aged in the small-scale tanks. The yield stress was higher than the specification of 15 Pa for both the feed aged in the laboratory and the feed aged in the tanks. The laboratory aging procedure is currently under development therefore the significance of the variations in the rheological measurements are not known.

Table 4.6.2 Physical Property and Rheology Data for Alternate HTM Flowsheet 2.

Alternate HTM Flowsheet 2[d]	g TO/L	pH (@ ≈22°C)	wt % solids	Density (g/ml)	Yield Stress (Pa[a])	Plastic Viscosity (mPa·s[b])	Correlation Coeff. (R^2)[c]
Preliminary Laboratory-Scale[e]:							
Before silica addition	277	8.0	37	1.29	6.7	30.5	0.99
After silica addition	464	8.0	45	1.41	6.4	27.3	0.98
Modified Laboratory-Scale:							
Before silica addition	236	8.3	29.2	1.22	9.2	19.6	0.92
After silica addition	403	8.3	43.5	1.29	7.3	15.17	0.92
Small-Scale:							
Before silica addition	234	8.3	28.3	1.2	17.8	15.7	0.59
After silica addition	422	8.4	43.2	1.3	16.3	19.3	0.74

(a) Laboratory rheological screening data value for the yield stress is 15 Pa. The yield stress was calculated by fitting the shear rate sweep data to the Bingham model.
(b) Laboratory rheological screening data value for the plastic viscosity is 25 mPa·s. The plastic viscosity was calculated by fitting the shear rate sweep data to the Bingham model.
(c) Least squares correlation coefficient of shear rheology data fit to the Bingham equation.
(d) Alternate HTM Flowsheet 2 is the alternate reductant, glycolic acid processed flowsheet.
(e) Rheology measurements were taken at 25°C for the preliminary laboratory-scale feeds and at 50°C for the modified laboratory-scale feeds and the small-scale feeds.

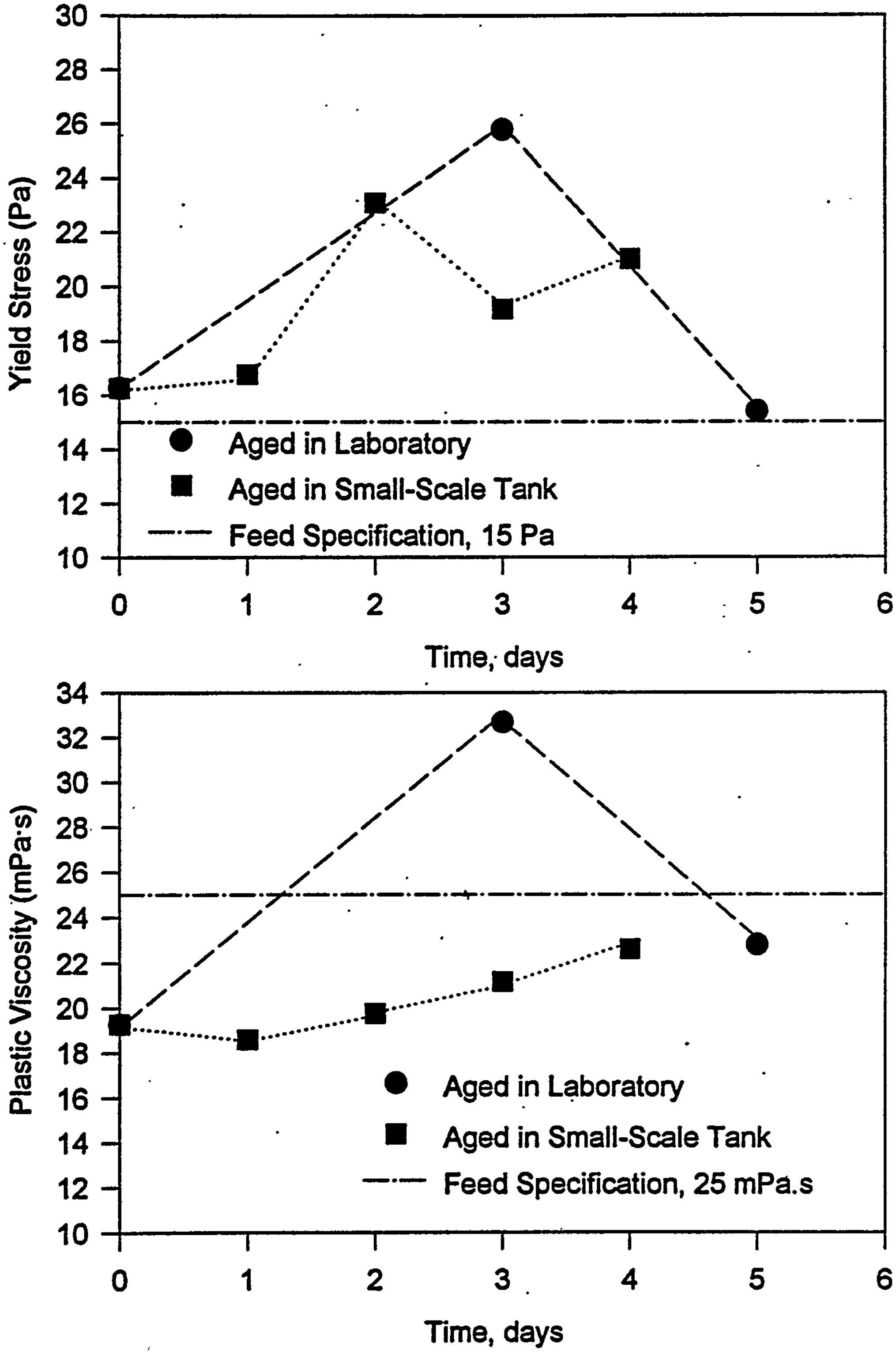

Figure 4.6.2 Plastic Viscosity and Yield Stress as a Function of Aging Time for Alternate HTM Flowsheet 2 Feed Prepared in the Small-Scale System.

Summary

Due to the sampling procedure described in section 3.2, some caution must be taken with the application of the rheological and physical property data. At a gTO/L of 354, the high temperature melter feed prepared using Alternate HTM Flowsheet 1 in the small-scale tanks, has plastic viscosities and yield stresses within the specifications of 25 mPa•s and 15 Pa. At a gTO/L of 422, the high temperature melter feed prepared using Alternate HTM Flowsheet 2 in the small-scale tanks, has plastic viscosities within the specification of 25 mPa•s and yield stresses of 16 to 22 Pa, which is above the specification of 15 Pa (see Figures 4.6.1.and 4.6.2).

From a rheological performance perspective, the glycolic acid treated feed is a better choice than the nitric acid treated feed because the glycolic acid treated feed has higher oxide loadings for similar rheological properties. In addition, the nitric acid treated feed is slightly rheopectic (increases in viscosity under constant shearing conditions). However, the glycolic acid treated feed gels when allowed to sit without continual stirring. These properties will need to be considered if there is a possibility of not being able to continually stir the feed or if the feed needs to be transported over long distances.

For both flowsheets, the modified laboratory-scale processing runs predicted lower yield stresses than what were measured for the waste and melter feed simulants (except for the waste simulant treated with nitric acid before silica addition) produced during the small-scale processing runs. Although the gTO/L, pH, wt% solids, and plastic viscosities were similar for both Alternate HTM Flowsheets 1 and 2, the yield stresses of the melter feeds and the waste simulants prepared in the laboratory-scale processing runs were 35% lower than the yield stresses of the melter feeds prepared in the small-scale processing runs (see Tables 4.6.1 and 4.6.2).

For both Alternate Flowsheets 1 and 2, the plastic viscosities remained below the specification of 25 mPa•s for the feed aged in the laboratory as well as for the feed aged in the small-scale system (except for the Alternate Flowsheet 2 feed aged in the laboratory). For both Alternate Flowsheets 1 and 2, the yield stresses were higher for the feed aged in the laboratory and for the feed aged in the tanks (except for the Alternate Flowsheet 1 feed aged in the small-scale system) than the specification of 15 Pa. The laboratory aging procedure is currently under development therefore the significance of the variations in the rheological measurements is not known.

4.7 Standard Crucible Redox Testing

Introduction

This section addresses the measurement of a glass oxidation state indicator, the $Fe^{+2}/\Sigma Fe$ ratio for both laboratory- and small-scale preparations. Two melter feeds and two methods of glass preparation are discussed for each of the two Alternate HTM Flowsheets. Two melter feeds for each flowsheet, one prepared in the laboratory and one prepared in the small-scale feed preparation system were melted using a standard crucible method. The $Fe^{+2}/\Sigma Fe$ ratios of glass samples collected from the small-scale melter was also determined for each flowsheet. The measured $Fe^{+2}/\Sigma Fe$ ratios are given in Table 4.7.

Discussion

Alternate HTM Flowsheet 1

The relative quantities of oxidants are given in Table 4.7 (a reductant was not added during Alternate HTM Flowsheet 1 processing). A slightly lower, 10-20%, quantity of oxidants were present in the small-scale melter feed relative to the laboratory-scale melter feed. Sensitivity of the $Fe^{+2}/\Sigma Fe$ ratio to differences of this order of magnitude is unknown. The $Fe^{+2}/\Sigma Fe$ ratio of glasses prepared from the two melter feeds, laboratory- and small-scale, using the standard crucible method were 0.063 and 0.067 (mean values), respectively. The $Fe^{+2}/\Sigma Fe$ ratio of glasses collected from the bottom drain of the SSHTM and a canister pour ranged from 0.419 to 0.302. Comparison of the crucible and small-scale glass redox values suggest that glass prepared in the SSHTM with the nitric acid treated feed was significantly more reduced. Further analyses of the cold cap and high temperature redox chemistries will be addressed in the SSHTM-1 letter report, milestone T3C-95-129.

Alternate HTM Flowsheet 2

The relative quantities of oxidants and reductants in the laboratory- and small-scale melter feeds are similar (refer to Table 4.7). Relative to the laboratory-scale melter feed, a slightly higher ratio of reductant to oxidant was measured for the small-scale; however, the sensitivity of the $Fe^{+2}/\Sigma Fe$ ratio to differences of this order of magnitude is unknown. The $Fe^{+2}/\Sigma Fe$ ratio of glasses prepared from the two melter feeds using the standard crucible method were 0.061 and 0.084 (mean values) for the laboratory- and small-scale feeds, respectively. The small-scale melter feed produced a slightly more reduced glass. The $Fe^{+2}/\Sigma Fe$ ratio for glass samples collected from the bottom drain of the SSHTM varied from 0.061 to 0.175. Significant differences between the laboratory- and small-scale $Fe^{+2}/\Sigma Fe$ ratios are not evident from the current limited data base.

Summary

Insufficient data and analyses are available at this time to provide an accurate assessment of the redox chemistry and scaling factors. Further analyses of the cold cap, high temperature redox chemistries, and potential scaling factors will be addressed in the SSHTM-1 letter report, milestone T3C-95-129.

Table 4.7 Standard Crucible Redox Test Data for Both Laboratory- and Small-Scale Melter Feed Alternate HTM Flowsheet 1 and 2 Testing.

	Final		Moles Oxidant[a]		Moles Reductant[b]	Glass: $Fe^{+2}/\Sigma Fe$	
	pH (@ ≈22°C)	(gTO/L)	NO_3^-	NO_2^-	(glycolate)	Crucible	Melter
Alternate HTM Flowsheet 1[c]							
laboratory melter feed[1]	7.4	339	1.14	0.41	N/A	N/A	N/A
dried melter feed/glass	N/A	N/A	----	----	N/A	0.0633	N/A
	N/A	N/A	----	----	N/A	0.0627	N/A
small-scale melter feed[2]	7.9	354	1.05	0.35	N/A	N/A	N/A
dried melter feed/glass	N/A	N/A	----	----	N/A	0.0655	0.419[d]
	N/A	N/A	----	----	N/A	0.0717	0.302[e]
	N/A	N/A	----	----	N/A		0.302[f]
Alternate HTM Flowsheet 2[g]							
laboratory melter feed[3]	8.3	403	0.64	0.23	0.48	N/A	N/A
dried melter feed/glass	N/A	N/A	----	----	----	0.0610	N/A
	N/A	N/A	----	----	----	0.0599	N/A
small-scale melter feed[4]	8.4	422	0.60	0.31	0.54	N/A	N/A
dried melter feed/glass	N/A	N/A	----	----	----	0.0792	0.0687[h]
	N/A	N/A	----	----	----	0.0882	0.0719[i]
	N/A	N/A	----	----	----		0.0614[j]
	N/A	N/A	----	----	----		0.1753[k]

(1) Laboratory melter feed made from the T95-SSHTMHNO3-1 test slurry on Nov. 11, 1994.
(2) Small-scale melter feed sample corresponds to rheology samples hno30a, hno3d0b, hno3-5d0, and hno35d0a taken from the small-scale feed preparation system on Aug. 19, 1994.
(3) Laboratory melter feed made from the T95-SSHTMGLYC-1 test slurry on Nov. 10, 1994.
(4) Small-scale melter feed sample corresponds to rheology sample SSHTM1-11.1.12-1 taken from the small-scale feed preparation system on Aug. 14, 1994.
(a) Reported moles of NO_3^- are after addition of $NaNO_3$. The $NaNO_3$ contributed 0.47 moles of nitrate per 125 gWO.
(b) Reductant used are moles of $C_2H_3O_3^-$ per 125 gWO.
(c) Alternate HTM Flowsheet 1 is the no reductant, nitric acid process flowsheet; laboratory data from test T95-SSHTMHNO3-1.
(d) Sample number SSHTM1-85; sampled on Aug. 30, 1994 at 0650 hours. Glass sample is a bottom drain sample taken during melter operation.
(e) Glass sample retreived from SSHTM-1 Canister #3 on Nov. 4, 1994. This glass pour was the third of five total pours. Glass was not supposed to contain boron oxide, but was found to contain approximately 2.5 wt% B_2O_3. Glass sample poured on Aug. 30, 1994 at 0620 hours. Value is the mean of two duplicate analyses; standard deviation is 0.001.
(f) Sample number SSHTM1-109; sampled on Sept. 1, 1994 at 0540 hours. Glass sample is a bottom drain sample taken during melter operation.
(g) Alternate HTM Flowsheet 2 is the alternate reductant, glycolic acid process flowsheet; laboratory data from test T95-SSHTMGLYC-1.
(h) Glass sample was retreived from an SSHTM-1 canister and supplied by DA Lamar.
(i) Sample number SSHTM1-24; sampled on Aug. 17, 1994 at 0300 hours. Glass sample is a bottom drain sample taken during melter operation.
(j) Sample number SSHTM1-42; sampled on Aug. 18, 1994 at 0710 hours. Glass sample is a bottom drain sample taken during melter operation.
(k) Sample number SSHTM1-50; sampled on Aug. 18, 1994 at 2009 hours. Glass sample is a bottom drain sample taken during melter operation.

5.0 CONCLUSIONS

This data package is a brief observation and operation report on available data for the Small-Scale High Temperature Melter-1 (SSHTM-1) feed preparation activities. The test was conducted in two melter feed batch segments prepared from two different feed preparation flowsheets. Testing primarily addressed alternate flowsheet options tested in the laboratory to mitigate potential safety issues related to generation of hydrogen and ammonia, to produce acceptable melter feed rheological properties, to maximize total waste oxide loading in the glass, to simplify the vitrification flowsheet, and to increase vitrification flowsheet processing rate. The two flowsheets tested include 1) no reductant addition and titration with HNO_3 to provide an acceptable melter feed rheology near the target oxide loading (Alternate HTM Flowsheet 1), and 2) titration with glycolic acid, an alternate reductant to HCOOH (Alternate HTM Flowsheet 2). This data package does not discuss small-scale high temperature melter operation or glass pool melt/glass product data and analysis (which will be presented in later reports); therefore, the vitrification flowsheet processing rate is not discussed.

Several laboratory-scale test versions of the SSHTM-1, modified small-scale processing tests were conducted so that the basis of comparison between the two scales would be as close as possible. This allowed for a good comparison and evaluation of potential correlations between the two scales.

Preliminary analyses show a direct correlation between the laboratory- and small-scale systems with respect to off-gas, and slurry and condensate chemistries when the scaling difference is taken into account. The scale factor between the two systems based on processing volume is approximately 1200. The reliability of laboratory-scale tests to predict processing activity (off-gas and slurry and condensate chemistry) on the small-scale is very good. Specific findings at this time include: 1) No H_2 was observed during Alternate HTM Flowsheet 1 tests on either the laboratory- or small-scale. Hydrogen production was observed during Alternate HTM Flowsheet 2 processing, a non-noble metal containing slurry simulant, on both processing scales in similar quantities (on the order of 1% of amounts observed with formic acid processing of noble metal containing slurry simulants); 2) Ammonia did not appear to be a reaction product for either flowsheet on either scale; 3) Off-gas total production and peak generation rates were similar within a factor of about two for H_2 while NO_x was over predicted by up to 35%. Those numbers for CO_2 were predictable within 10 to 20%; within the estimated order of reproducibility for these tests. The N_2O was present in quantities near or below the analytical detection limits; 4) Laboratory- and small-scale nitrite and nitrate levels essentially paralleled one another; 5) Similar amounts of organic carbon were found in both laboratory- and small-scale glycolic acid prepared feeds and indicated that little glycolate had been consumed on either scale; 6) Condensates were also generally consistent in their compositions containing mainly nitrate, with the small-scale a little more acidic than their laboratory equivalent (as expected since the small-scale tests employed air as a sweep gas which would have oxidized NO to NO_2 producing more nitrate in the condensate). The small-scale test condensates were contaminated in varying amounts with slurry due to foaming making detailed comparisons inappropriate; 7) Comparison of Alternate HTM Flowsheets 1 and 2 suggests that more nitrite is destroyed when glycolic acid is used than when nitric acid is used in treating the waste simulant for the same equivalents of acid added.

The two feed preparation systems both exhibited difficulty in mixing the high total oxide loaded melter feeds. Sufficient agitation in the small-scale feed preparation system was difficult to achieve. The agitation in tank HB-32 was found to be much less efficient than in tank HB-33. The nitric acid processed feed concentration was stopped short of the target value because of insufficient mixing in tank HB-32. The glycolic acid feed was concentrated as required but it was right at the limit of the capability of the equipment to keep it mixed. Although the melter feed tank agitator in tank HB-33 performed better than the agitator in tank HB-32, melter feed slurries had stagnant areas in both tanks. In the small-scale feed preparation system mixing characteristics of the feed was a limiting factor in acid addition and percent oxide concentration.

For both Alternate HTM Flowsheet 1 and Alternate HTM Flowsheet 2, melter feed was prepared in the laboratory (500 ml) to test the rheologic properties which were then compared to the small-scale results. In addition, the same melter feed was used to test the redox potential of the melter feed. Due to the sampling procedure described in Section 3.2, some caution must be taken with the application of the rheological and physical property data.

At a gTO/L of 354, the high temperature melter feed prepared using Alternate HTM Flowsheet 1 in the small-scale tanks, has plastic viscosities and yield stresses within the specifications of 25 mPa•s and 15 Pa. At a gTO/L of 422, the high temperature melter feed prepared using Alternate HTM Flowsheet 2 in the small-scale tanks, has plastic viscosities within the specification of 25 mPa•s and yield stresses of 16 to 22 Pa, which is above the specification of 15 Pa.

The glycolic acid treated melter feed has higher oxide loadings than the nitric acid treated melter feed for similar rheological properties. The nitric acid treated feed is slightly rheopectic (increases in viscosity under constant shearing conditions). The glycolic acid treated feed gels when allowed to sit without continual stirring. These properties will need to be considered if there is a possibility of not being able to continually stir the feed or if the feed needs to be transported over long distances.

For both flowsheets, the modified laboratory-scale processing runs predicted lower yield stresses than what were measured for the waste and melter feed simulants (except for the waste simulant treated with nitric acid before silica addition) produced during the small-scale processing runs. Although the gTO/L, pH, wt% solids, and viscosities were similar for both Alternate HTM Flowsheets 1 and 2, the yield stresses of the melter feeds and the waste simulants prepared in the laboratory-scale processing runs were 35%

lower than the yield stresses of the melter feeds prepared in the small-scale processing runs.

For both Alternate Flowsheets 1 and 2, the plastic viscosities remained below the specification of 25 mPa•s for the feed aged in the laboratory as well as for the feed aged in the small-scale system (except for the Alternate Flowsheet 2 feed aged in the laboratory). For both Alternate Flowsheets 1 and 2, the yield stresses were higher for the feed aged in the laboratory and for the feed aged in the tanks (except for the Alternate Flowsheet 1 feed aged in the small-scale system) than the specification of 15 Pa. The laboratory aging procedure is currently under development therefore the significance of the variations in the rheological measurements is not known.

Insufficient data and analyses are available at this time to provide an accurate assessment of the redox chemistry and scaling factors. Further analyses of the cold cap, high temperature redox chemistries, and potential scaling factors will be addressed in the SSHTM-1 letter report, milestone T3C-95-129.

6.0 RECOMMENDATIONS

This data package is a brief observation and operation report on available data for the Small-Scale High Temperature Melter-1 (SSHTM-1) feed preparation activities. A complete letter report will be prepared and issued in July 1995 to fulfill milestone number T3C-95-129. This letter report will include a summary of this data package and small-scale high temperature melter operation and glass pool melt/glass product data and analysis. The letter report will include a comprehensive recommendation section based on a more holistic view of the entire test available at that time.

7.0 REFERENCES

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