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**Dry-Out and Low Temperature
Calcination of DST/SST Waste Blend
High Temperature Melter Feed**

H. D. Smith
E. M. Tracey

February 1996

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

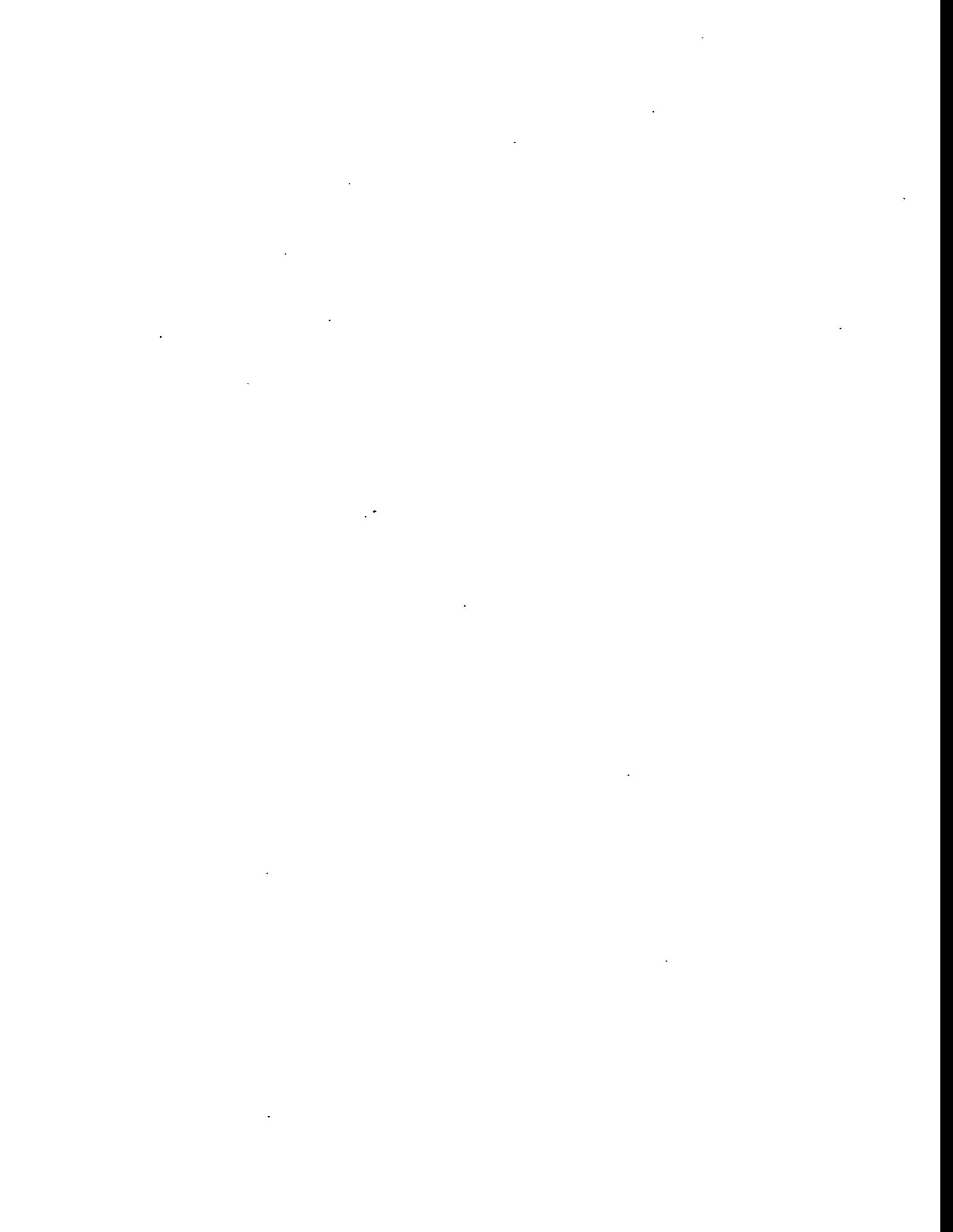
Pacific Northwest National Laboratory
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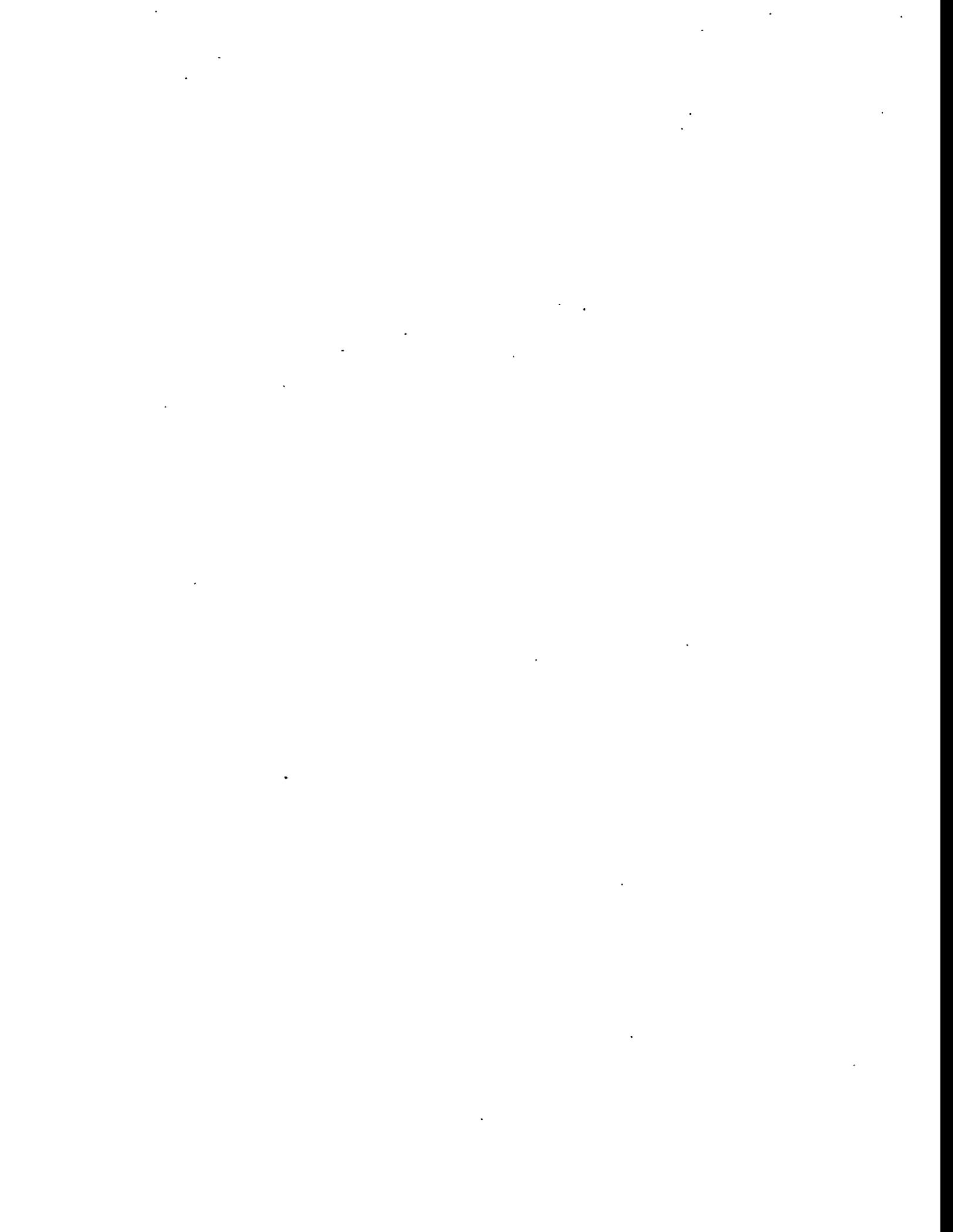
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The FY1994 DST/SST blend was prepared in accordance with the DST/SST blend feed specification^(a). The laboratory preparation steps and observations were compared with an existing experience base to verify the acceptability of the feed specification for simulant make-up.

The most significant test results included a variety of features. Ferrocyanide breaks down to NH_3 plus formate during the low-temperature calcining phase of the tests. Ferrocyanide displayed no redox reactivity with the nitrates and nitrites contained in the slurry in the absence of sugar. Sugar displays a redox reaction with the nitrates and nitrites in the blend similar to the redox reaction observed in the LLW feed simulant.

Boiling of a free flowing slurry occurs at temperatures below about 120°C . When about 45% of the total water loss has occurred, the feed slurry congeals and continues to lose water, shrinking and developing shrinkage cracks. Water stops coming off between 350°C and 400°C . Slurry shear strength and viscosity strongly increase as the weight percent solids increases from 20 wt% to 45 wt%. The 45 wt% solids corresponds to approximately a 40 % water loss.

The principle heat sensitivity for this material is the exothermic reaction which is activated when the temperature exceeds about 250°C . The breakdown of ferrocyanide to ammonia and formate under strongly basic conditions may begin at temperatures less than 100°C , but the rate increased strongly with increasing temperature and appeared to be completed in the time of our tests. Differential thermal analysis (DTA) results on feed slurry without and with ferrocyanide showed only endothermic behavior. This is consistent with the dry out and low temperature calcine studies which did not indicate any exothermic behavior for the feed slurry with and without ferrocyanide. Feed slurry containing sugar equal in weight to the nitrate plus nitrite content (20% of the total oxides per liter (TO/L)), displayed a distinctly exothermic activity with light and smoke production.

Physical property observations include the following: The feed slurry coats both glass and stainless steel in the liquid state. The material spalls and falls off as it dries leaving a thin, more adherent, film behind. The only phase separation observed during these tests occurred as a result of the water condensate leaching from the slurry boil spatter. Salt containing condensate re-evaporated as it ran down the side of the reaction vessel leaving a ring of separated white salts on the vessel wall. The sugar containing slurry simulant exhibited a volume expansion as a result of the exothermic reaction between sugar and nitrate and nitrite. A yellow salt separated from the glass melt made during the quartz crucible test which looks like salts observed to separate from other HLW simulant melts (NCAW based) and identified as sodium sulfate with a small amount of potassium chromate.

(a) E. M. Tracey, M.D. Merz, G. K. Patello, and K. D. Wiemers. 1995. Feed Specification for the Double-Shell Tank/Single Shell Tank Waste Blend for High-Level Waste Vitrification Process and Melter Testing, C95-02.02H

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1.0 Introduction

A high level waste (HLW) Vitrification Facility (HVF) will be constructed at Hanford to convert pretreated HLW and transuranic (TRU) waste to a durable vitrified form for final disposal in a federal geologic repository. Recent renegotiation of the Hanford Federal Facility Agreement and Consent Order (known as the Tri-Party Agreement (TPA)) invoked several baseline changes which affected the planned approach for disposal of Hanford Site tanks wastes. The HLW program was expanded to encompass the retrieval and remediation of all underground storage tanks, including Single Shell Tanks (SSTs) as well as previously planned Double Shell Tanks (DSTs). To meet the high capacity requirements to the new HVF, two melter technologies, the joule-heated, high-temperature melter (HTM) system and the cold-crucible melter (CCM) were selected for further technical assessment^(a). A DST/SST waste blend composition developed by WHC^(b), will be used to assess the performance of these dryers and calciners. The DST/SST composition will also provide the reference composition for the feed preparation process flowsheet development. Specific technology development needs related to the baseline process flowsheet requirements are identified by Orme (1994).

The overall investigation addressed three primary areas:

- preparation of the DST/SST waste blend simulant to verify the feasibility of the make-up steps as given in the feed specification (milestone C95-02.02H) and to provide a source of simulant for laboratory testing,
- laboratory evaluation of feed preparation process flowsheets for the HTM and CCM systems, and
- laboratory evaluation of dry-out and calcination process steps.

This report focuses on the last of these three general investigation objectives.

(a) R.B. Calmus. 1995. High Level Waste Melter Alternatives Assessment Decision, Letter to L. Erickson. #9546834

(b) R.W. Powell. 1995. Double-Shell Tank/Single Shell Tank Waste Blend Composition for High-Level Waste Vitrification Process Testing, Letter to J.M. Creer. #945712

2.0 Test Objectives

The primary test objective was to provide a preliminary assessment of DST/SST melter feed drying and calcining which could be used in the CCM or HTM vitrification flowsheet prior to feeding the melter to increase melter feed processing capacity. Assessment of dry-out and calcining included:

1. Gas composition and generation rate

The offgas generation rates were measured as a function of time. From this information the maximum generation rate and the total amount of gas evolved was determined. It was important to identify toxic, flammable, and/or explosion hazard species so that the plant off-gas system is designed to mitigate the hazards associated with them. In addition, it was important to know the rate of gas generation so that the dry-out, calciner system will not over-pressurize during operation.

2. Feed composition

The feed composition (wet, dry, and calcined; with and without glass formers) was taken to be the target slurry simulant composition and target feed composition.

3. Water Loss Characteristics

The water loss during dry out and low temperature calcination was determined as a function of time and temperature. Also, it was important to correlate water loss with the rheological properties of the feed, so that the slurry behavior in a calciner can be predicted.

4. Transport/rheological properties

The rheological properties and density were determined as a function of weight percent solids. These properties strongly influenced the rate of calcination and the nature of the calcine product produced, i. e., thin and scaley, thick and blocky, dense, porous, etc.

5. Bulk Properties

Calcined bulk density provided a measure of the volume of material that would be produced by the calcination process. It would also provide information on the thermal conductivity of the dried feed. The bulk density was estimated from pieces of calcined feed that were weighed and, because of their regular geometry, their volume could be approximated. The hygroscopic characteristics of the calcined feed were determined from the measured weight gain of a fragment with time standing in laboratory air.

6. Heat sensitivity

This was an observed characteristic which was noted during the test or from viewing the video tape of the test. Changes of rheology as a function of temperature would be an example of this property.

7. Enthalpy changes

Samples of slurry were evaluated by DTA to identify exotherms and endotherms.

8. Stickiness

Based on visual observations, the tendency for the slurry to adhere to the vessel walls and the stainless steel stirrer as dry out and calcining occur was documented.

9. Abrasiveness, hardness

The feed cake abrasiveness was expected to be a function of its batch materials until its components begin to react and/or fuse together during calcination. The composite hardness was expected to be a function of the degree of calcination. Over the range of the present test conditions, the silica sand would be the principle abrasive phase. No specific measurements for this property were planned.

10. Phase separation

The dried-out /calcined material was examined visually for a separated phase. Segregated salts were the most likely to occur.

11. General observations (color changes, caking, etc.)

These observations were taken as part of the test record and were correlated with the other properties measured during this study.

3.0 Procedures, Equipment, and Materials

3.1 Transport and Physical Properties

The DST/SST waste blend simulant with glassformers was gradually dried out by heating. At several stages of drying, weight percent solids, density, and rheological properties were measured.

Density and weight percent solids were measured using HWVP technical procedure WTC-006-4. To determine density, a measured volume of slurry simulant at ambient temperature was weighed and from that grams per unit volume was calculated. Weight percent solids was determined by weighing a slurry sample and then weighing the sample after it was dried for 24 hours at 105°C and calculating the remaining percentage of weight.

Rheological characterization was performed at 50°C using the same procedure. The rheological values were measured using the Haake M5 measuring system with the MV2 sensor. Rheograms were generated by increasing the applied shear rate from 0 to 451 s⁻¹ in a 2 minute interval. The increasing shear rheology data were fit with the Bingham equation:

$$\tau = \tau_0 + \mu\dot{\gamma}$$

where

τ = shear stress,
 τ_0 = yield stress,
 $\dot{\gamma}$ = shear strain rate, and
 μ = plastic viscosity.

Bulk density and hygroscopy were also measured. After the melter feeds were calcined at low temperatures (section 3.3), pieces of the reacted feed were carefully measured and weighed. From their calculated volume and their weight, a density was calculated. To test the hygroscopic nature of the calcined feeds, several pieces from the first three tests were allowed to stand exposed to the laboratory atmosphere for up to 140 days. The fragments were weighed before the exposure started and then reweighed periodically to identify any changes in weight that would indicate the uptake of water.

3.2 Thermal Analysis

Thermal gravimetric analysis and differential thermal analysis were performed on the DST/SST waste blend simulant with and without sodium nickel ferrocyanide. A model SDT 2960 Simultaneous DTA-TGA manufactured by TA Instruments, Inc., New Castle, Delaware was used to perform the analysis. The samples were heated from 30°C to 1350°C at 30°C/min in alumina oxide crucibles.

3.3 Low-Temperature Calcination

The system that was used to calcine (boiling to 500°C) the simulant materials is shown in Figure 3.3.1 and is described below. The instrumented reaction vessel consists of a 2-L Pyrex kettle placed in a temperature controlled heating mantle. The Pyrex kettle lid is modified to accept several thermocouples, an agitator shaft connected to a stir blade, condenser, a divided sweep gas inlet (one jet to the bottom of the vessel and the other directed at the vessel lid to keep a window clear for the video camera). A second condenser is added in series to the first condenser connected to the vessel lid. The sweep gas, argon with a helium tracer, carries off-gas from the reaction vessel plenum, through the condensers to the off-gas measuring system (Figure 3.3.2). Three thermocouples are placed in the reaction vessel to detect temperature gradients.

Figure 3.3.2 is a schematic of the off-gas measuring equipment configuration. Because of the dynamic nature of the dry-out/calcination chemistry and resultant gas generation, real time monitoring capabilities are employed to characterize the generation rates of the major gaseous reaction products. The emission rate behaviors of H₂, CO₂, N₂O, CO, O₂, and N₂ are monitored using a gas chromatograph (GC). A Chemiluminescent NO/NO_x analyzer is used to measure NO_x. Over 95% of the NO_x measured was NO₂. The nominal sample rate of the GC is approximately 80 s, while the nominal sample rate of the NO_x analyzer is 60 s. A Fourier transform infrared (FTIR) spectrometer analyzes gas samples on an approximately 3 minute cycle time which provided a backup analysis for each of the above gases, except for H₂ and O₂, plus NH₃. The spectrometer is also used for the detection of other unknown, infrared (IR) sensitive gaseous species, such as volatile organics and cyanide. Note sscpm on Figure 3.3.2 stands for standard cubic centimeters per minute.

The dry out and calcination laboratory processing and characterization methods are as follows:

1. Four hundred mL of prepared melter feed slurry was placed in the reaction vessel. The sweep gas flow through the plenum of the reaction vessel was established (1.95 L per min), and stirring of the slurry at about 60 rpm was started. The slurry surface appearance was recorded using a video tape recorder and was viewed through the reaction vessel lid.
2. The slurry was heated in a stepwise fashion using thermocouple #4 as the control thermocouple. The temperature was allowed to reach a maximum for a given control setting, and then the control point was reset to 5°C above the maximum temperature attained at the previous control value. For these tests, the temperature was set first to 100°C. Typically there was a thermal overshoot of several degrees, so the temperature set point was usually incremented by 8°C to 12 °C. This procedure was continued until the slurry was dry and cracked, then the temperature increments were increased to 20°C above the maximum (increase the set point by 25°C to 30°C). This routine was continued until the temperature attained at the center of the reaction vessel was approximately 350°C. This temperature was held for 20 to 30 minutes and then the power was turned off.
3. Coincident with the above heating, the temperatures were recorded at 1 to 3 minute intervals, the off-gas was analyzed as described below, measured amounts of condensate were taken at regular time intervals, and the video camera was recording the surface of the slurry. In addition, the times at which the set point for the mantle heater was changed were recorded in an observation log.

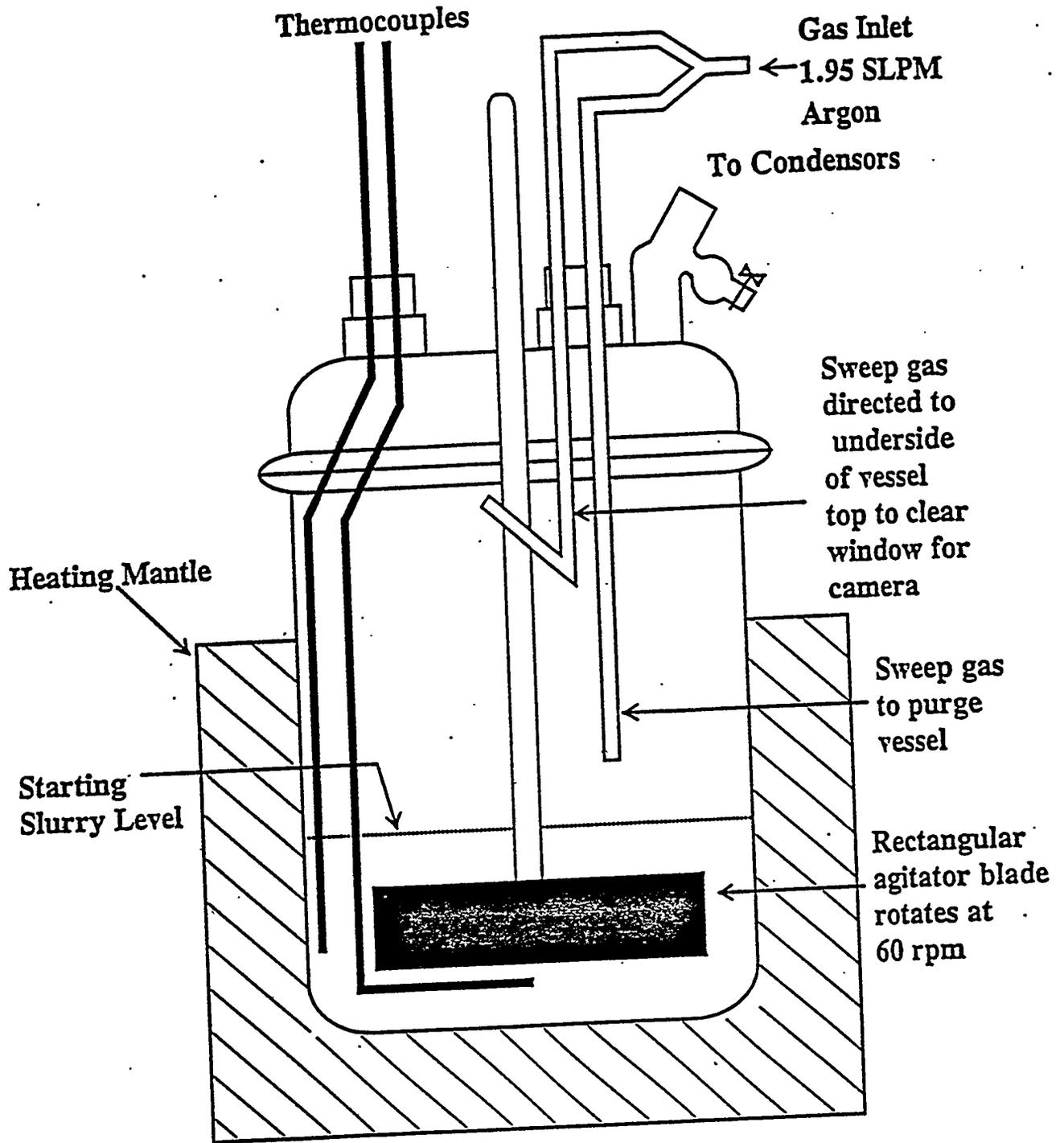
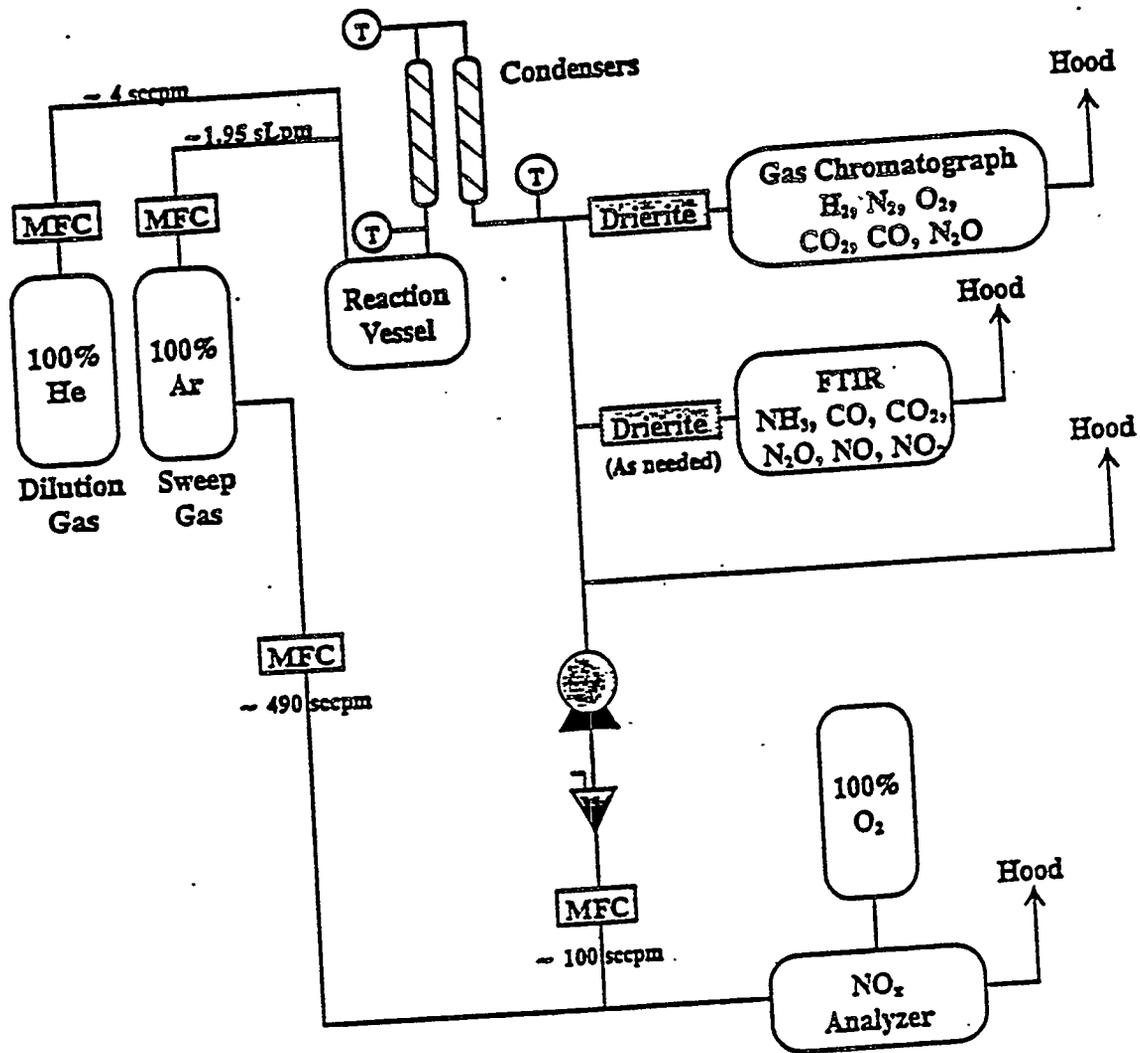


Figure 3.3.1. Schematic Configuration of the Reaction Vessel for the Blend Dry-Out/Low-Temperature Calcine Testing



MFC	Mass Flow Controller	<u>Detection Limits</u>	
T	Temperature Probe	NO_x Analyzer	NO_x 1 ppm
	Metal Bellows Pump	GC	H₂ 10 ppm
	Needle Valve		N₂ 100 ppm
			O₂ 100 ppm
			CO₂ 50 ppm
			CO 200 ppm
			N₂O 50 ppm

Figure 3.3.2. Schematic of the Laboratory-Scale Offgas Equipment Configuration for the Blend Dry-Out/ Low-Temperature Calcine Testing

4. At the conclusion of the test, when the dried and calcined melter feed had cooled enough to allow the reaction vessel to be opened, additional video pictures were taken of the melter feed as it was being removed from the vessel to show the degree of adherence to the vessel walls and the stainless steel stirrer.

3.4 High-Temperature Calcination

This system consists of a quartz crucible reactor equipped with an on-line chromatograph-mass spectrometer and viewing port (Figure 3.4)^(a) in which the dried simulant can be calcined up to 1300°C in a furnace.

The DST/SST waste blend simulant was dried at 105°C in air for 24 hours then crushed for 2 minutes in an agate disc mill to -120 mesh. Samples were stored at atmospheric conditions before use in the quartz crucible. Three grams of dried melter feed were transferred to the quartz crucible. An ultrasonic cleaner was used to remove feed from the quartz crucible sides. The slurry feed samples were heated in the quartz crucible reactor from room temperature to 1300°C at a rate of 10°C/min..

Offgas was analyzed by Gas Chromatograph-Mass Spectrophotometer (GC-MS) (Hewlett Packard models 5890 and 5971, respectively). The GC Pora PLOT Q column was maintained at 90°C. The inlet pressure was 6.1 psi and a corresponding backpressure regulator was set at 6.1 psi (to avoid baseline upsets). GC injections of 0.5 ml were made once a minute by a valve rotator which allowed the gas species to be identified every 10°C. An Ar + 1% He sweep gas was introduced to the quartz crucible at a flow of 400 ml/min while maintaining an overall gas pressure of roughly 42 KPa (6.1 psi). The mass spectrometer was operated in a scanning mode.

3.5 Materials

The FY1994 DST/SST blend was prepared in accordance with the DST/SST blend feed specification^(b). The laboratory preparation steps and observations were compared with existing experience base to verify the acceptability of the feed specification for simulant make-up. The DST/SST blend simulant was used for the dry out and calcine assessment tests. The batching compounds and target composition are given in Table 3.5.

-
- (a) P. A. Smith, J.D. Vienna, and M. D. Merz. 1994. NCAW Feed Chemistry: Effect of Starting Chemistry on Melter Offgas and Iron Redox, C94-03.02K
- (b) E. M. Tracey, M.D. Merz, G. K. Patello, and K. D. Wiemers. 1995. Feed Specification for the Double-Shell Tank/Single Shell Tank Waste Blend for High-Level Waste Vitrification Process and Melter Testing, C95-02.02H

Table 3.5. Blend Simulant Make Up

<u>Oxides</u>	<u>Batching Compound</u>	<u>moles elem. / 118g WO/L</u>	<u>Wt% Oxide</u>
Ag ₂ O	AgNO ₃	0.00005	0.0044
Al ₂ O ₃	Al(OOH), NaAlSi ₃ Si ₂ O ₂₄ (NO ₃) ₂ (Cancrinite)	0.33900	15.3000
B ₂ O ₃	H ₃ B ₃ O ₃	0.00286	0.0301
BaO	Ba(OH) ₂ ·8H ₂ O	0.00619	0.0230
Bi ₂ O ₃	Bi(NO ₃) ₃ ·5H ₂ O	0.01110	2.0700
CaO	Ca(OH) ₂	0.04880	2.1900
CaO	Ca(OH) ₂	0.00094	0.0963
CaO ₂	Ca(NO ₃) ₂ ·6H ₂ O	0.02110	2.9000
Cl	NaCl	0.00122	0.0346
Ca ₂ O ₃	Ca(NO ₃) ₂ ·6H ₂ O	0.00016	0.0108
Cr ₂ O ₃	Cr(NO ₃) ₃ ·9H ₂ O	0.00790	0.4800
Ca ₂ O	CaNO ₃	0.00011	0.0129
CaO	Cu ₂ SO ₄ ·5H ₂ O	0.00015	0.0096
F	NaF(LaF ₃ , NdF ₃)	0.03880	0.5890
Fe ₂ O ₃	Fe(NO ₃) ₃ ·9H ₂ O	0.18300	11.7000
Ga ₂ O ₃	Ga ₂ O ₃	0.00000	0.0000
H ₂ O	H ₂ O	0.00005	0.0038
K ₂ O	KOH	0.00626	0.2360
La ₂ O ₃	LaF ₃ , La(OH) ₃	0.00349	0.4550
Li ₂ O	Li ₂ O	0.00006	0.0007
MgO	Mg(NO ₃) ₂ ·6H ₂ O	0.00253	0.0417
MnO ₂	Mn(NO ₃) ₂ , KMnO ₄	0.02780	1.9300
MoO ₃	MoO ₃	0.00068	0.0781
Na ₂ O	NaOH	1.08000	26.9000
Na ₂ O ₃	Na(NO ₃) ₃ ·6H ₂ O, NaF ₃	0.06830	9.1900
NiO	Ni(NO ₃) ₂ ·6H ₂ O	0.04040	2.4100
P ₂ O ₅	Na ₃ PO ₄	0.03810	5.0000
PbO	Pb(NO ₃) ₂	0.00178	0.3410
PdO	Pd(NO ₃) ₂	0.00016	0.0157
Pr ₂ O ₃	Pr(NO ₃) ₃ ·6H ₂ O	0.00015	0.0201
Rb ₂ O	Rb(NO ₃)	0.00009	0.0075
Ra ₂ O ₇	Ra ₂ O ₇	0.00000	0.0004
Rh ₂ O ₃	Rh(NO ₃) ₂	0.00013	0.0136
Ru ₂ O ₃	RuNO(NO ₃) ₃	0.00050	0.0498
Sb ₂ O ₃	Sb ₂ O ₃	0.00019	0.0219
SeO ₂	SeO ₂	0.00029	0.0259
SiO ₂	SiO ₂	0.22100	10.6000
Sm ₂ O ₃	Sm(NO ₃) ₃ ·6H ₂ O	0.00000	0.0004
SnO ₂	SnCl ₂ ·2H ₂ O	0.00000	0.0002
SO ₃	Na ₂ SO ₄	0.00566	0.3620
SrO	Sr(NO ₃) ₂	0.00530	0.4400
Ta ₂ O ₅	Ta ₂ O ₅	0.00000	0.0004
TaO ₂	TaO ₂	0.00002	0.0031
TiO ₂	TiO ₂	0.00012	0.0074
WO ₃	Na ₂ WO ₄ ·2H ₂ O	0.00100	0.1150
Y ₂ O ₃	Y(NO ₃) ₃ ·6H ₂ O	0.00012	0.0105
ZnO	Zn(NO ₃) ₂ ·6H ₂ O	0.00028	0.0185
ZrO ₂	ZrO(NO ₃) ₂	0.07700	7.5900
		2.28685	100.0045

<u>Anions</u>	<u>Batching Compound</u>	<u>g Anion/L (at 118 g oxide/L)</u>
NO ₃ -	NaNO ₃	32.9
NO ₂ -	NaNO ₂	1.74
OH-	NaOH	22.8
CO ₃ --	Na ₂ CO ₃	2.14
I-	NaIO ₃	0.0000395
TOC	Na ₂ C ₂ O ₄	0.411
CN-	Na ₂ NiFe(CN) ₆	2.8

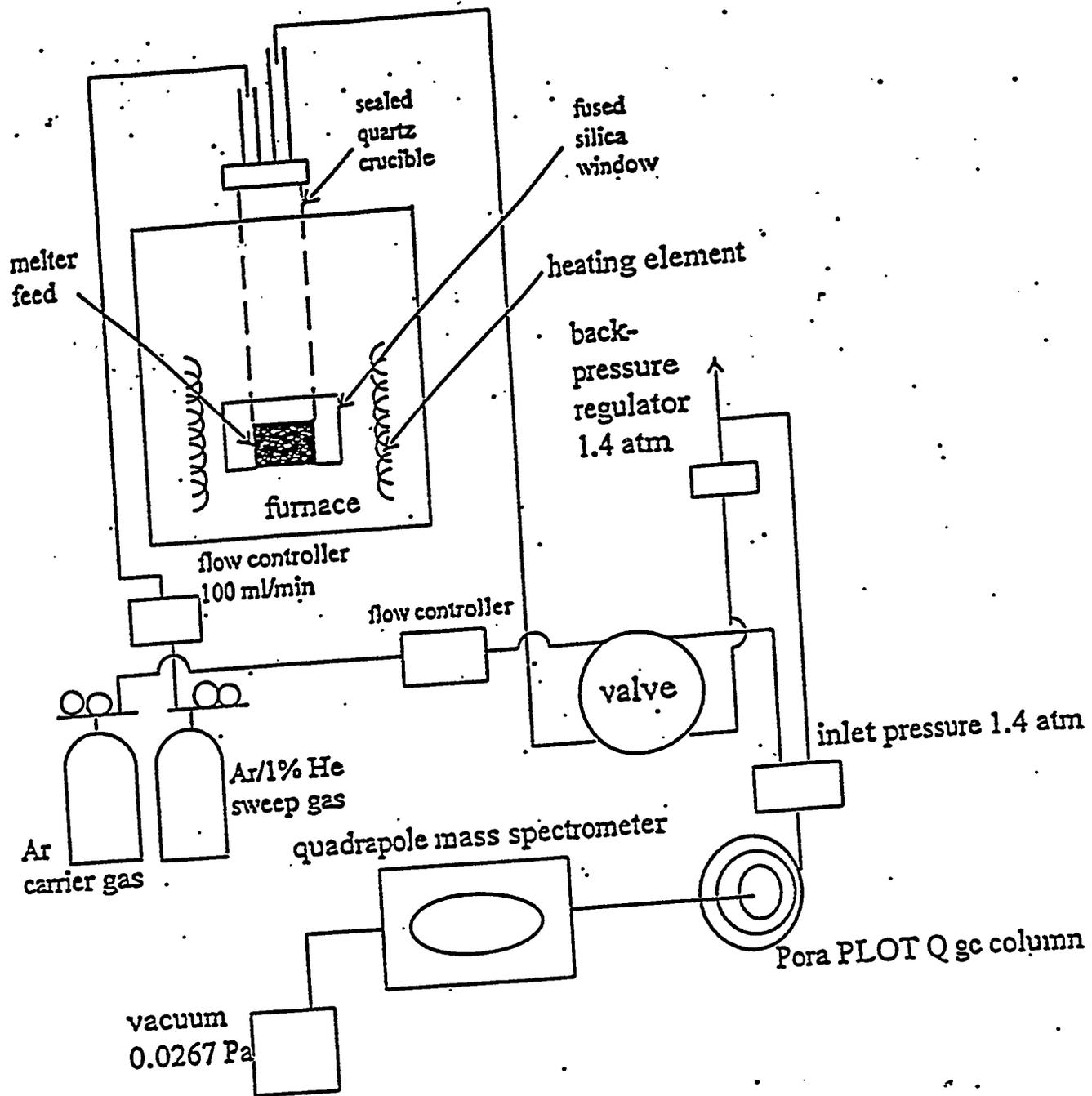


Figure 3.4. Schematic Configuration of the Quartz Crucible High Temperature Calcine/Melting System Used to Test Blend Feed Specimens Including its Offgas Apparatus

4.0 Results and Discussion

The principle objectives of this work were to characterize the changes that occur in the DST/SST waste blend simulant as a function time and temperature. Since time was the only independent variable, all the variables are presented as a function of time and any dependence of the variables on temperature is determined from their dependence on time.

The five tests performed are described in Table 4.0. They include two tests of the blend simulant without ferrocyanide, with two levels of ferrocyanide, and with ferrocyanide plus sugar. All but the test containing sugar were made up to a melter feed composition that was 65% waste oxides and 35% SiO_2 . The variability was the result of adding silica based on assumed gWO/L values which were subsequently found to be high, hence, the excess silica. Chemically this should not affect the melter feed behavior because of the inertness of silica sand. Physically, the additional sand raises the solids loading and may shift the rheological properties to higher values. The "mass delta" represents the difference between the starting weight and the sum of the parts (condensate, residue, offgas, and any samples taken). This number is highest for the tests with the most water. This suggests that water vapor escapes through leaky joints in the system and the saturates the dry sweep gas. The final columns give the gWO/L and gTO/L based on measured values.

4.1 Low-Temperature Calcination

4.1.1 Water

Following the procedure described above, water was driven off at a rate that increased until the temperature was uniform throughout the slurry, as shown in Figures 4.1.1.1 to 4.1.1.5. The rate of water loss was maintained at about 3.5 g/min until the slurry began to solidify at the vessel walls. (The evaporation of water at this rate takes about 130 watts of power.) The net affect was to collect water toward the center of the vessel and then the same relationship between solidification and temperature rise was observed at the center of the vessel. Though at the center of the vessel, the temperature transition was more rapid because it involved a much smaller volume of slurry. The slurry did not cease releasing water until the slurry had reached a maximum temperature between 350 and 400°C. Figure 4.1.1.6 is a comparison plot with the water loss rate plotted as "percent H₂O" and the total water loss plotted as "cumulative percent H₂O," both as a function of time. The figure shows that the dry out profiles for the last four tests are similar. The first test was a scoping test to allow us to see what to expect during these tests.

During the dry-out, the slurry appeared to first congeal to a dark uniform material which did not inhibit the stirring action of the rotating blade. As more water was driven off, the slurry agitated by the blade became thicker and piled up in front of the mixer blades. The slurry beneath the blades solidified before the slurry that was agitated by the blades. The solidified slurry contained numerous air holes through which boiling still could be observed. After solidification, shrinkage cracks developed in the solid feed which appeared to grow continually until water ceased coming out of the vessel.

Table 4.0-Blend Test Summary

<u>Test</u>	<u>Fe/CN16 level</u>	<u>reductant</u>	<u>Glass Comp.**</u>	<u>Initial Slurry Mass (g)</u>	<u>Dried Feed Final Wt. (g)</u>	<u>gWO1</u>	<u>Start Vol.(ml)</u>	<u>ToO1</u>
T95-HTM-DR-C-1	none	negligible	SiO2-0.65g/g	649.2	207.2	186	523.4	294.0
T95-HTM-DR-C-2	none	negligible	SiO2-0.81g/g	495.5	110.2	150	419.1	261.3
T95-HTM-DR-C-3	0.9 g CN/ 118 gWO	FeCN	SiO2-0.57g/g	509.7	133.8	172	415.4	262.1
T95-HTM-DR-C-4	2.8 g CN/ 118 gWO	FeCN	SiO2-0.54g/g	597.7	144.6	149	515.4	222.3
T95-HTM-DR-C-5	2.8 g CN/ 118 gWO	FeCN+Sugar#	none	578.7	94	149	500.0	149.0

* analyzed value

sugar was added equal to 20% of the gWO

** Target silica addition was 0.54 g per gram of waste oxides.

T95-HTM-DR-C-1

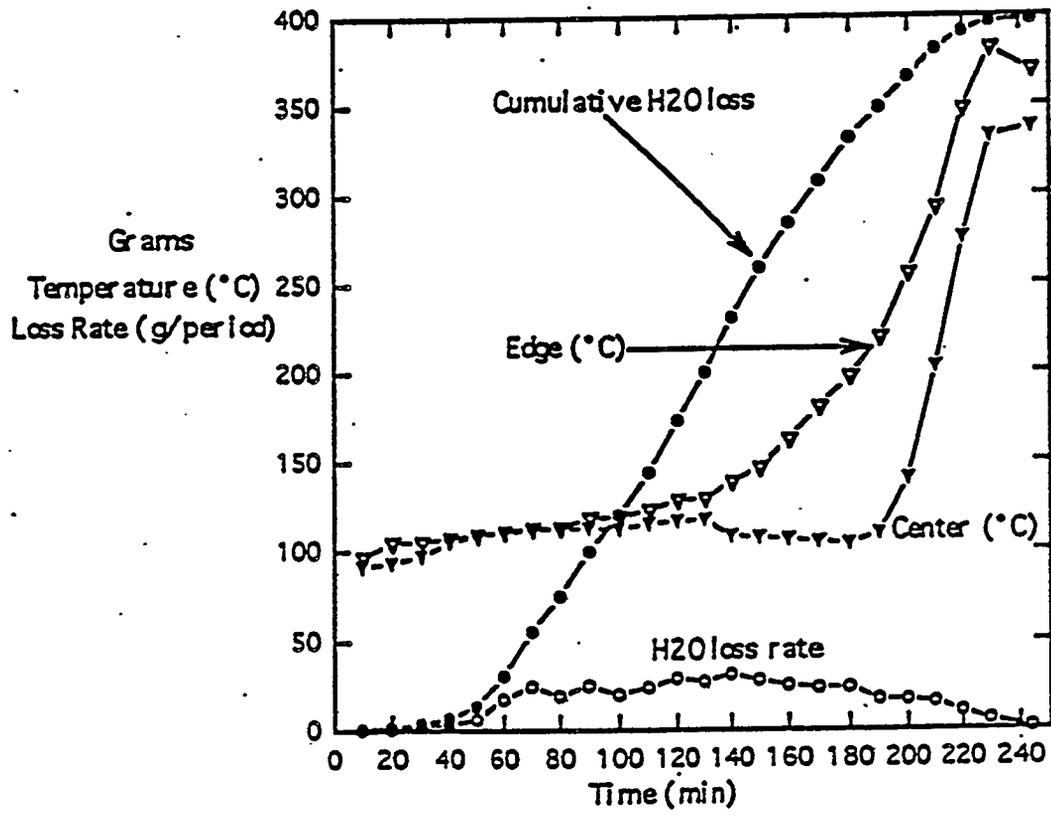


Figure 4.1.1.1

Water Loss as a Function of Time, Temperature for Test T95-HTM-DR-C-1

T95-HTM-DR-C-2

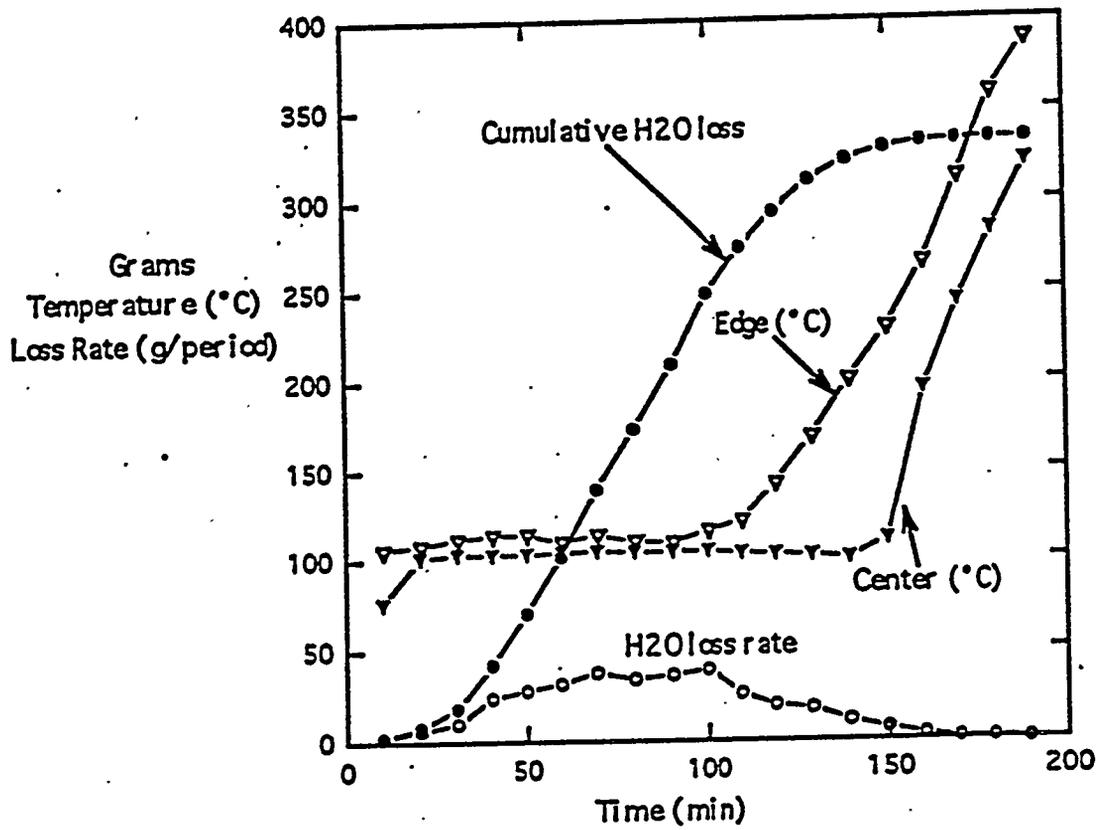


Figure 4.1.1.2 Water Loss as a Function of Time, Temperature for Test T95-HTM-DR-C-2

T95-HTM-DR-C-3

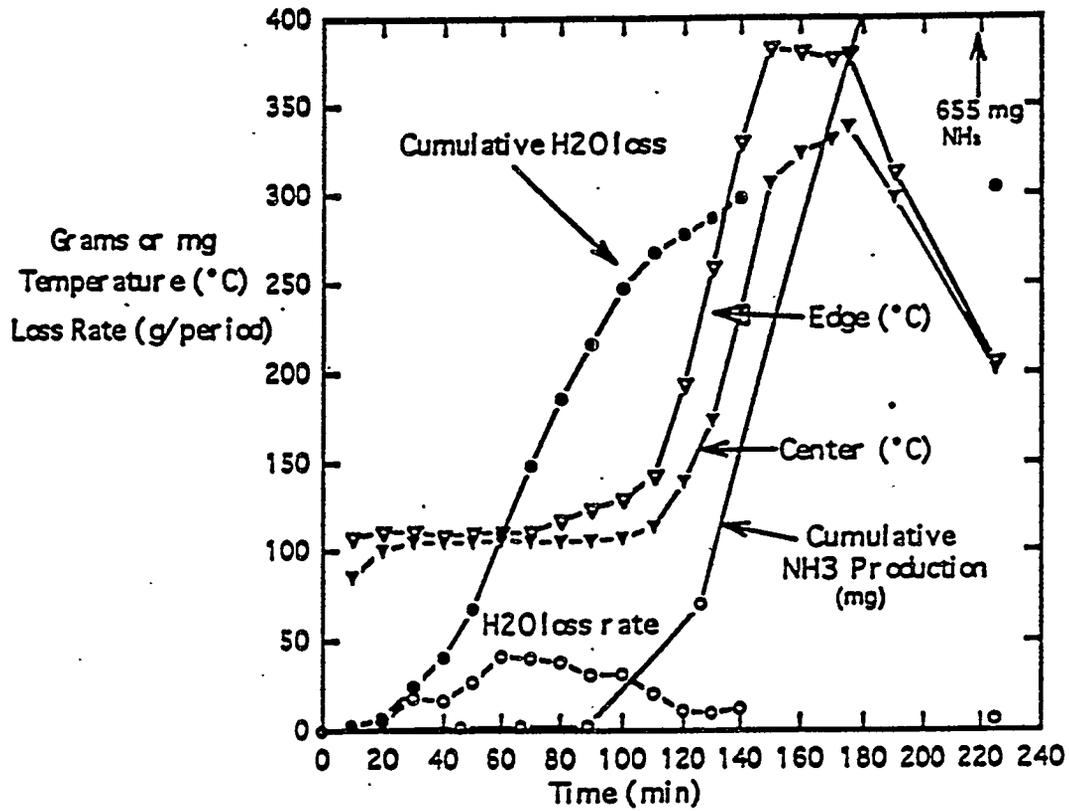


Figure 4.1.1.3

Water Loss as a Function of Time, Temperature for Test T95-HTM-DR-C-3

T95-HTM-DR-C-4

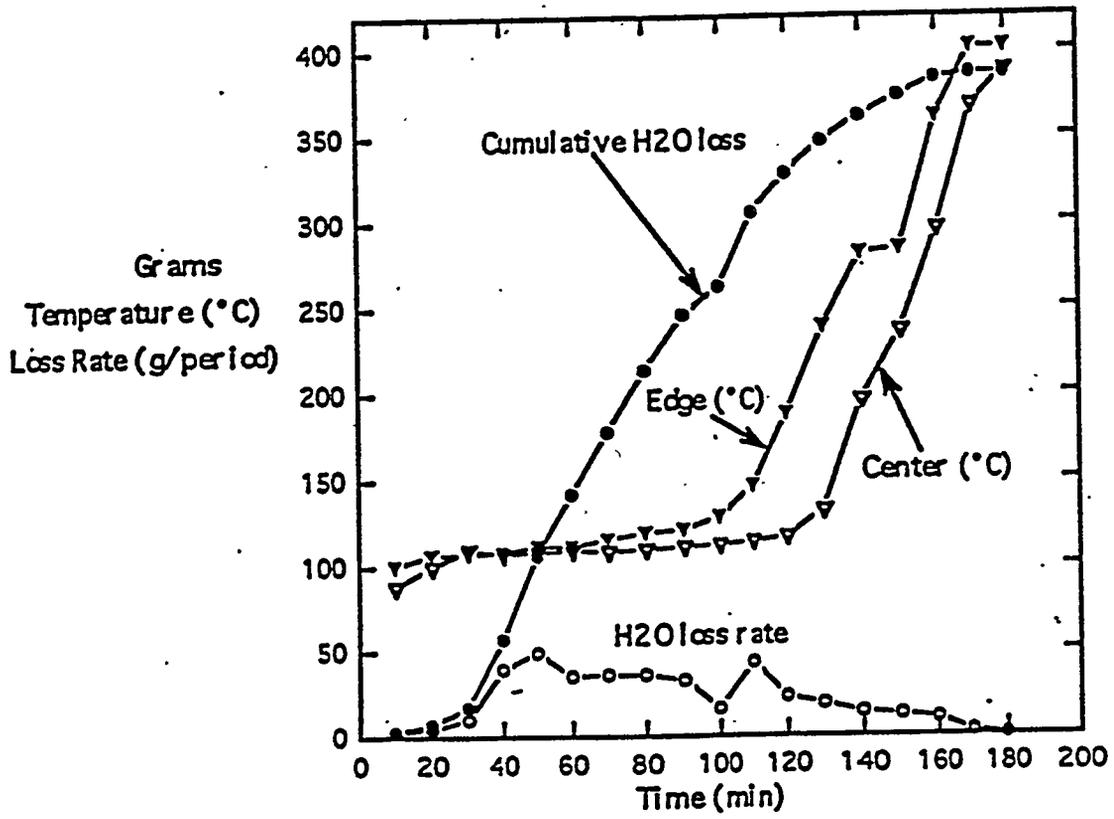


Figure 4.1.1.4 Water Loss as a Function of Time, Temperature for Test T95-HTM-DR-C-4.

T95-HTM-DR-C-5

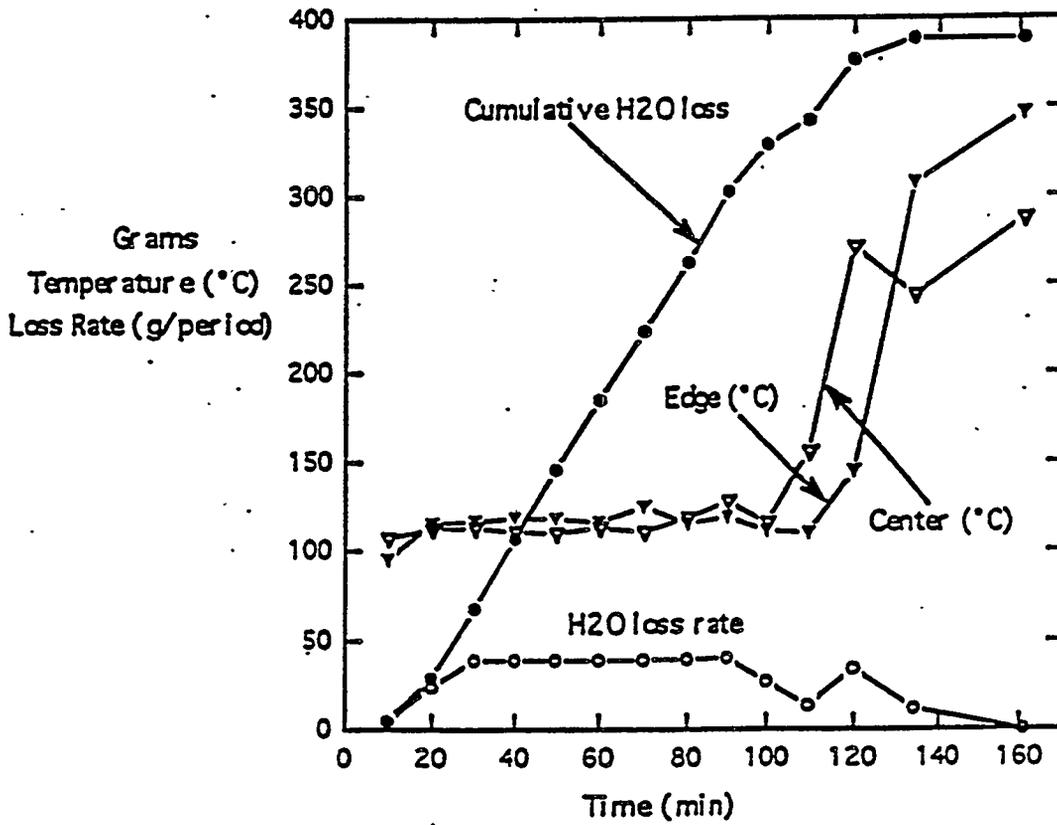


Figure 4.1.1.5

Water Loss as a Function of Time, Temperature for Test T95-HTM-DR-C-5

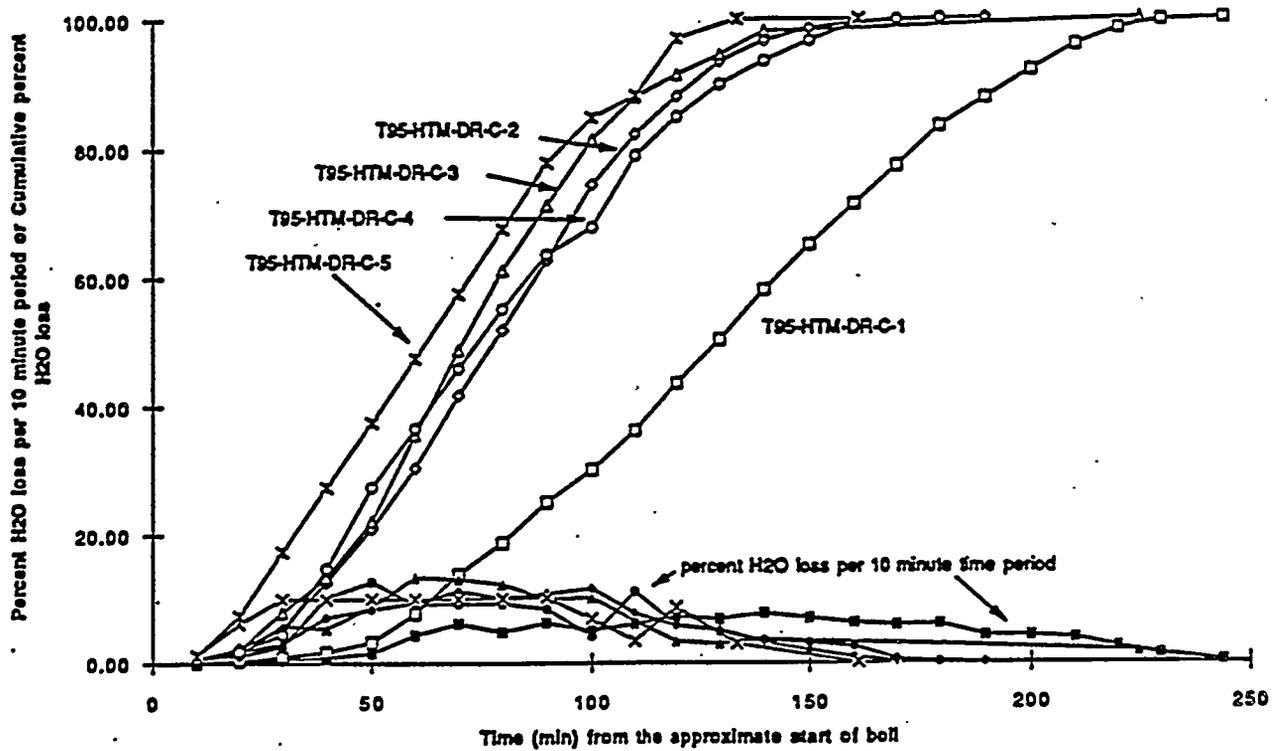


Figure 4.1.1.6

Comparison of the Water loss as a Function of Time for Each of the Five Tests

If the stirring blade had agitated the entire volume of slurry, it appears that the slurry would have solidified as a single mass rather than in stages as observed. This will be further discussed below under physical properties.

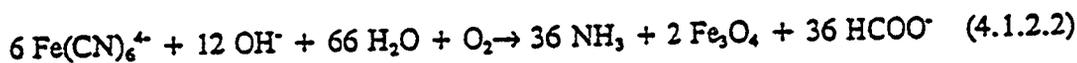
4.1.2 Other Gases

The offgas totals and peak rates are given in Table 4.1.2.1 and the evolution rates as a function of time (temperature) are shown in Figures 4.1.2.1 to 4.1.2.5. Test T95-HTM-DR-C-1 was a scoping test and the last portion of the off-gas data was lost, therefore no N₂O, CO, or H₂ were observed. Little offgas activity was noted from the melter feed slurries made up from blend waste simulant containing no ferrocyanide. When approximately 30 wt% of the target ferrocyanide has been added (T95-HTM-DR-C-3), there is a significant increase in the amount of CO₂ generated, but other gases do not appear to be significantly influenced. When the blend simulant is fully loaded with ferrocyanide, as it was for test T95-HTM-DR-C-4, there was significant increase in all of the nitrogen containing gases and in CO₂. Nitric Oxide displayed the largest release increase followed by N₂O and CO₂. Ammonia is also a significant product as discussed below.

The addition of sugar to the feed results in a significant exothermic reaction which heats the reacting areas to incandescence. The exothermic reaction was also indicated by the temperature spikes shown in Figure 4.1.2.5. Multiple spikes in the temperature and offgas generation were observed because the reaction took place in limited areas as the dry out of the slurry simulant progressed.

Ammonia results are presented in Table 4.1.2.2 and in Figure 4.1.2.6. Ammonia generation during the dry out and low temperature calcine tests was monitored and semiquantitatively measured using the FTIR and acid (H₂SO₄) bubbler traps. The amounts of NH₃ evolved from the blend feeds appears to be proportional to the amounts of ferrocyanide present in the feeds suggesting that the NH₃ is a breakdown product of the ferrocyanide. In addition, the NH₃ generation occurs after dry out of the feed as indicated by Figure 4.1.2.6. According to Tan and Teo (1987) and Robuck and Luthy (1989) a reaction between the ferrocyanide and base (NaOH) will produce NH₃ and NaCOOH plus other products. Their work was performed under atmospheric pressure at temperatures less than boiling and under hydrothermal conditions for temperature up to about 180°C. The reaction is pH dependent with the reaction going to completion at a pH of 10 or greater but not at a pH of 6.2.

They describe the reaction with the following equations:



According to our results, essentially all of the nitrogen associated with the CN anion reacts to form NH₃, consistent with the findings of the above authors. Our results are also consistent with the reaction kinetics described by the above authors. Some reaction is observed under boiling conditions but most of the reaction in the blend based melter feed appears to occur after the free water is gone. The reaction must be occurring between hydroxides, hydrates, and the ferrocyanide in the blend melter feed.

Table 4.1.2.1. Blend Dry-Out and Low-Temperature Calcine Test Offgas Data

Offgas Analyses - All values in mmoles or mmoles per min.

T95-HTM-DR-C-1		<u>CO2</u>	<u>H2</u>	<u>NOx</u>	<u>N2O</u>	<u>N2</u>	<u>CO</u>	<u>CH4</u>
Peak Rate		0.027	0.0004	0.0758	0.013	0.032	0	0.0016
Total		0.96	0.005	1.96	0.059	4.94	0	0.006
T95-HTM-DR-C-2		<u>CO2</u>	<u>H2</u>	<u>NOx</u>	<u>N2O</u>	<u>N2</u>	<u>CO</u>	<u>CH4</u>
Peak Rate		0.0097	0.0039	0.039	0.027	0.0158	0.0063	0.0025
Total		0.17	0.123	1.8	0.762	1.81	0.154	0.0038
T95-HTM-DR-C-3		<u>CO2</u>	<u>H2</u>	<u>NOx</u>	<u>N2O</u>	<u>N2</u>	<u>CO</u>	<u>CH4</u>
Peak Rate		0.124	0.0025	0.4	0.0227	0.0183	0.025	0.0024
Total		3.46	0.056	1.2	0.483	1.56	0.399	0.0037
T95-HTM-DR-C-4		<u>CO2</u>	<u>H2</u>	<u>NOx</u>	<u>N2O</u>	<u>N2</u>	<u>CO</u>	<u>CH4</u>
Peak Rate		1.13	0.00336	1.61	0.324	0.332	0.113	0.0041
Total		14.3	0.0411	26.6	3.12	4.94	0.628	0.0247
T95-HTM-DR-C-5		<u>CO2</u>	<u>H2</u>	<u>NOx</u>	<u>N2O</u>	<u>N2</u>	<u>CO</u>	<u>CH4</u>
Peak Rate		4.61	0.131	5.91	0.548	0.927	0.831	0.0082
Total		45.4	1.81	71.2	4.68	8.76	8.04	0.058

4.1.2.2. Blend Dry-Out and Low-Temperature Caliche Test Ammonia Offgas Data

T93-HTM-DR-C-1
 Sample
 Primary Condensate
 Secondary Condensate
 NH3
 1.9 mg/L
 53 mg/L

Ammonia Trap Sample
 none - not indicated on FTIR
 Expected NH3 - 0 mg

Expected NH3 - 0 mg

T93-HTM-DR-C-2
 Ammonia Trap Sample
 none - not indicated on FTIR

T93-HTM-DR-C-3
 Expected NH3 - 366 mg

Sample	Fraction of Argon Flow Rate	Ammonia Trap Samples							
		Trap Vol./wt.	NH3 mg/L	sum NH3(mg)	cum.(mg)	Cum. Time	Time Period	Rate(mg/min)	
NH3-1	0.08	65.1	19.6	16.39	0.00	0	0min	0.05	1.04
NH3-2	0.08	60	22.5	2.26	2.26	46	46	0.02	0.99
NH3-3	0.08	55	23.2	0.50	2.76	67	21	0.01	1
NH3-4	0.08	49.7	23.4	0.13	2.89	89	22	1.83	0.97
NH3-5	0.08	42.5	146.0	67.74	70.63	126	37	6.22	1.05
NH3-6	0.08	37.2	1355.0	584.67	655.30	220	94		
				671.89					

T93-HTM-DR-C-4
 Expected NH3 - 1157 mg

Sample	Fraction of Argon Flow Rate	Ammonia Trap Samples							
		Trap Vol./wt.	NH3 mg/L	sum NH3(mg)	cum.(mg)	Cum. Time	Time Period	Rate(mg/min)	
NH3-1	-0.2	55.5	30	8.33	8.33	140	180	0.05	
NH3-2	-0.2	49.3	4300	1052.56	1060.88	167	27	38.98	
NH3-3	-0.2	42.9	6600	493.35	1554.23	184	17	29.02	
				1354.23					

T93-HTM-DR-C-5
 Expected NH3 - 1157 mg

Sample	Fraction of Argon Flow Rate	Ammonia Trap Samples							
		Trap Vol./wt.	NH3 mg/L	sum NH3(mg)	cum.(mg)	Cum. Time	Time Period	Rate(mg/min)	
NH3-1	-0.12	56.4	290	136.30	136.30	65	65	2.10	
NH3-2	-0.12	51.2	420	55.47	191.77	81	16	3.47	
NH3-3	-0.12	46.7	810	151.78	343.54	98	17	8.93	
NH3-4	-0.12	42.3	1900	384.23	727.77	143	45	8.54	
				727.77					

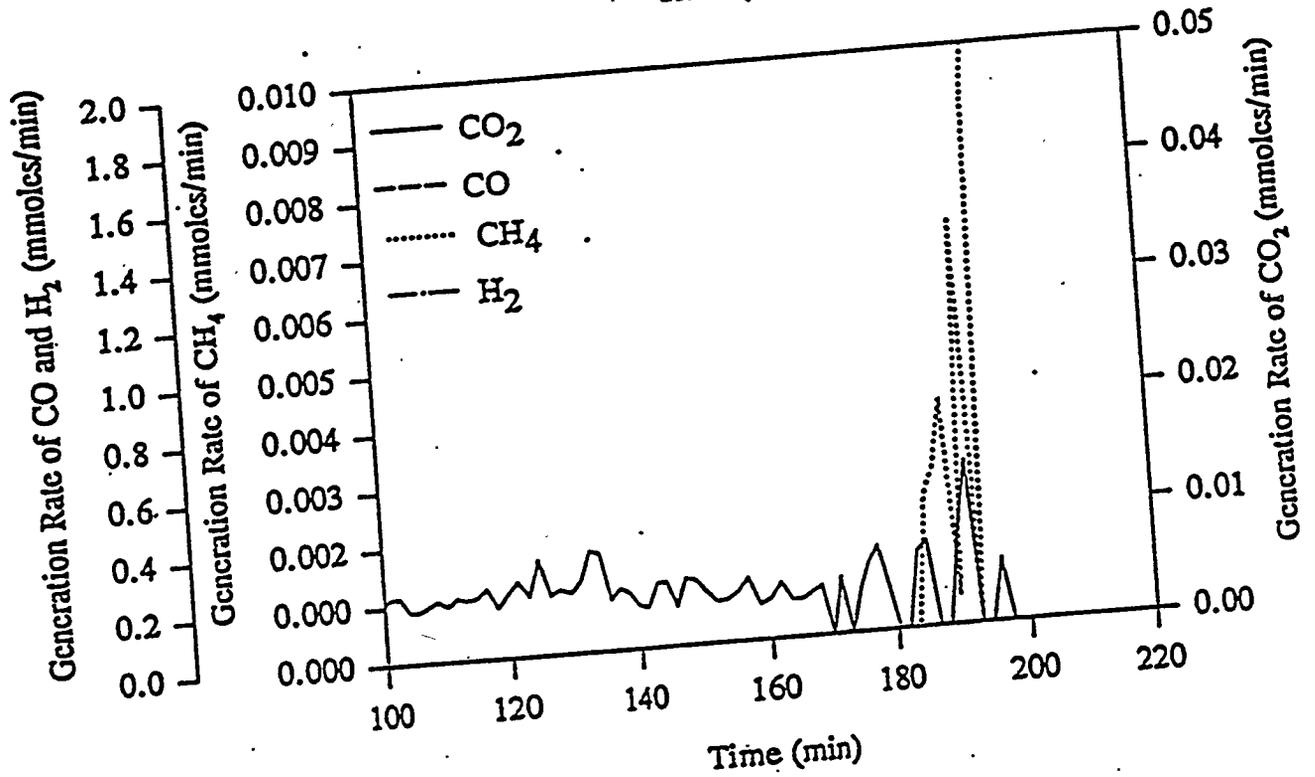
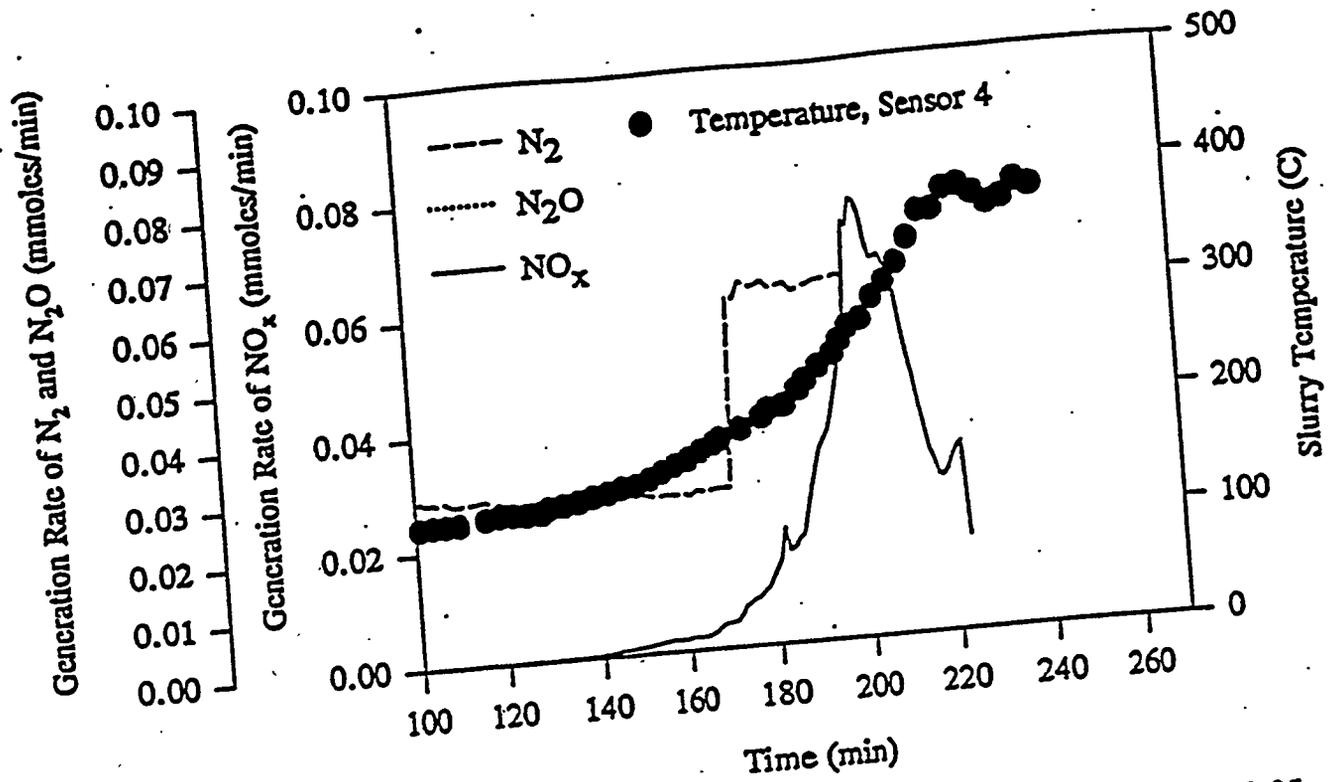


Figure 4.1.2.1 Offgas Profiles as a Function of Time and Temperature for Test T95-HTM-DR-C-1

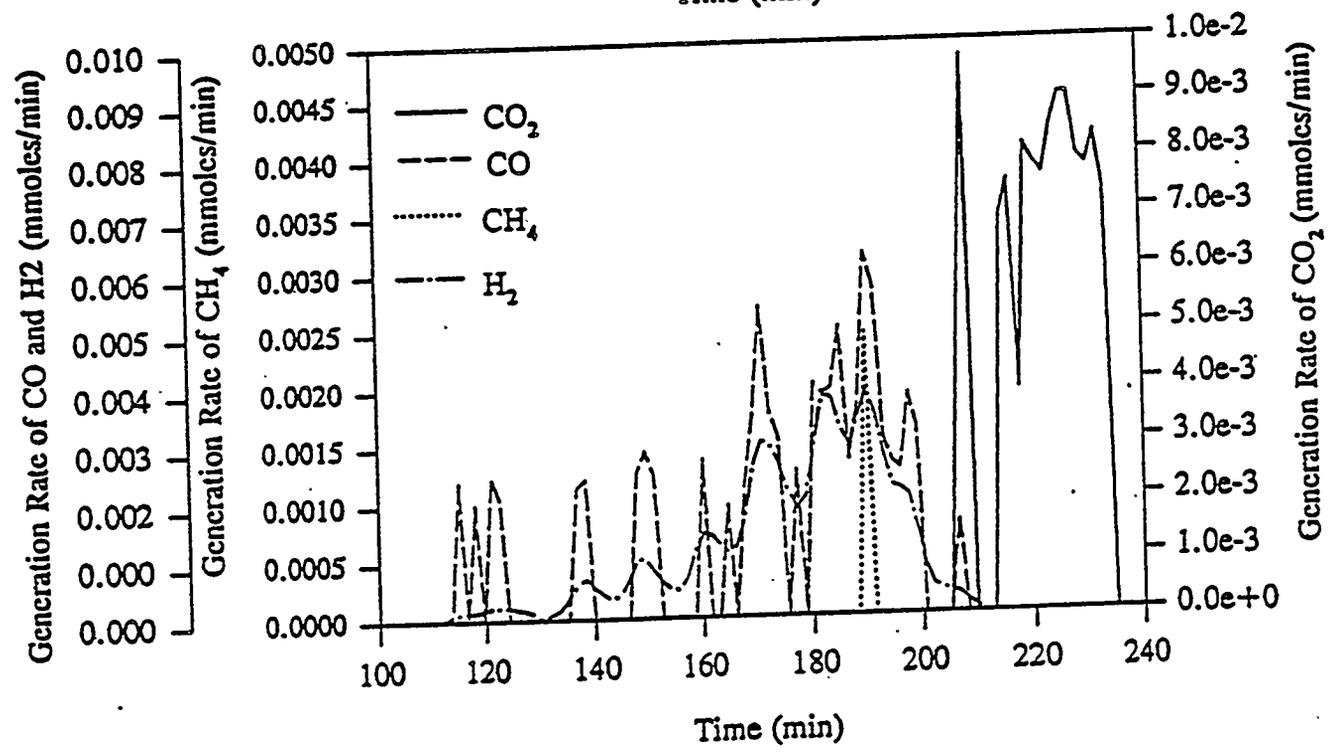
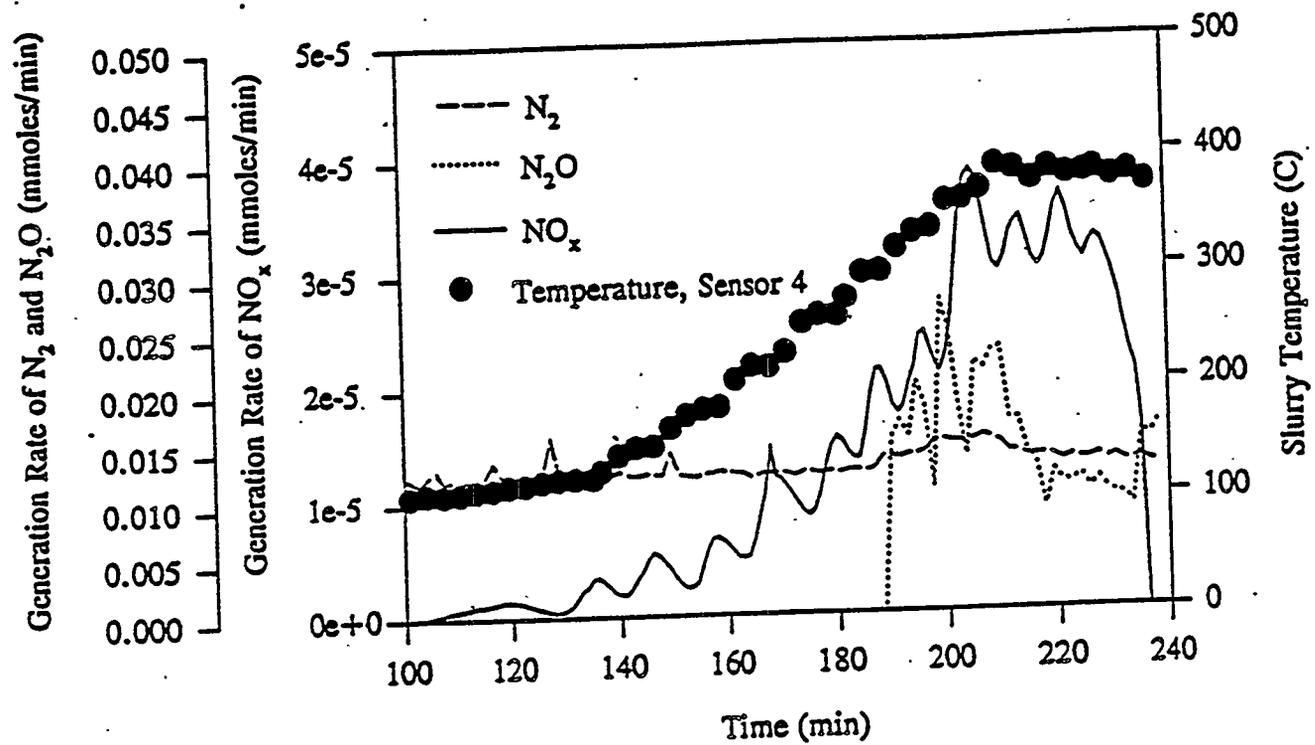


Figure 4.1.2.2 Offgas Profiles as a Function of Time and Temperature for Test T95-HTM-DR-C-2

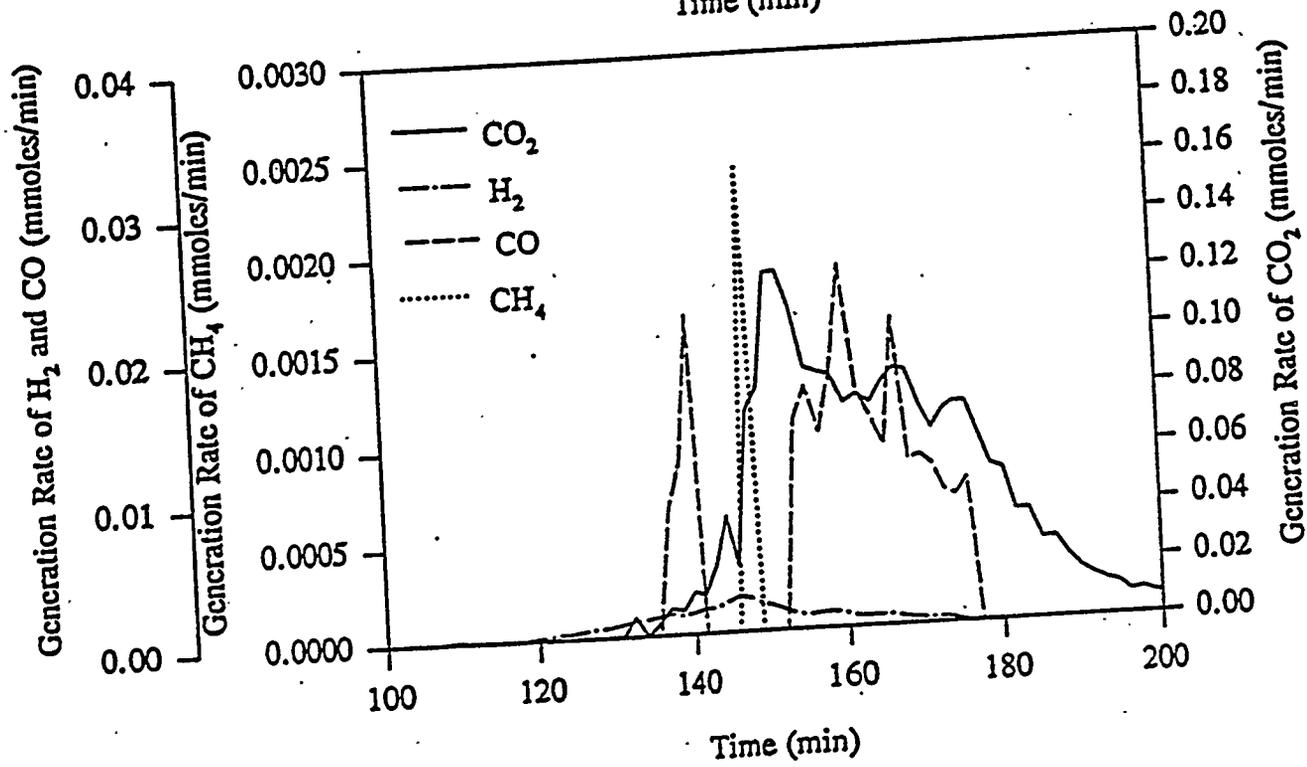
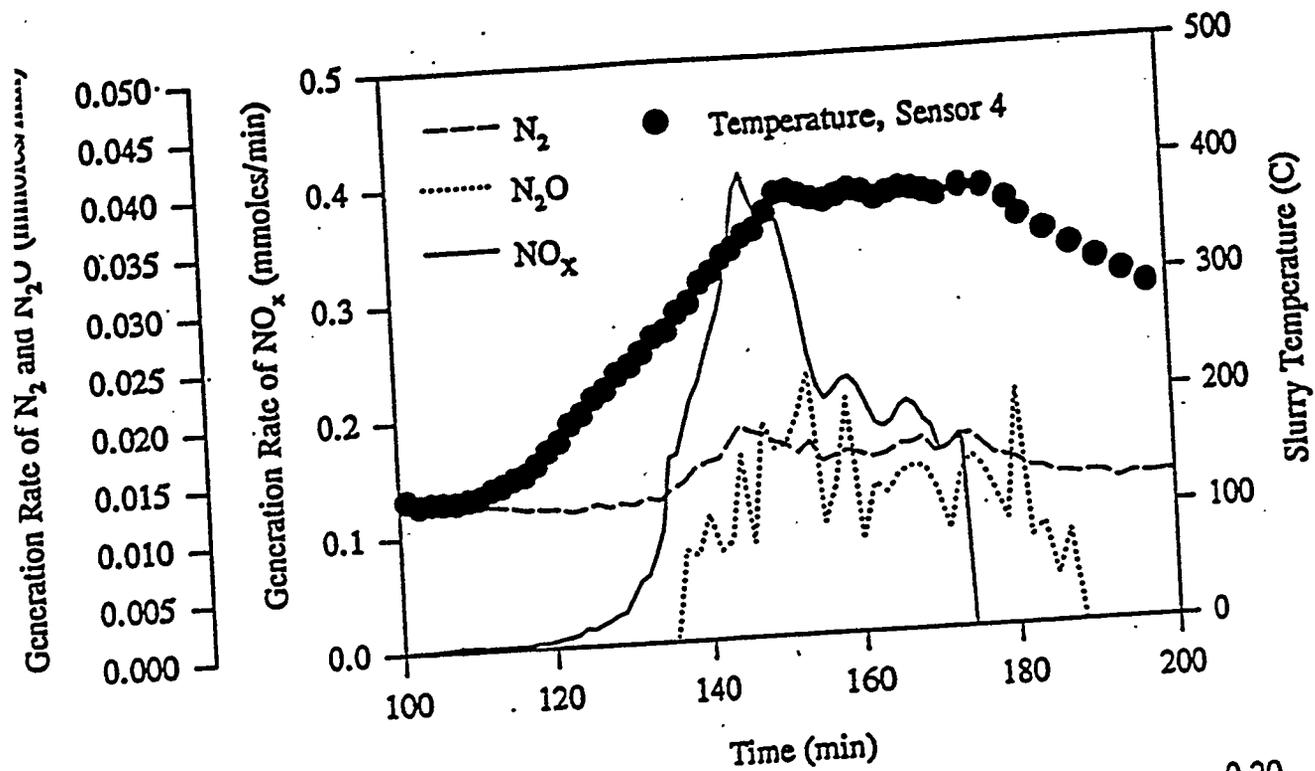


Figure 4.1.2.3 Offgas Profiles as a Function of Time and Temperature for Test T95-HTM-DR-C-3.

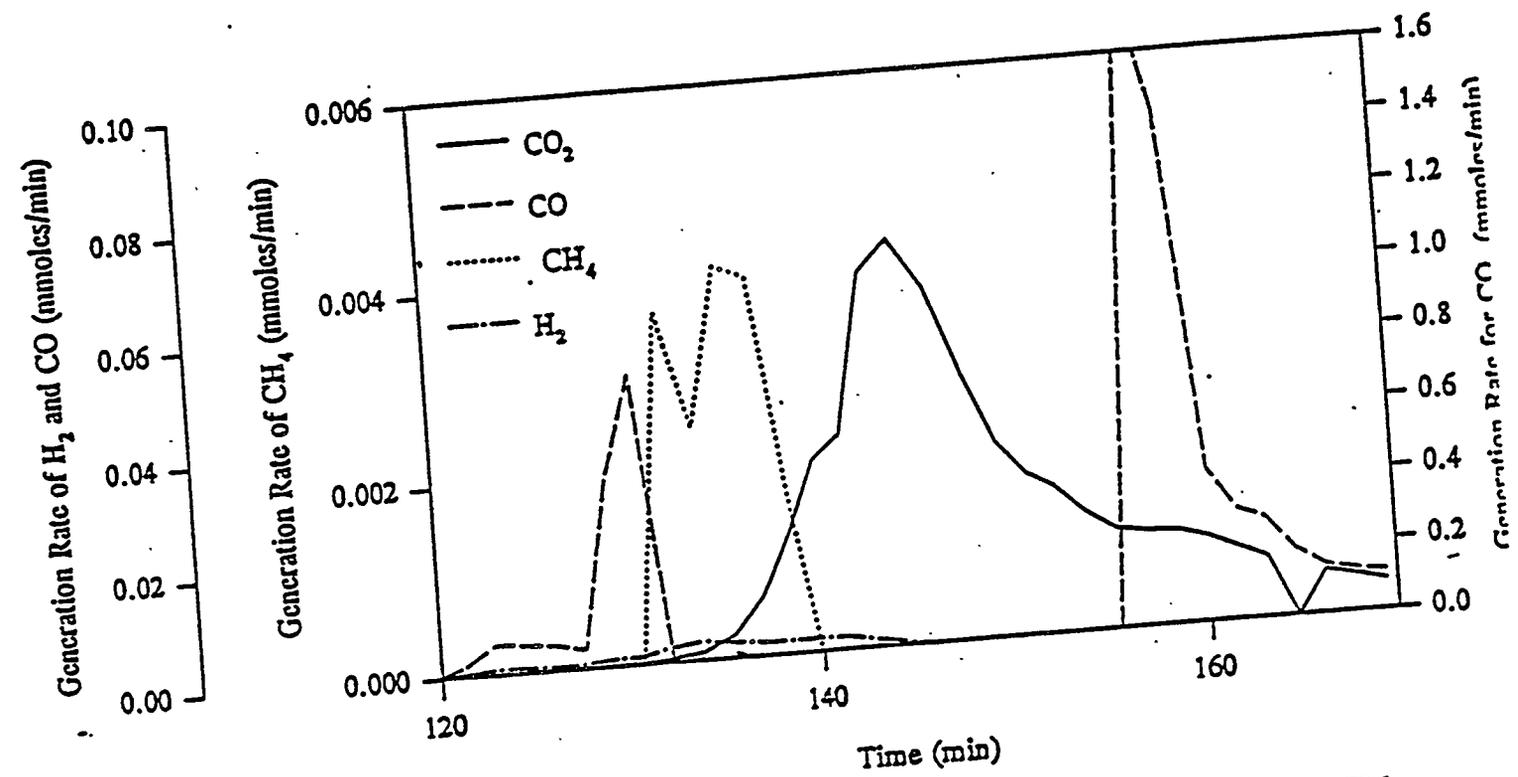
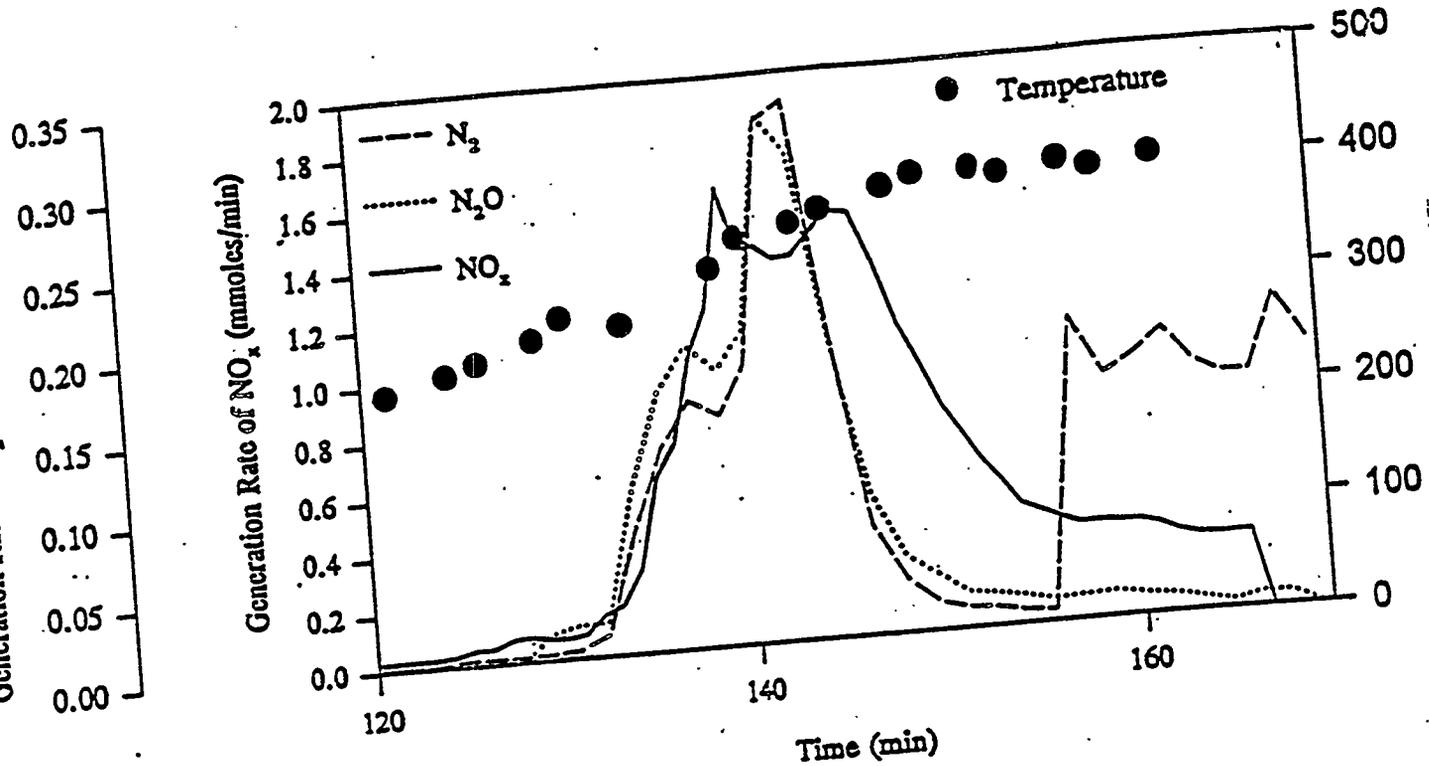


Figure 4.1.2.4 Offgas Profiles as a Function of Time and Temperature for Test T95-HTM-DR-C-4

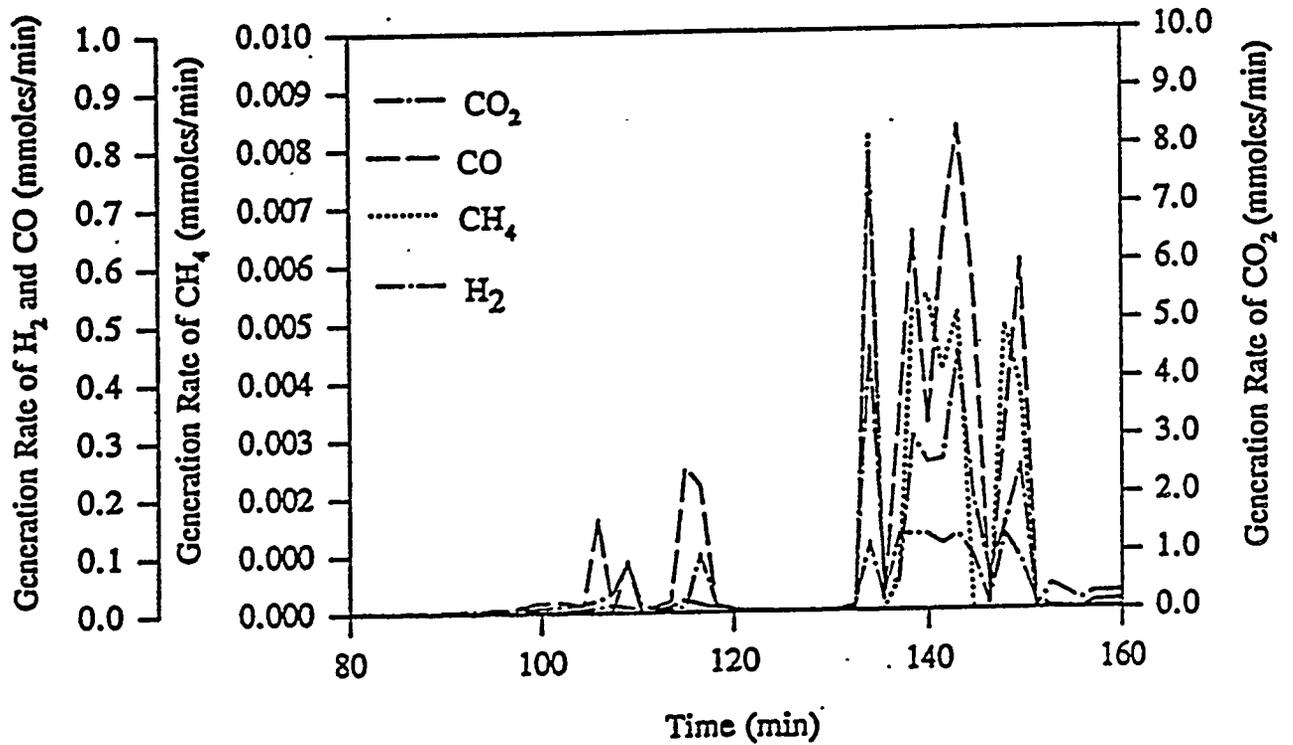
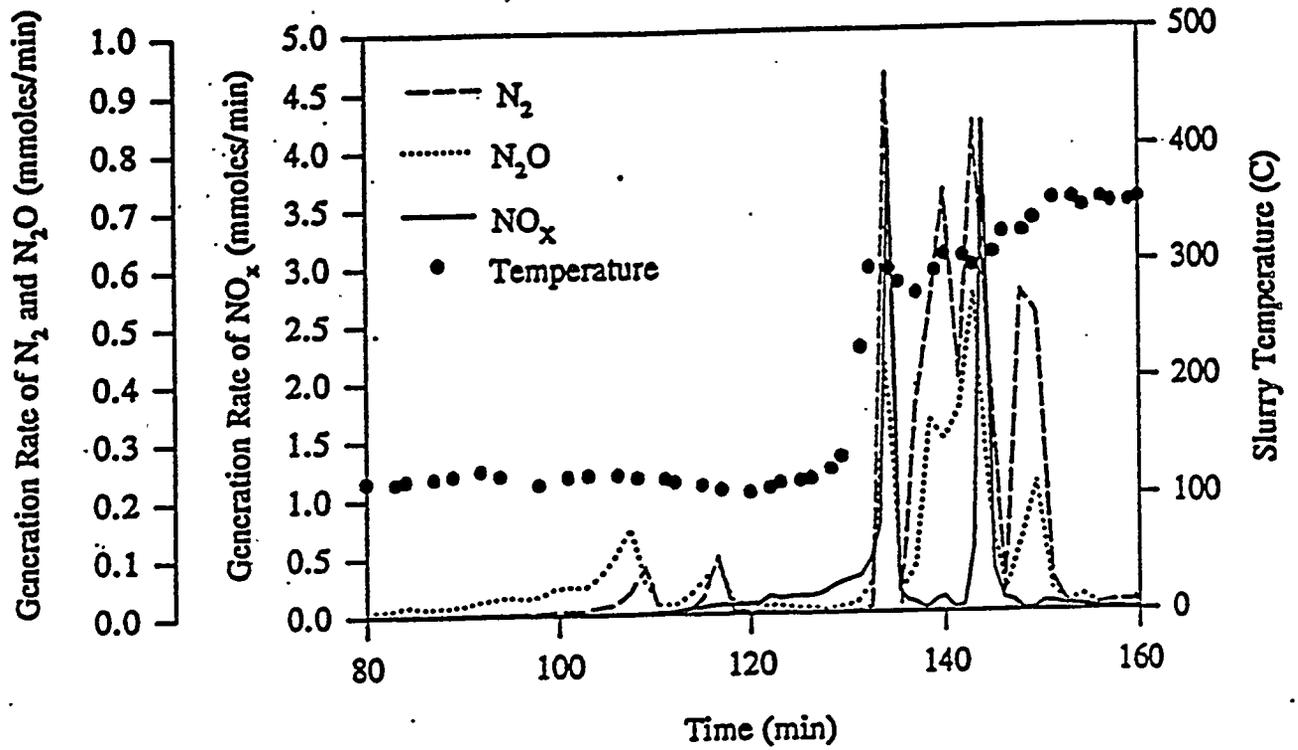


Figure 4.1.2.5 Offgas Profiles as a Function of Time and Temperature for Test T95-HTM-DR-C-5

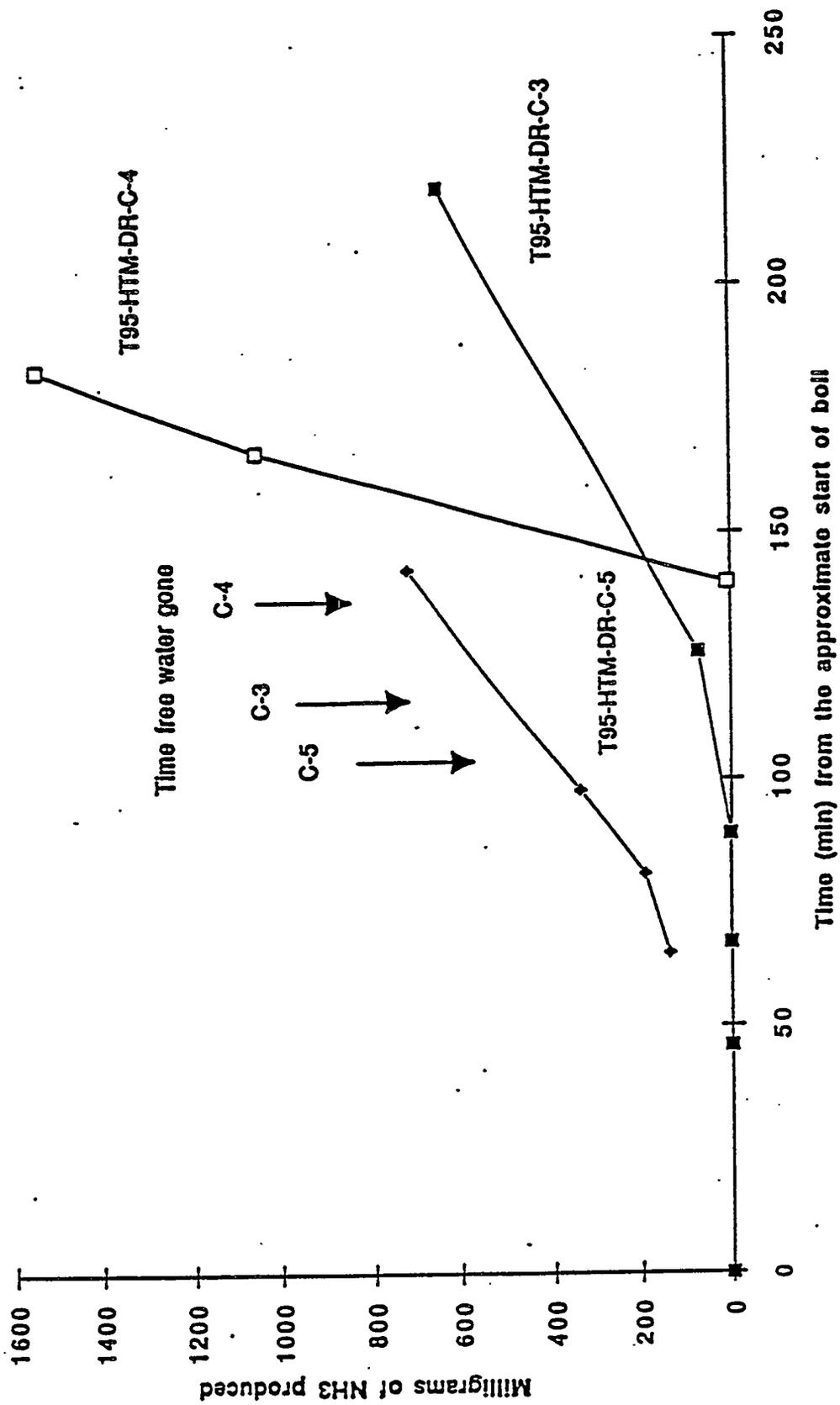
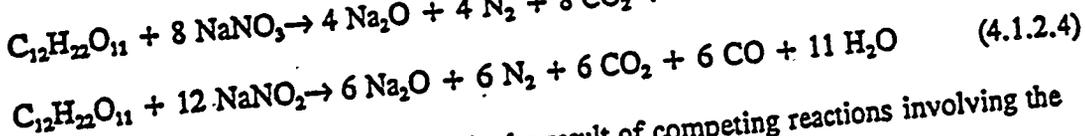
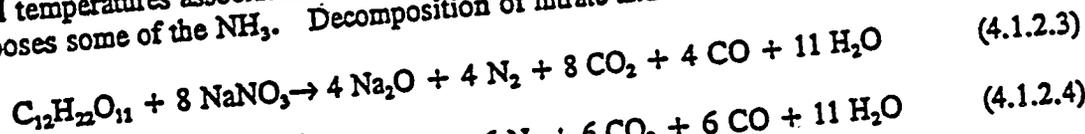


Figure 4.1.2.6

Ammonia Production During the Dry-Out and Low-Temperature Calcine Tests as a Function of Time from the Start of Slurry Feed Simulant Boiling

When sugar is added, the amount of NH_3 appears to be reduced. Possibly, the more elevated temperatures associated with the exotherm resulting from the sugar-nitrate-nitrite reaction also decomposes some of the NH_3 . Decomposition of nitrate and nitrite by sugar is as follows:

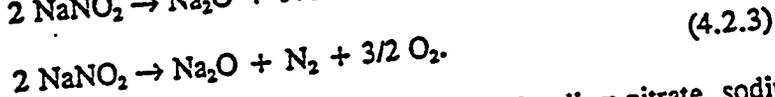
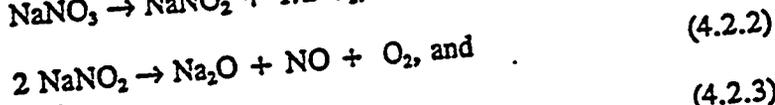
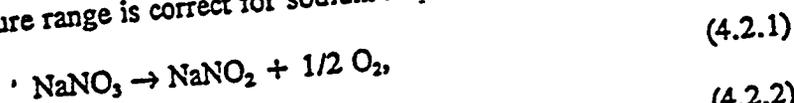


Another possibility is that the reduced NH_3 is the result of competing reactions involving the ferrocyanide complex.

4.2 High-Temperature Calcination

The off-gases produced from the high-temperature calcination of the DST/SST waste blend simulant with sodium nickel ferrocyanide (Figure 4.2) were CO_2 , H_2 , N_2 , NO , and O_2 . N_2 , O_2 , and NO generation started at 600°C and peaked at 900°C . The CO_2 offgased earlier, starting at 300°C and peaking at 650°C . No CH_4 or CO were observed.

The temperature range is correct for sodium nitrate and sodium nitrite reduction by:



A mole balance was performed assuming complete destruction of sodium nitrate, sodium nitrite, sodium carbonate, sodium ferrocyanide, and sodium oxalate.

Table 4.2. Elemental Balance

Element	Start (mmoles/g dried feed)	Off-Gas (mmoles/g dried feed)
N	2.27	1.39
C	0.36	0.98
O	6.78	6.00

Less N and O was measured than what was in the starting materials and more carbon was off-gased. Since NH_3 was not measured and ferrocyanide decomposes to NH_3 plus other species, the nitrogen deficit may be due to ammonia generation. The excess CO_2 may represent take up of CO_2 from the atmosphere which would be expected for a very basic slurry such as the blend.

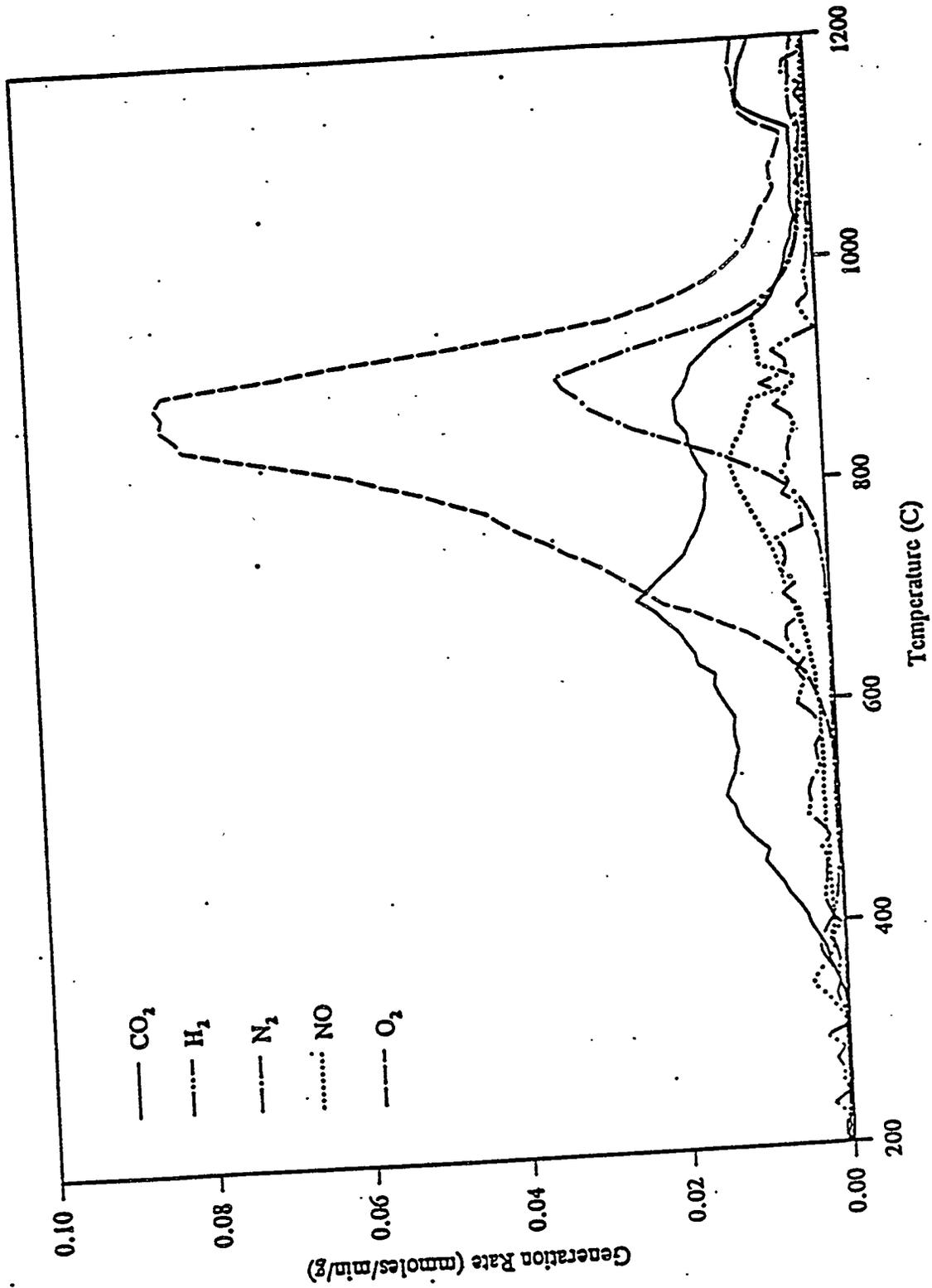


Figure 4.2. Offgas Profiles for a Blend Specimen Equivalent to T95-HTM-DR-C-3 Melted in the Quartz Crucible System. The specimen was heated to 1300°C, heating at 10°C per minute

A black glass (brown through a thin layer) was produced by the heat treatment. A thin salt deposit was present on the surface of the glass pool. The salt had a yellow color and appeared to be the same kind of a salt deposit observed on high temperature melts made using an NCAW type simulant. In the case of the NCAW type melts, the separated salt was shown to be predominantly sodium sulfate with a trace of potassium chromate, which would account for the yellow color. Since the "blend" and the NCAW based waste have similar sulfate contents (0.36 wt% vs 0.67 wt%), it is believed that this is the same kind of separated salt deposit.

4.3 Physical Properties, Transport Properties, and Thermal Analysis

4.3.1 Transport and Physical Properties

Density, yield stress, and plastic viscosity increase with increasing weight percents solids as shown in Figure 4.3.1. At the lowest weight percent solids, the viscosity is 10.0 cp and the yield stress is 2.6 Pa. These values increase exponentially to a viscosity of 107 cp and a yield stress of 66.5 Pa at a weight percent solids of 44.

4.3.2 Thermal Analysis

The TGA-DTA results for both the DST/SST waste blend simulant with and without sodium nickel ferrocyanide showed two regions of weight loss associated with two endotherms. These samples had been dried at 105°C for 24 hours prior to this testing. The two endotherms are indicated by the drops in the temperature difference between the sample and the blank. For both simulants, the weight loss was 40%. The first endotherm occurs at 150°C and the second occurs at 750°C. These are shown in Figure 4.3.2.

The first large endotherm of the TGA/DTA analysis was not associated with any offgases. The second endotherm occurred at approximately the same temperature as the off-gas peak of O₂, N₂, and NO.

4.3.3 Shrinkage, Adherence, Material Strength

Table 4.3.3.1 summarizes the development of features during the dry out and calcining process as a function of percent of water loss. The comments indicate that the slurry goes through a process of thickening, congealing, and shrinkage with accompanying cracking during the final stages of drying. In this table, the total oxides per liter were calculated from the starting values and the measured water loss. This is known to be an approximation but gives a good indication of slurry concentration at the various stages of dry out.

These results compare consistently with the rheology data (Section 4.3.1). The rheology parameters, viscosity and shear strength, are both observed to be strongly increasing at 45 wt% solids (i.e., the weight of material remaining after drying the slurry at 105°C for 24 hours). This is equivalent to about 450 TO/L (weight oxides is equivalent to about 70 wt% of the solids content). In this range of TO/L, the feed slurry is partially congealed and this is the approximate time that the temperature gradient begins to increase between the outside and the inside of the drying batch (see Figures 4.1.1.1 to 4.1.1.5). This reflects the fact that heat was no longer circulating to the center via fluid flow but by conduction which requires the establishment of a temperature gradient. Hence, the

Table 4.3.3.1. Annotated Water Loss Log for Each Dry-Out and Low-Temperature Calcine Test

TPS-HTM-DR-C-1

442

Water Loss Log

Time period	amount(g)	Cum. Time	Wt % lost	Cumulative %	TOI _g	Comments
12:16-12:26	0.5	10	0.13	0.13	294.31	
10min	1.0	20	0.25	0.38	294.94	• slurry thickening at vessel edge
10min	2.2	30	0.53	0.93	296.33	• surface film tearing as a result of stirring action
10min	3.3	40	0.83	1.76	298.44	• slurry definitely appears thicker
10min	6.2	50	1.56	3.32	302.48	
10min	17.6	60	4.43	7.75	314.59	• slurry build up on stir rod
10min	24.6	70	6.19	13.94	333.23	
10min	19.4	80	4.88	18.82	349.56	
10min	25.0	90	6.29	25.11	373.13	• pudding like consistency of slurry
10min	20.1	100	5.06	30.17	394.52	
10min	24.0	110	6.04	36.21	423.50	
10min	29.0	120	7.30	43.51	464.76	
10min	27.2	130	6.84	50.35	511.49	• slurry under stirrer congealed
10min	30.9	140	7.78	58.13	577.46	• cracks appearing in congealed slurry
10min	27.9	150	7.02	65.15	653.57	• cracks continue to grow
10min	25.1	160	6.32	71.46	741.49	
10min	23.5	170	5.91	77.38	848.34	
10min	24.0	180	6.04	83.42	994.72	• cracks continue to grow
10min	17.1	190	4.30	87.72	1134.16	• solid material breaking off sides of vessel
10min	16.9	200	4.25	91.97	1316.56	• solidified material appears to be breaking up into small pieces
10min	13.4	210	3.88	95.85	1542.63	
10min	10.0	220	2.52	98.36	1736.21	
10min	5.4	230	1.36	99.72	1862.42	
14min	1.1	244	0.28	100.00	1890.41	
	397.4					
to 13:04	11.8					
76min	8.3					

TPS-HTM-DR-C-2

385.3

Water Loss Log

Time period	amount(g)	Cum. Time	Wt % lost	Cumulative %	TOI _g	Comments
11:35-11:45	2.1	10	0.63	0.63	262.82	
10min	6.0	20	1.80	2.43	267.28	
10min	10.2	30	3.06	5.49	275.20	
10min	23.9	40	7.18	12.67	295.75	
10min	21.0	50	8.41	21.07	324.09	• Slurry coating walls of vessel and building up on stirrer shaft
10min	31.4	60	9.43	30.50	363.13	
10min	37.5	70	11.26	41.76	424.13	
10min	34.0	80	10.21	51.97	500.34	
10min	36.2	90	10.87	62.83	618.70	• Congealed slurry around edge beginning to crack, bottoms congealing

Table 4.3.3.1. Annotated Water Loss Log for Each Dry-Out and Low-Temperature Calcine Test

Time	amount(g)	Cum. Time	Wt. % lost	Cumulative %	TO/Lk	Comments
10min	38.9	100	11.68	74.51	829.60	
10min	25.9	110	7.78	82.29	1073.15	• Congealed slurry cracking throughout
10min	19.3	120	5.79	88.08	1373.67	• Dried slurry spalling off stir bar
10min	17.5	130	5.25	93.34	1841.17	• Dried slurry has flakey appearance, some disturbed by stir bar
10min	10.9	140	3.27	96.61	2336.44	• No further change observed
10min	6.6	150	1.98	98.59	2791.04	
10min	3.0	160	0.90	99.49	3061.83	
10min	0.9	170	0.27	99.76	3153.63	
10min	0.7	180	0.21	99.97	3228.92	
10min	0.1	190	0.03	100.00	3239.97	
	333.1					
all	14.2					

T95-HTM-DR-C-3

Water Loss Log time period	amount(g)	Cum. Time	Wt. % lost	Cumulative %	TO/Lk	Comments
10:25-10:35	2.0	10	0.66	0.66	263.42	• slurry appears to have thickened some - temperature affect?
10min	4.4	20	1.45	2.11	266.38	• slurry at edge congealing - some breaking off and mixing back in
10min	17.7	30	5.85	7.96	278.99	
10min	16.4	40	5.42	13.38	291.79	
10min	26.6	50	8.78	22.16	315.24	• Obvious thickening, build up around edges increasing
10min	40.9	60	13.51	35.67	359.69	• stirrer blades showing, slurry between edge and stirring blade appears dry
10min	39.8	70	13.14	48.81	416.90	• remaining fluid slurry piling up around stirring shaft-dilutant?
10min	37.6	80	12.42	61.23	490.62	• cracking of congealed slurry,
10min	30.4	90	10.04	71.27	572.45	
10min	30.9	100	10.20	81.47	689.33	
10min	19.8	110	6.54	88.01	793.08	• cracking and shrinkage have broken up the congealed slurry
10min	10.2	120	3.37	91.38	859.75	
10min	9.1	130	3.01	94.39	929.45	
10min	11.4	140	3.76	98.15	1034.51	• congealed slurry breaking off stirring blades
85min	5.6	225	1.85	100.00	1095.34	
	302.8					
to 12:29	9.7					
101min	3.5					

T95-HTM-DR-C-4

Water Loss Log time period	amount(g)	Cum. Time	Wt. % lost	Cumulative %	TO/Lk	Comments
9:56-10:06	2.7	10	0.70	0.70	223.67	
10min	4.5	20	1.17	1.86	226.00	
10min	10.1	30	2.62	4.48	231.41	
10min	39.8	40	10.31	14.79	255.51	
		453.1				

Table 4.3.3.1. Annotated Water Loss Log for Each Dry-Out and Low-Temperature Calcine Test

Time	Amount (g)	Cum. Time	Wt. % lost	Cumulative %	TO/L	Comments
10min	49.0	50	12.69	27.47	293.09	
10min	33.4	60	9.17	36.64	327.93	• layer of congealed slurry on vessel wall
10min	35.9	70	9.30	45.93	372.88	• slurry congealed to edge of stir blade sweep
10min	35.9	80	9.30	55.23	432.11	• slurry piling up in front of stir blade, congealed slurry beginning to crack
10min	32.6	90	8.44	63.67	504.94	
10min	16.2	100	4.19	67.87	551.11	
10min	43.0	110	11.13	79.00	727.69	• slurry is all cracked up
10min	23.0	120	5.96	84.96	878.20	
10min	19.0	130	4.92	89.88	1039.17	
10min	13.9	140	3.60	93.47	1247.19	
10min	12.3	150	3.18	96.66	1479.61	
10min	10.1	160	2.62	99.27	1746.94	
10min	2.3	170	0.60	99.87	1821.90	
10min	0.5	180	0.13	100.00	1839.06	
	386.2					
	12.7					

to 12:38:00

TPJ-ITM-DR-C-3

Water Loss Log time expired to 9:40	Amount (g)	Cum. Time	Wt. % lost	Cumulative %	TO/L	Comments
10 min	4.8	10	1.24	1.24	150.81	
10 min	24.0	20	6.18	7.42	160.35	• slurry appears to be thickening
10 min	38.9	30	10.02	17.44	179.31	
10 min	39.0	40	10.05	27.49	203.12	• slurry is caking on stir shaft, thick judging by the boiling action
10 min	38.9	50	10.02	37.51	234.12	
10 min	39.0	60	10.05	47.55	276.43	
10 min	39.1	70	10.02	57.57	337.19	• slurry congealing on sides of vessel, appears very thick
10 min	39.8	80	10.07	67.65	432.83	
10 min	26.8	90	10.25	77.90	608.52	• light and smoke observed when congealed slurry contacts vessel wall
10 min	13.3	100	6.90	84.80	837.39	• stirring interrupted, then decided to continue
10 min	33.8	110	3.43	88.23	1029.57	• slurry appears congealed, cracking
14 min	11.6	120	8.71	96.93	2470.31	• exothermic activity, dried slurry appears to expand
27 min	0.3	134	2.99	99.92	4732.92	• stirrer grids up some slurry, entanglement with a TC stopped rotation
	388.2	161	0.08	100.00	4869.28	• slurry looks like gray black ash
	17.7					

to 12:01

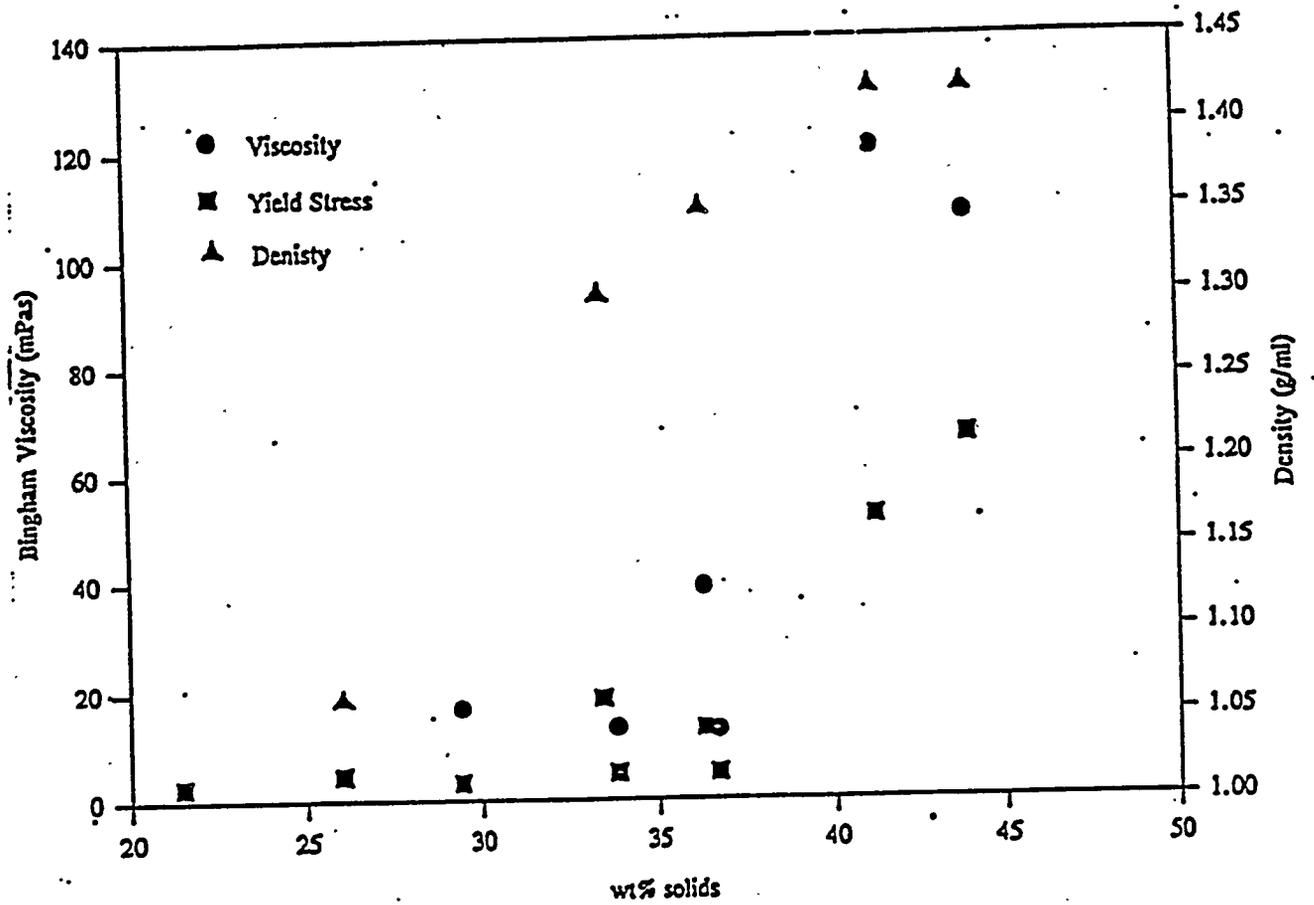


Figure 4.3.1. Viscosity, Yield Stress, and Density of the Blend Feed Equivalent to T95-HTM-DR-C-2 as a Function of Wt% Solids

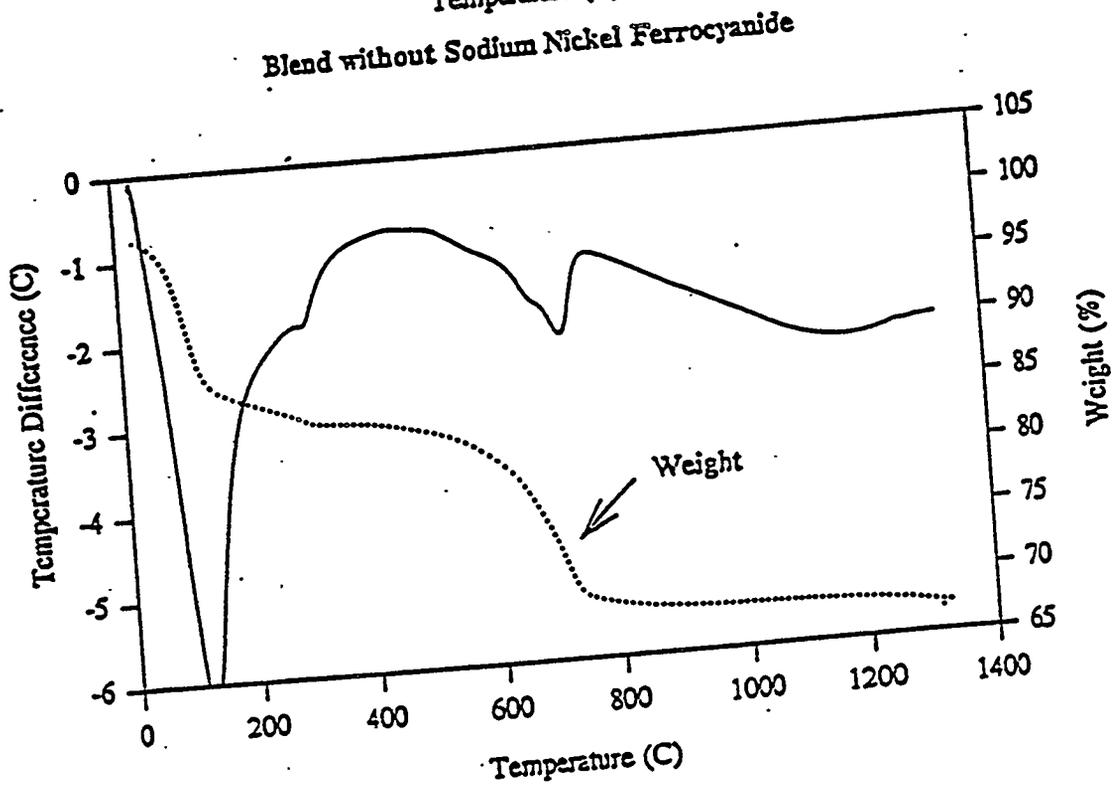
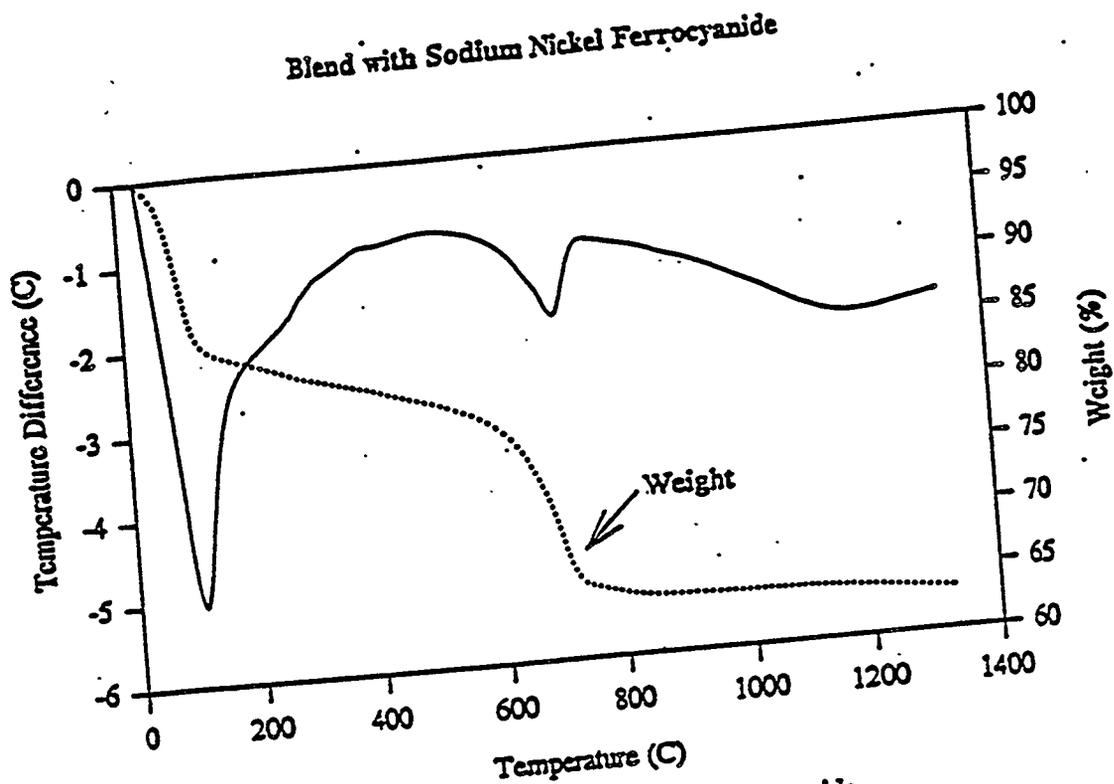


Figure 4.3.2. DTA of Blend Feed Simulant with and without Ferrocyanide (Equivalent to T95-HTM-DR-C-2 and 3)

visual observations presented in Table 4.3.3.1 are consistent with property measurements and temperature profiles. The slurry feed appears to congeal at boiling temperature with about 45 % water loss.

Pieces of dried and low temperature calcined feeds were selected for their regular geometry, carefully measured, and weighed. From their measured volume and weight, a density was calculated. These values ranged from a low of about 0.54 g per cc to about 3.07 g per cc. From visual observations of the calcined material, the range of density values was not surprising. Some pieces from surface areas appear quite dense while interior pieces contain a large number of voids. Table 4.3.3.2 and Figure 4.3.3. show the hygroscopic nature of the calcined feeds. For samples from Tests 1 and 2, the percent weight gain increased to about 5% within a few days and then seemed to level out. When all of the samples were reweighed again after another 130 days, the weight gains had increased to 7-9% over the initial weights. Since the initial series of weighings were made in April and the last set of weighings were made in August the increase of from 5% to 7-9% may be the result of increased humidity in the laboratory as well as the extended time. Note that observed relative humidity values for the building where these samples were housed typically runs between 30% and 60% with an average of about 50%. After the above weight gains the calcined feed slurry still appeared and handled as a dry material.

Table 4.3.3.3. Hygroscopic Weight Gain of Dried and Calcined Blend Feed Samples

TEST	TARE	SAMPLE "A"	NET	% wt gain	days	TARE	SAMPLE "B"	NET	% wt gain	days	DATE
T93-HTM-DR-C-1	1.6g	4.0333	2.4333	0.00	0	1.5g	3.0345	1.5345	0.00	0	3/15/95
		4.169	2.569	4.72	20		3.0926	1.5926	3.79	20	4/4/95
		4.1765	2.5765	5.02	27		3.0967	1.5967	4.05	27	4/11/95
		4.1766	2.5766	5.03	35		3.0968	1.5968	4.06	35	4/19/95
		4.2747	2.6747	9.02	145		3.1454	1.6454	7.23	145	8/7/95
T93-HTM-DR-C-2	1.5742g	2.2796	0.7054	0.00	0	1.460g	2.107	0.647	0.00	0	3/29/95
		2.2969	0.7227	2.45	2		2.1296	0.6696	3.49	2	3/31/95
		2.2986	0.7244	2.69	6		2.1309	0.6709	3.69	6	4/4/95
		2.2991	0.7249	2.76	13		2.1346	0.6746	4.27	13	4/11/95
		2.2986	0.7244	2.69	21		2.1344	0.6744	4.23	21	4/19/95
		2.315	0.7408	5.02	131		2.153	0.693	7.11	131	8/7/95
T93-HTM-DR-C-3	1.6g	4.6934	3.0954	0.00	0	1.4944g	3.3532	1.8588	0.00	0	4/19/95
		4.892	3.292	6.35	110		3.4825	1.9881	6.96	110	8/7/95

Blend Calcine - Weight Gain in Air

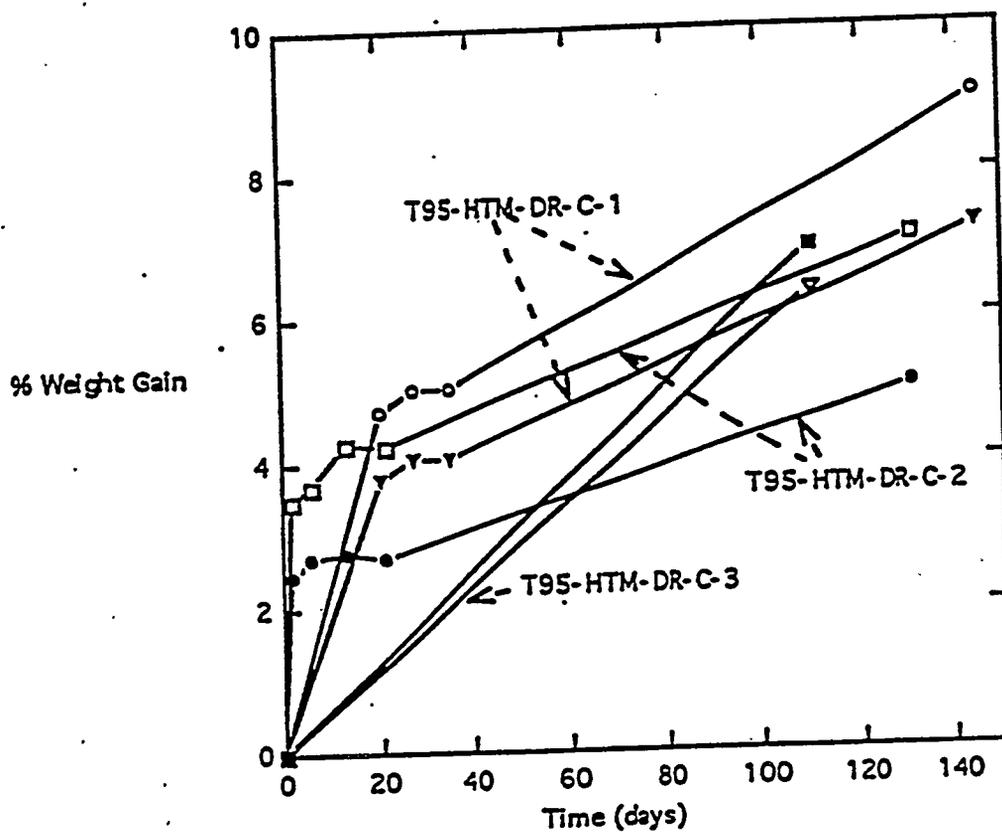


Figure 4.3.3. Observed Weight Gain of Dried and Calcined Blend Feed Samples Exposed to Laboratory Air under Ambient Conditions

5.0 Conclusions

1. Gas composition and generation rate (including water loss) -

A) Water is always the major component removed during drying with most of the water lost by the time the slurry temperature has reached 120°C.

B) Ferrocyanide breaks down to NH_3 plus formate during the calcining phase of the tests. Ammonia was observed in quantities proportional to the amount of ferrocyanide present in the feed slurry. Ferrocyanide displayed no redox reactivity with the nitrates and nitrites contained in the slurry.

C) Sugar displayed a similar redox reaction with the nitrates and nitrites in the blend as it did in the LLW feed simulant.

D) Other offgases such as NO and CO_2 come off at higher temperatures starting generally at 350°C to 400°C and, based on quartz crucible results, continue to 1300°C with a major O_2 peak around 800°C.

2. Water Loss Characteristics -

Boiling of a free flowing slurry occurs at temperatures below about 120°C. When about 45% of the free water has been lost, the feed slurry congeals and continues to lose water, shrinking and developing shrinkage cracks. Essentially water stops coming off between 350°C and 400°C.

3. Transport/rheology properties -

Slurry shear strength and viscosity strongly increase as the weight percent solids increases from 20 wt% to 45 wt%. This corresponds to an approximately 40 % water loss.

4. Bulk Properties -

As the percent solids increases from 20 to 45 wt%, the slurry density increases from 1.07 g/cc to 1.43 g/cc. The dried and low temperature calcined material has a large variation in porosity which resulted in a large range of values for the bulk density for this material ranging from about 0.5 g/cc to about 3.0 g/cc.

5. Heat sensitivity -

The principle heat sensitivity for this material is the exothermic reaction which is activated when the temperature exceeds about 250°C. The breakdown of ferrocyanide to ammonia and formate under strongly basic conditions may begin at temperatures less than 100°C, but the rate increases strongly with increasing temperature and appeared to be completed in the time of our tests.

6. Enthalpy changes -

DTA results on feed slurry without and with ferrocyanide shows only endothermic behavior. This is consistent with the dry out and low temperature calcine studies which did not indicate any exothermic behavior for the feed slurry with and without ferrocyanide. Feed slurry with sugar added equal to the nitrate plus nitrite content (20% of the TO/L) displayed a distinctly exothermic activity with light and smoke production.

7. Stickiness -

The feed slurry coats both glass and stainless steel in the liquid state. The material spalls and falls off as it dries with thin more adherent film left behind.

8. Abrasiveness, hardness -

The abrasiveness of the feed slurry is a function of the silica sand content and sharpness.

9. Phase separation -

The only phase separation observed during these tests occurred as a result of the water condensate leaching of slurry boil spatter. Salt containing condensate re-evaporated as it ran down the side of the reaction vessel leaving a ring of separated white salts on the vessel wall just above the original slurry line. A yellow salt separated from the glass melt made during the quartz crucible test which looks like salts observed to separate from other HLW simulant melts (NCAW based) and identified as sodium sulfate with a small amount of potassium chromate.

10. General observations (color changes, caking, ...) -

One notable difference between feed slurry with sugar and the other slurry feeds was the effect of sugar. The sugar containing feed exhibited a volume expansion as a result of the exothermic reaction. The dried, reacted waste slurry broke up into a medium sized (< 1 cm) granular material.

6.0 References

Orem, RM. 1994. *Technology Development in Support of the TWRS Process Flowsheet, Revision 0*, WHC-SD-WM-DTP-033.

Tan, T. C. and W. C. Teo. 1987. *Destruction of Cyanides by Thermal Hydrolysis*, Plating and Surface Finishing, April, pp 70-73.

Robuck, Stephen J. and Richard G. Luthy. 1989. *Destruction of Iron-Complexed Cyanide by Alkaline Hydrolysis*, Water Science Technology, Vol. 21, Brighton, pp. 547-558.

Appendix A

Low-Temperature Calcine Test Data Summary

T95-HTM-DR-C-1		Olfas Analysis - All values in samples or samples per min.		Sample Data - Chemical Analysis		Ammonia Trap Samples		Water Loss Log	
Sample	Time Period	NOx	NO2	NO3	NO2	NO3	NO2	NO3	Time Period
Peak Rate	0.027	0.004	0.013	0.032	0	0.0016			
Total	0.96	0.005	0.059	4.94	0	0.006			
Simulian mass	649.2 g total feed mass								
Sample	Time period	amount	Sample Density	NO3	NO2	NH3			
Primary Condensate	all	see below	1	<0.003 mg/L	0.92 mg/L	1.9 mg/L			
Secondary Condensate	all		1	<0.007 mg/L	60 mg/L	53 mg/L			
Sample	Reaction of Argon Flow Rate		Ammonia Trap Volume	NH3					
Sample	Water Loss Log	amount (g)							
Primary Condensate	Time period	12:16-12:26	0.5	Start wt.	649.2				
Primary Condensate	10min	1		Final wt	207.2				
Primary Condensate	10min	2.2		Net wt change	442				
Primary Condensate	10min	3.3		wt Condensate	417.5				
Primary Condensate	10min	6.2		wt Offgas					
Primary Condensate	10min	17.6		wt Samples					
Primary Condensate	10min	24.6		difference	24.5				
Primary Condensate	10min	19.4							
Primary Condensate	10min	25							
Primary Condensate	10min	20.1							
Primary Condensate	10min	24							
Primary Condensate	10min	29							
Primary Condensate	10min	27.2							
Primary Condensate	10min	30.9							
Primary Condensate	10min	27.9							
Primary Condensate	10min	25.1							
Primary Condensate	10min	23.5							
Primary Condensate	10min	24							
Primary Condensate	10min	17.1							
Primary Condensate	10min	16.9							
Primary Condensate	10min	15.4							
Primary Condensate	10min	10							
Primary Condensate	10min	5.4							
Primary Condensate	14min	1.1							

