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K. D. Wiemers

March 1996

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

Pacific Northwest National Laboratory
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SUMMARY

The Hanford Waste Vitrification Plant (HWVP) is being designed for the Department of Energy to immobilize pretreated radioactive high-level waste (HLW) as glass for geological disposal. In the HWVP formic acid will be added to the pretreated HLW prior to vitrification. The formic acid is added to adjust the feed rheology and to provide a reductant which maintains the feed in the melter within an acceptable redox range. This study was conducted to evaluate the effect of nitrate and carbonate concentrations in the pretreated neutralized current acid waste (NCAW) feed on the amount of formic acid required to obtain an acceptable glass redox state in the melter. The glass redox state was measured by the Fe^{+2}/Fe^{+3} ratio in the vitrified product.

Thirteen runs were conducted, providing 19 data points. The physical properties and chemical composition of preformated and formated test simulants were characterized. The redox state of the vitrified product was evaluated as a function of formic acid addition for different combinations of nitrate and carbonate content in the feed. Data from this study and Farnsworth (1987) were compiled to evaluate the relationship between formic acid addition requirements, nitrate concentration, and glass redox adjustment. Results from this study suggest that the formic acid requirements are more accurately prescribed by the stoichiometry of redox reactions rather than neutralization reactions. The primary redox participants in this study were nitrate, ferric ion, and formic acid. An acceptable glass redox was observed when $HCOOH/NO_3 = 3$ and $Fe/NO_3 \leq 4$. In the presence of high iron ($Fe/NO_3 > 4$) the formic acid requirements for acceptable glass redox were less, $HCOOH/NO_3 = 1.5$ to 2.5. It is speculated that the variation in the formic acid requirements can be correlated to differences in the ratio of nitrate redox reaction products, NO, NO_2, N_2O and NH_3. Wiemers (1987) reported the presence of CO_2, NO_x, N_2O, and H_2 in offgas released during formating. Ammonia was qualitatively detected during the study reported herein. The relationship of other active redox species such as nitrite and organics to formic acid requirements for glass redox remains to be established.

The threshold requirement, $HCOOH/NO_3 = 3$, was independent of the simulant carbonate content. The carbonate content ranged from 6 to 39 g carbonate/g WO (8 to 54 g carbonate/L). Thus, formic acid adjustments for glass redox are not required. However, evaluation of limited mass balance data suggests that the step in which nitrate reduction occurs (formating or vitrification) may be dependent on the pH (i.e., carbonate content) of the feed. Lower nitrate consumption during formating was observed in high carbonate (more alkaline) simulants.

The physical properties of the feed were similar to those observed for PSCM-23 (Goles 1989). No apparent trends related to nitrate or carbonate concentration were observed for the physical properties measured during this study.

The control of glass redox behavior couples two chemical systems: 1) formating during which formic acid is added to the feed and 2) vitrification, the product from which the Fe^{+2}/Fe^{+3} ratio is measured. A preliminary mass balance flowsheet was derived which begins to tie together the chemistry of these two systems.

1.0 INTRODUCTION

The Hanford Waste Vitrification Plant (HWVP) is being designed for the Department of Energy to immobilize pretreated radioactive high-level waste (HLW) as glass for geological disposal. Formic acid will be added to the pretreated HLW in the HWVP prior to vitrification. The formic acid is added to adjust the feed rheology and to provide a reductant which maintains the glass redox state in the melter within an acceptable redox range. A sufficient quantity of reducing agent is needed to assure that the glass will not foam by reboil in the melting process, thereby decreasing process rates. Excess reducing agent will result in the reduction of metal oxides to their metallic state. The reduced metals can form a conductive sludge at the bottom of the ceramic melter; shorting the melter electrodes; leading to premature failure of the melter.

Experimental work was conducted to determine the relationship between the nitrate and carbonate concentration in a test simulant and the amount of formic acid necessary to provide an acceptable glass redox state. The glass redox state is measured by the Fe^{+2}/Fe^{+3} in the vitrified sample. A Fe^{+2}/Fe^{+3} range of 0.005 to 0.3 has been found to provide acceptable glass behavior for melter operation. The test simulant prepared in this study was based on a reference pretreated NCAW composition with the exception of not containing nitrite or organics. The adjustments in formic acid addition required for nitrite and organics remain to be defined.

This study addresses Technology Plan (Sexton 1988) issue 2.2.1 Redox Control and was originally authorized in the fiscal year (FY) 1989 Letter of Instruction to Pacific Northwest Laboratory (PNL) under WBS 1VJ0010300. Additional experimental work was performed per the FY 1990 Letter of Instruction under WBS 1.2.2.03.03. This report satisfies the requirements for deliverable 1.2.2.03.03A, "Issue report on glass redox behavior as a function of feed components."

This report describes the test approach, apparatus, and measurements; and discusses the results in terms of formating chemistry and plant application. Conclusions and recommendations are listed first.

2.0 CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are made from the results and analyses of this study.

- An acceptable glass redox was observed when HCOOH/NO3 = 3 and Fe/NO3 $\leq$4. In the presence of high iron (Fe/NO3 > 4) (Farnsworth 1987) the formic acid requirements for an acceptable glass redox were less, HCOOH/NO3 = 1.5 to 2.5.
- The presence of ammonia in formated simulant indicates a higher degree of nitrate reduction than previously reported in Wiemers 1987. Reduction of nitrate to ammonia would require more formic acid stoichiometrically, than reduction of nitrate to gaseous nitric oxides. The amount of NH_3 produced was not quantified in this study.
- The threshold requirement, HCOOH/NO3 = 3 was independent of the carbonate concentration. Thus, no formic acid adjustments for glass redox are required to accommodate the presence of carbonate in the range of 6 to 39 g carbonate/g WO (8 to 54 g carbonate/L).
- High levels of carbonate resulted in more alkaline endpoints for equivalent formic acid additions. The minimum pH in high carbonate samples was 5. At an equivalent formic acid addition to low carbonate slurries the minimum pH was 3. Based on limited mass balance data, the amount of nitrate reduction during the formating step increased with an increase in acidity (low carbonate simulants). However, as noted above, the threshold requirement for $HCOOH/NO_3$ was independent of carbonate loading.
- Evaluation of solubility behavior suggests that 25-50% of the chromium, manganese, and molybdenum are reduced during formating.
- The physical properties of the simulant were similar to those reported for PSCM-23 (Goles and Nakaoka 1989). No apparent trends related to nitrate or carbonate concentration were observed for the physical properties measured.

The following recommendations are made based on the results of this study:

- Hanford high-level wastes to be treated in the HWVP will contain nitrite and organics. The effects of these components on the current correlation for redox adjust chemical requirements needs to be investigated. Off gas analysis should be included in these studies.

- Current plans are to add a maximum of 30 ml 90 wt% formic acid; additional reductant would be supplied by sugar. These redox adjustment components were used successfully during PSCM-23 (Goles and Nakoaka, 1990) after lab-scale testing to establish requirements. Assessment of the supplemental reductant requirements should be firmly established now via lab-scale studies to minimize lag time during actual processing.

- Glass redox in the melter is significantly affected by the melter environment, cold cap chemistry, and glass/cold cap dynamics. Correlation of glass redox models from laboratory studies with large scale feed processing and melter operation is required to ensure the validity of correlations for HWVP feed makeup.

- The amount of ammonia released during formating should be quantified. The impact of ammonia release during formating on the off gas ventilation system needs to be considered. The potential for formation of ammonia nitrate on filters may propose some safety concerns. The dissolution of ammonia in the scrubber may alter the scrubbers trapping efficiency.

- The generation rate of H_2 and any organics needs to be further defined in order to assess if the explosion limit can be approached during formating. The release of H_2 during formating has been discussed. CO was not detected above 0.1 mole% (detection limit for mass spectroscopy analysis) in the off gas collected during formating (Wiemers 1987).

- Nitrate reduction may occur in the SRAT and/or in the melter. The dependence of melter throughput on where the nitrate reduction occurs requires evaluation.

- The potential for magnetic particles to impact subsequent process steps should be considered.

3.0 OBJECTIVE

The objective of this study was to provide a predictive model by which the amount of formic acid required to obtain an acceptable glass redox state may be determined based on the nitrate and carbonate composition of the feed. The redox state of the vitrified product was evaluated as a function of three key variables: concentrations of carbonate and nitrate in the feed and the amount of formic acid added.

4.0 TEST APPROACH

Ten runs were conducted to complete a parametric test in which the Fe^{+2}/Fe^{+3} of vitrified samples was measured for various combinations of nitrate and carbonate simulant content and amounts of formic acid added. Results from this initial test indicated that redox reactions rather than neutralization reactions should provide the primary basis for specifying formic acid requirements for glass redox adjustments. Subsequently, three additional runs were completed in which the amount of formic acid added was based on the initial nitrate concentration. Nitrate was the major oxidant in the test simulants.

This section describes the selection criteria for the test parameters; the test matrix; the feed preparation and formating procedures; and the analyses.

4.1 BASIS FOR TEST PARAMETERS

Sources of nitrate and carbonate in the actual waste and bounding case concentration levels as estimated by Westinghouse Hanford Company (WHC) are based upon core sample analyses and flowsheet evaluation. These data are reported in the Hanford Waste Vitrification Plant Technical Data Package (Wright 1988). A summary of the selection criteria is given for the bounding cases used in this study.

Nitrate - The primary source of nitrate in the NCAW is the nitric acid used in the PUREX Plant during the dissolution and processing of the fuel. In the B-Plant the waste will be washed to remove nitrate to meet HWVP acceptance criteria. Target bounding case concentration levels estimated by WHC and used in this study were 3 to 36 g·NO_3/100·g waste oxides. The nominal concentration of nitrate was 9 g NO_3/100 g waste oxides. The high and nominal concentrations were obtained from the Technical Data Package (Wright 1988). The target minimum nitrate concentration is based on the nitrate remaining after washing of the precipitated hydroxides during simulant preparation (Wiemers 1987).

Carbonate - NCAW is currently stored in double shell tanks (DST). After pretreatment in B-Plant, the waste will be stored in DST prior to routing to the HWVP. During storage in the double shell tanks, air lift circulators are used to prevent the accumulation of excessive heat from radiolytic decay by suspending solids and removing heat by forced convection. Equilibration of the HWVP feed with carbon dioxide from the air is the primary source of carbonate in the feed. The target range used in this study was 3 to 30 g/100 g waste oxides. The low end of this range represents dissolved CO_2 from the surrounding laboratory air. The target nominal CO_3 concentration level was 17 g/100 g oxides. The nominal and maximum levels of CO_3 were obtained from a memo to O. L. Kruger from R. A. Watrous dated March 1, 1989 concerning Engineering Change Notices 400073 and 400074.

Formic Acid - For the parametric test minimum (first 10 runs) selection of the formic acid addition, 16 ml 90 wt% formic acid/L feed, assumed a Fe^{2+}/Fe^{3+} ratio of 0.10 would be achieved (see Figure 7, Farnsworth 1987). The nominal level was 22 ml 90 wt% formic acid/L as used for the similar simulant feed composition during PSCM-23 (Goles and Nakaoka 1989).(a) The maximum level of formic acid addition was defined as the amount of formic acid required to reach a pH of 7 (essentially neutralize the added bicarbonate) with a high carbonate, low nitrate feed. This amount was 31 ml 90 wt% formic acid/L.

For the 3 runs which followed the parametric test, the amount of formic acid added was based on the initial nitrate concentration. The ratio, $HCOOH/NO_3$, ranged from 1.5 to 10 to bound the initial predicted threshold, $HCOOH/NO_3 = 3$, for obtaining an acceptable glass redox state.

4.2 TEST MATRICES

This study consisted of thirteen runs. The first ten runs were defined by a parametric design. Based on results from the parametric test and

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(a) Differences in simulant composition are: ~2X more La in PSCM-23; Nd in PSCM-23 = ~3/4 of current study; Zn included in PSCM-23 not in current study; noble metals included in current study not in PSCM-23 (refer to Table 4.1 (Goles and Nakaoka 1989) with Table 4.2 of this report).

analyses of Farnsworth 1987 data, three additional runs were performed to provide supplemental data. A summary of parameters used in each of the runs is given in Table 4.1.

The experimental matrix for the parametric test as described in Test Plan HWVP-89-IVJ00100300A was revised as $NaNO_3$ and $NaHCO_3$ levels specified by the design would have resulted in sodium concentrations above the range of the reference sodium composition. Per the Test Plan the maximum amount of formic acid added during the parametric test was defined as that required to neutralize the high level carbonate/low level nitrate simulant (Test 6). Neutralization was defined as the point at which the slurry pH became <7.

TABLE 4.1. Range for Test Parameters

	Slurry Composition							
	Nitrate[a]			Carbonate[b]			Formic Acid Added	
Run No.	g/L	moles/L	g/100g WO[c]	g/L	moles/L	g/100g WO	ml/L	moles/L
1	28	0.45	20	21	0.35	15	22	0.47
2	40	0.72	32	21	0.35	15	31	0.67
3	8	0.13	6	3	0.05	2	16	0.34
4	43	0.67	31	21	0.35	15	16	0.35
5	8	0.13	6	38	0.63	27	15	0.32
6	8	0.13	6	38	0.63	27	32	0.69
7	54	0.87	39	3	0.05	2	31	0.67
8	8	0.13	6	3	0.05	2	31	0.66
9	53	0.85	38	3	0.05	2	16	0.35
10	20	0.33	14	21	0.35	15	22	0.48
11	22	0.35	18	38	0.63	27	23	0.50
							32	0.34
							53	1.15
12	26	0.42	21	3	0.05	2	54	1.17
							90	1.95
							151	3.27
13	8	0.13	6	38	0.63	27	24	0.53
							38	0.82
							55	1.19

(a) Nitrate values reported from analytical data.
(b) High and nominal carbonate values are based on target composition. Low carbonate value based on analytical data may be in error by 50%.
(c) Runs 1-10 simulants were 140 g waste oxide (WO)/L prior to formatting. Runs 11-13 simulants were adjusted to 125 gWO/L prior to formatting.

However, the application of this formic acid loading, 31 to 32 ml 90 wt% HCOOH/L feed, resulted in only two of the ten runs (Run 6 and Run 8) with ferrous ion above the detection level (ferrous/ferric ≥ 0.005). Insufficient data were available for statistical analysis.

Subsequently, three follow-up experiments were completed (Runs 11-13). These runs differed from the previous parametric study in two ways:

1. The formating procedure and apparatus were modified to accommodate removal of simulant during the addition of formic acid. Three formated samples for each tests were obtained. This provided a continuum (as defined by three points) for the glass redox values as a function of formic acid addition amount at a given initial carbonate and nitrate feed concentration.
2. The amount of formic added was based on the initial target nitrate molarity rather than the neutralization reactions.

4.3 TEST SIMULANT PREPARATION

A 20 L batch of test simulant was prepared via precipitation of hydroxide salts from dissolved nitrate salts. Four major constituents (Ni, Fe, Al, and Zr) were precipitated separately. The remaining minor constituents were co-precipitated or added as insoluble salts. The precipitated hydroxide salts were washed and filtered to remove excess sodium and nitrate. The sodium and nitrate concentration prior to adjustment was 5 and 8 g/L, respectively. The precipitated hydroxide salts were blended and aged for a minimum of 2 weeks prior to commencement of testing.

Individual 1.5 L aliquots were removed from the stock batch and spiked with sodium bicarbonate and/or sodium nitrate as prescribed by the test matrix. When required, additional sodium was added as sodium hydroxide to satisfy sodium target values. The simulant target composition is shown in Table 4.2.

4.4 FORMATING AND VITRIFICATION PROCEDURE

After adjustment of the carbonate and nitrate concentrations, the simulant was heated to 95 ± 3°C and maintained at this temperature for 10 minutes. Formic acid (90 wt%) was added to the simulant at a rate of

TABLE 4.2. Simulant Target Composition(a)

Basic Oxide	Target Wt%	g WO/L(b)	Element	Target g Element/L(c)	Simulant g Element/L(d)
Al_2O_3	9.35	11.69	Al	7.42	7.43
BaO	0.42	0.52	Ba	0.56	0.52
B_2O_3	0.10	0.12	B	0.05	0.05
CaO	0.31	0.39	Ca	0.33	0.52
CdO	3.12	3.90	Cd	3.64	2.98
CeO_2	0.62	0.78	Ce	0.76	0.56
Cr_2O_3	0.52	0.65	Cr	0.53	0.56
Cs_2O	0.62	0.78	Cs	0.88	(e)
CuO	0.62	0.78	Cu	0.74	0.48
F	1.25	1.56	F	1.88	(e)
Fe_2O_3	29.09	36.36	Fe	30.52	28.92
La_2O_3	3.01	3.76	La	3.85	1.60
MgO	0.38	0.48	Mg	0.34	0.42
MnO_2	0.62	0.78	Mn	0.59	0.92
MoO_3	1.25	1.56	Mo	1.25	1.20
Na_2O	18.70	23.38	Na	20.81	5.37
Nd_2O_3	3.74	4.68	Nd	4.81	3.75
NiO	2.39	2.99	Ni	2.82	2.69
P_2O_5	0.91	1.14	P	0.30	0.29
Pr_6O_{11}	0.43	0.54	Pr	0.53	0.31
SO_3	0.68	0.85	SO_3	1.02	0.98
SiO_2	4.16	5.20	Si	2.92	2.52
Sm_2O_3	0.21	0.26	Sm	0.27	(e)
SrO	0.42	0.52	Sr	0.53	0.34
Y_2O_3	0.21	0.26	Y	0.25	0.27
ZrO_2	15.59	19.49	Zr	17.31	17.15
RuO_2	0.66	0.82	Ru	0.75	0.78
PdO	0.21	0.26	Pd	0.27	0.39
Rb_2O	0.21	0.26	Rb	0.29	(e)
Rh_2O_3	0.21	0.26	Rh	0.26	0.26
Total	100.01	125.02	Total	106.48	

(a) The wt% values vary slightly from values given in Wright (1988) due to substitution/deletion of selected oxides and renormalization of composition.

(b) Per Test Plan HWVP-89-1VJ0010300A, based on 125 gWO/L.

(c) Per Test Plan HNVP-89-1VJ0010300A, based on 150 gWO/L.

(d) Sodium level adjusted by addition of $NaNO_3$, $NaHCO_3$, and/or NaOH.

(e) Fluoride data was not reproducible. P, Pr, Pd, and Rh measurements were not analyzed by approved impact level II procedures, and are listed for information only. Cs and Rb not measured.

1 ml/min. At the completion of formic acid addition, the formated simulant was refluxed at 95 ± 3°C for 2 hrs. The reflux period was provided to allow for completion of reactions with formic acid. The simulant was continuously agitated with a propeller type blade. The feed pH and temperature were monitored throughout the heating, formating, and reflux steps. These steps simulated those currently planned for HWVP operation.

Runs 11-13 simulant samples were collected during formic acid addition by removing the pH electrode and siphoning the simulant into a tared vessel. The receiving vessel was weighed, the sample volume marked, and the vessel placed into a heating mantle to reflux the sample for two hours at 95 ± 3°C.

A 500 ± 50 g total oxide (TO)/L simulant was prepared by the addition of frit (weight ratio of waste oxide to frit oxide being 125/375). An aliquot of the formated simulant + frit was vitrified by stepwise additions of an aliquot of the mixture to a crucible. The crucible and its contents were heated to 1000°C in a muffle furnace between additions. The Fe^{+2}/Fe^{+3} ratio was determined spectrophotometrically.

4.5 ANALYTICAL TESTS

The test simulant composition was characterized using ion chromatography (IC) for sulfate and nitrate; specific ion electrode for fluoride ion; and inductively coupled plasma spectroscopy (ICP) for the metallic elements. The sludge and supernate fractions of the slurry were analyzed independently to determine the total inorganic and organic carbon in Runs 1-10 and by ICP and IC for Runs 12 and 13.

The following physical and rheological properties of Runs 1-10 simulants were measured: yield stress, apparent viscosity as a function of shear rate, wt% total oxides, wt% total solids, gTO/L feed, pH, density, and settling rate.

Similar analyses were performed for Runs 11-13, with the exception that the rheological properties, settling rate, and carbon concentration were not determined.

5.0 EQUIPMENT DESCRIPTION

The formating apparatus consisted of a 2 L glass kettle placed in a temperature controlled heating mantle. The kettle lid was modified to accept a simulant thermocouple, formic acid addition tube, pH electrode and automatic temperature compensator, an agitator shaft, and condenser. The formic acid was introduced into the kettle below the simulant surface through a teflon tube using a peristaltic pump to control the addition rate. Both simulant temperature and pH were monitored during the process. A schematic of the simulant formating apparatus is shown in Figure 5.1.

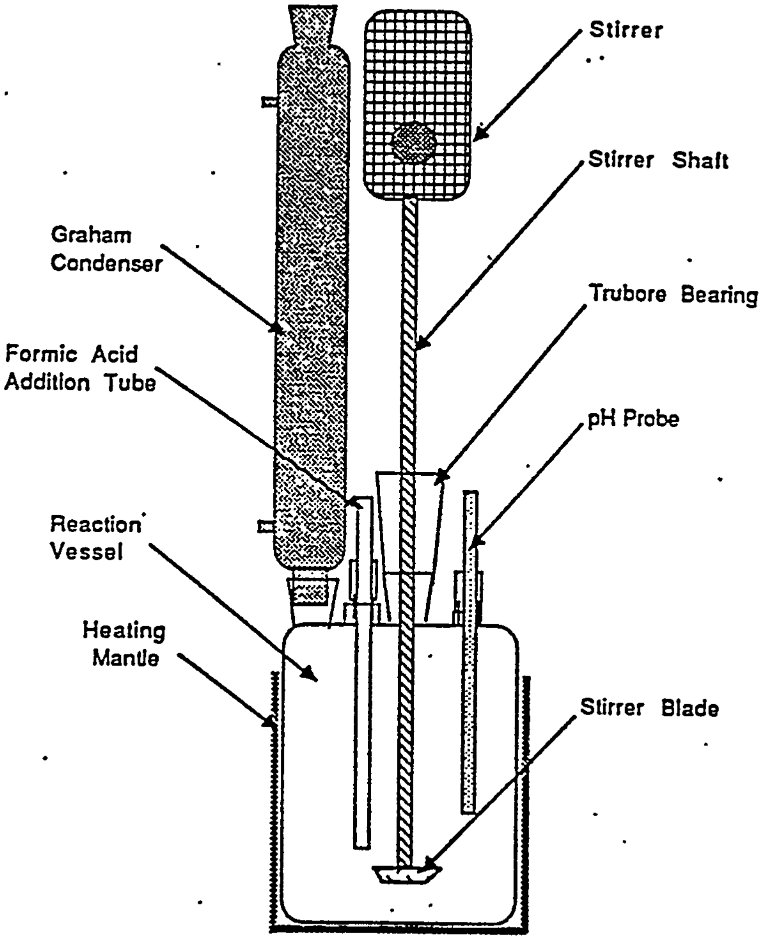

FIGURE 5.1. Schematic of the Formating Apparatus

6.0 HIGHLIGHTS

Observations recorded in addition to measurements specified in the Test Plan are discussed. These include the detection of ammonia and magnetic particles in the formated simulant and the apparent dilatant behavior of a melter feed simulant.

The presence of ammonia was qualitatively detected in Runs 1-11 and 13 formated simulant. All of these runs had an alkaline post reflux pH; the ammonia therefore being presence primarily as the easily detectable NH_3 species. Run 12, Sample 3 was the only sample with a post reflux pH < 7. If ammonia was present it would be as the ammonium ion, NH_4^+ ion, and not detected by odor. When base (NaOH) was added to make Run 12, sample 3 alkaline, NH_3 was detected also. This observation suggested an alternative route for the nitrate reduction step.

During Run 12, when the adjustment of low oxide content by evaporation in sample 2 was carried out by use of a heating plate and stir bar instead of in a furnace, magnetic particles in the formated feed were observed clinging to the stir bar. Magnetic particles were subsequently identified by use of a hand held magnet, in sample 1, and all vitrified samples. The feed (prior to formic acid addition) and Sample 3 (151 ml 90 wt% formic acid/L) did not contain a detectable amount of magnetic particles. The crystalline composition of the magnetic particles from the formated simulant (prior to vitrification) was determined by X-ray diffraction to be a combination of the following phases: $(NiFe)Fe_2O_4$, $NiFe_2O_4$, Fe_2O_3, $FeO(OH)$, and Fe_3O_4. The existence of these particles will require further consideration should the presence of a magnetic field be identified in subsequent process steps.

The maximum amount of formic acid added in this study was 151 ml 90 wt% formic acid/L. The rheological behavior of the melter feed prepared by the addition of frit to this formated sample was not quantified. However, the material appeared to be dilatant. The surface of the material was shiny and moist-like in a static condition. When stirred, the surface became dull, and the resistance to flow increased greatly. This behavior was not observed at a loading of 90 ml 90 wt% formic acid/L. Using the formic acid requirement criteria of $HCOOH/NO_3 = 3$, the maximum amount of formic acid required for maximum nitrate loadings would approach the formic acid loading in which the dilatant behavior was observed. The addition of sugar as a reductant to reduce the amount of formic acid required may resolve this potential problem. However, the rheology of the feed with formic acid and sugar should be measured.

7.0 RESULTS

The simulant composition and physical data are presented and compared with previous studies. Neutralization and redox chemistry are related to the observed solubility behavior and glass redox state. A preliminary mass balance for redox reactions which take place during formating and vitrification is described.

7.1 SIMULANT COMPOSITION

Table 7.1 lists the actual and target compositions of the simulants for Runs 1-10. The four major components on a weight percent basis, Fe, Na, Al, and Zr, are within 10% of the target concentrations. Deviations in minor constituent composition are similar to those reported for past simulants (Wiemers 1987). Differential losses may be due to the extraction of more soluble species during washing and nonrepresentative sampling of minor, insoluble salts such as lanthanum fluoride. The carbon analytical data was suspect due to contamination of the instrument detector. In runs where carbonate additions were made target compositional values were assumed for evaluation of tests results.

The compositions of the formated simulants for Runs 1-10 are listed in Table 7.2. Compositional data for Run 11 is listed in Table 7.3. As expected no significant differences in the individual component concentration exists between the initial simulant and formated simulant except for nitrate. The decrease in nitrate concentration with addition of formic acid can be explained by the reduction of the nitrate to gaseous products, NO_x, N_2O, and ammonia. SRL (Zamecnik) has reported a recycle of the nitrate in their pilot scale operations via the following disproportionation and decomposition reactions in the condenser:

$$NO + 1/2\ O_2 \rightarrow NO_2$$
$$2\ NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$
$$3\ HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O$$

TABLE 7.1. Composition of Simulant for Runs 1-10, g/L

Element[a]	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Runs 1-10 Average	Percent RSD	Target	Average Runs 1-10 Percent Deviation
Al	7.23	6.94	7.24	6.85	7.21	7.39	6.87	7.49	6.97	7.08	7.13	3.08	7.42	3.95
B	0.04	0.05	0.04	0.26	0.04	0.05	0.19	0.06	0.08	0.05	0.09	87.21	0.05	-73.81
Ba	0.51	0.49	0.49	0.48	0.50	0.51	0.49	0.52	0.50	0.50	0.50	2.17	0.56	11.19
Ca	0.53	0.50	0.50	0.54	0.54	0.55	0.51	0.58	0.55	0.54	0.53	4.80	0.33	-61.79
Cd	2.93	2.82	2.80	2.79	2.87	2.92	2.88	2.95	2.95	2.90	2.88	2.07	3.64	20.90
Ce	0.57	0.61	0.58	0.72	0.59	0.57	0.66	0.61	0.69	0.66	0.63	8.49	0.76	17.69
Cr	0.54	0.54	0.54	0.53	0.55	0.57	0.54	0.57	0.57	0.56	0.55	2.89	0.53	-4.12
Cu	0.47	0.43	0.44	0.42	0.46	0.46	0.43	0.48	0.44	0.43	0.45	4.77	0.74	39.73
Fe	27.74	28.17	27.07	27.50	27.44	27.92	27.96	28.39	28.78	28.63	27.96	1.94	30.52	8.39
La	1.10	1.43	1.06	1.27	1.30	1.28	1.65	1.43	1.67	1.51	1.37	15.10	3.85	64.41
Mg	0.42	0.39	0.38	0.39	0.41	0.41	0.40	0.43	0.40	0.39	0.40	3.60	0.34	-17.98
Mn	0.91	0.87	0.85	0.86	0.87	0.90	0.87	0.90	0.88	0.89	0.88	2.23	0.59	-49.07
Mo	1.19	1.19	1.16	1.14	1.15	1.20	1.20	1.23	1.23	1.14	1.18	2.98	1.25	5.25
Na	19.76	25.42	18.72	23.67	19.49	18.92	24.00	20.70	23.53	18.03	21.22	12.54	20.81	-1.99
Nd	3.64	3.74	3.54	3.64	3.63	3.60	3.75	3.78	3.80	3.81	3.69	2.54	4.81	23.22
Ni	2.62	2.59	2.71	2.52	2.52	2.59	3.21	2.69	2.57	2.60	2.66	7.64	2.82	5.58
Ru	0.76	0.71	0.71	0.66	0.62	0.69	0.79	0.68	0.80	0.77	0.72	8.28	0.75	4.15
SO_3	1.57	1.15	1.02	1.01	1.01	1.01	1.13	1.13	1.14	1.13	1.26	0.45	1.02	0.24
Si	2.48	2.74	2.48	2.61	2.37	2.59	2.49	2.70	2.51	2.52	2.55	4.33	2.92	12.64
Sr	0.34	0.32	0.33	0.32	0.33	0.34	0.32	0.34	0.33	0.32	0.33	2.36	0.53	37.73
Y	0.27	0.23	0.25	0.23	0.26	0.26	0.24	0.26	0.24	0.24	0.25	4.69	0.25	0.80
Zr	17.41	16.03	15.79	15.89	16.91	16.89	16.30	17.87	16.56	16.34	16.60	4.06	17.31	4.11
NO_3	28.5	45.8	8.01	42.8	7.73	7.77	54.3	8.26	53.7	20.3	N/A[b]	N/A	N/A	N/A
CO_3[c]	21	21	3	21	38	38	3	3	3	21	N/A	N/A	N/A	N/A

(a) Fluoride data was not reproducible. P, Pr, Pd, and Rh measurements were not analyzed by approved impact level II procedures, and are listed for information only. Cs and Rb not measured.

(b) Not applicable.

(c) Values listed for Runs 1, 2, 4, 5, 6, and 10 are based on the amount of CO3 added. Values for Runs 3, 7, 8, and 9 represent carbonate derived from equilibrium with room air and may include carbonate contaminants from chemicals used to prepare the simulant. The carbonate value listed for these tests is based on analytical data averaged over these four tests. The analytical data may be in error by as much as 50%.

TABLE 7.2. Composition of Formated Simulant for Runs 1-10, g/L

Element[(a)]	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Average	Percent RSD
Al	6.60	5.96	6.84	5.79	8.29	6.66	5.91	6.70	5.99	6.53	6.53	11.19
B	0.04	0.06	0.04	0.07	0.05	0.04	0.11	0.05	0.07	0.04	0.06	37.23
Ba	0.45	0.41	0.46	0.41	0.50	0.46	0.41	0.45	0.42	0.46	0.44	7.01
Ca	0.48	0.43	0.50	0.48	0.55	0.52	0.43	0.50	0.46	0.52	0.49	8.28
Cd	2.66	2.41	2.70	2.39	3.00	2.66	2.36	2.59	2.51	2.72	2.60	7.47
Ce	0.51	0.53	0.53	0.61	0.59	0.52	0.54	0.54	0.58	0.62	0.56	7.07
Cr	0.51	0.47	0.51	0.47	0.58	0.52	0.46	0.51	0.49	0.53	0.51	6.91
Cu	0.43	0.38	0.43	0.37	0.47	0.43	0.37	0.42	0.37	0.41	0.41	8.55
Fe	25.24	24.05	25.22	23.52	28.34	25.90	23.87	25.44	24.39	26.51	25.25	5.70
La	0.88	0.86	1.06	0.83	1.46	0.83	0.65	0.97	0.82	1.11	0.95	23.44
Mg	0.38	0.34	0.40	0.34	0.42	0.39	0.34	0.37	0.34	0.38	0.37	8.14
Mn	0.81	0.73	0.81	0.73	0.89	1.11	0.72	0.79	0.75	0.82	0.82	14.04
Mo	1.09	1.01	1.09	0.99	1.19	1.10	1.01	1.10	1.05	1.15	1.08	5.87
Na	17.98	21.47	19.00	19.71	19.60	16.94	20.72	18.36	20.03	17.49	19.13	7.55
Nd	3.31	3.15	3.36	3.02	3.71	3.31	3.15	3.31	3.27	3.51	3.31	5.82
Ni	2.29	2.11	2.38	2.13	2.67	2.38	2.15	2.28	2.19	2.40	2.30	7.31
Ru	0.71	0.63	0.61	0.62	0.67	0.61	0.64	0.61	0.65	0.74	0.65	7.07
SO3	1.56	1.01	0.89	0.78	1.01	1.00	1.01	1.00	1.01	0.89	1.02	0.21
Si	2.26	2.11	2.32	2.12	2.56	2.31	2.14	2.28	2.19	2.34	2.26	5.97
Sr	0.30	0.27	0.31	0.26	0.43	0.31	0.27	0.29	0.28	0.30	0.30	16.21
Y	0.24	0.20	0.24	0.20	0.26	0.23	0.20	0.23	0.21	0.23	0.22	9.51
Zr	15.64	13.26	15.78	13.10	17.92	15.83	13.06	15.26	13.88	15.71	14.94	10.56
NO3	27.7	33.7	7.22	32.5	7.73	4.32	37.2	5.75	42.5	16.7	N/A[(b)]	N/A

(a) Fluoride data was not reproducible. P, Pr, Pd, and Rh measurements were not analyzed by approved impact level II procedures, and are listed for information only. Cs and Rb not measured.

(b) Not applicable.

TABLE 7.3. Run 11 Compositional Data, g/L(a)

Element	Target	Preformate Feed	23 ml Formic acid/L	32 ml Formic acid/L	53 ml Formic acid/L
Al	7.42	6.41	7.30	5.97	6.56
Ba	0.56	0.48	0.54	0.44	0.08
B	0.05	0.07	0.08	0.06	0.48
Ca	0.33	0.50	0.55	0.46	0.50
Cd	3.64	2.76	3.10	2.54	2.73
Ce	0.76	0.74	0.81	0.64	0.71
Cr	0.53	0.50	0.58	0.47	0.53
Cu	0.74	0.43	0.47	0.39	0.43
Fe	30.52	27.26	30.91	25.31	27.5
La	3.85	1.35	0.94	0.93	1.50
Mg	0.34	0.43	0.48	0.40	0.43
Mn	0.59	0.84	0.94	0.77	0.84
Mo	1.25	1.12	1.29	1.06	1.14
Na	20.81	22.17	25.54	21.06	22.5
Nd	4.81	3.69	4.13	3.40	3.68
Ni	2.82	2.49	2.67	2.23	2.43
P	0.30	0.37	0.40	0.31	0.51
SO_4	1.02	1.21	1.34	0.87	1.05
Si	2.92	0.49	0.58	0.43	0.63
Sr	0.53	0.32	0.36	0.29	0.32
Y	0.25	0.23	0.26	0.21	0.23
Zr	17.31	15.04	17.14	14.00	15.4
NO_3		22	15	13	5.5

(a) Fluoride data was not reproducible. CO_3, Cs, P, Pr, Sm, Pd, Rb, and Rh not measured.

It is not certain whether this scenario would occur during laboratory scale formating.

Similar trends in composition were observed for Runs 12 and 13. Compositional data for Runs 12 and 13 are discussed further in Section 7.4.

7.2 PHYSICAL CHARACTERISTICS

The physical characterization of the test simulant includes pH, rheology, density, wt% oxide, wt% solids, and settling rate. The physical properties observed are compared with those reported for previous simulants. Other than for pH, no significant trends in the physical properties related to carbonate or nitrate loadings were observed.

7.2.1 pH Data

The endpoint pH after equivalent formic acid addition was more alkaline with higher carbonate content. This is attributed to the high buffering capacity of the carbonate system. During the addition of formic acid, the pH decreased to a minimum of 5-6 in the presence of added carbonate. A minimum pH of 3-4 was observed for low carbonate and the maximum amount of formic acid added. During reflux the pH increased. The pH after reflux for Run 12 in which an excessive amount of formic acid was added, 151 ml/L increased only slightly to 4.2. For all other runs the pH increased to approximately 7-9 after reflux. Acceptable reproducibility between runs for the pH behavior was demonstrated by replicate Runs 1 and 10 (refer to Figure 7.1).

Two runs in the parametric test, numbers 6 and 8, resulted in an acceptable redox value ($Fe^{+2}/Fe^{+3} = 0.08$). Runs 6 and 8 had low nitrate loadings, the maximum amount of formic acid added, and high and low concentrations of carbonate, respectively. The pH variation (i.e., carbonate content) for these two runs (difference of 2 pH units) did not effect the glass redox value.

7.2.2 Rheology

Rheograms were obtained for Runs 1-10 preformate and formated (prior to frit addition) simulant. Tables 7.4, 7.5, and 7.6 list the flow index, n, the consistency factor, K, yield stress (Tau_y), and the apparent viscosity at selected shear rates for initial and formated simulants. Figure 7.2 shows fitted curves of the apparent viscosity as a function of shear rate. The apparent viscosities for Runs 1-10 were averaged at each shear rate for each curve. Rheological measurements for Runs 11-13 were not taken.

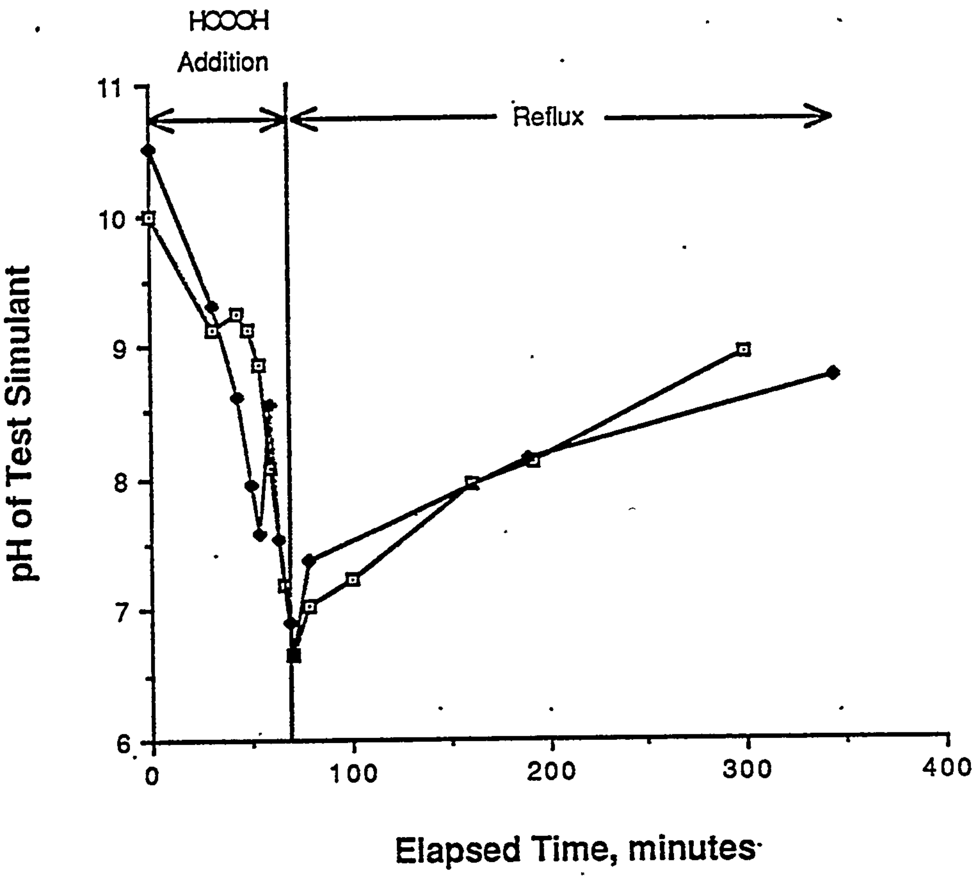

FIGURE 7.1. pH Change During Formic Acid Addition for Runs 1 and 10

The initial simulant exhibited a slight hysteresis (time dependency). Therefore, the apparent viscosity[a] for these samples was calculated for both the up and down curves. The apparent viscosity for the initial simulant

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[a] The apparent viscosity was calculated based on the following relationship:

apparent viscosity = tau/shear rate, $Pa \cdot sec^{-1}$

where Tau = Tau_y + K (shear rate)^n, Pa
Tau_y = yield stress, Pa
n = flow index, dimensionless
K = consistency factor, Pa-sec

A plot of the log of shear stress versus log of shear rate defines the values of n and K; n being the slope of the line and K being the y-intercept. A n value <1 indicates pseudoplastic behavior. For Newtonian fluids n = 1. Shear stress and shear rate are taken from the rheograms.

TABLE 7.4. Rheology Measurements for Simulant Up Curve

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	PSCM-23[(a)]
n	0.806	0.724	0.860	0.865	0.929	0.852	0.839	0.839	0.801	0.833	--
K	0.025	0.042	0.014	0.019	0.010	0.019	0.019	0.016	0.024	0.021	--
Tauy,	1.401	1.642	0.918	1.546	1.497	1.594	2.174	1.401	1.835	1.449	3.2-3.7
Apparent Viscosity, cP											
183 sec-1	16.856	18.840	11.652	17.603	15.375	17.331	20.280	14.619	18.396	16.557	31-34
383 sec-1	11.630	12.336	8.379	12.322	10.737	11.892	13.137	9.841	12.013	11.421	20-22
468 sec-1	10.66	11.829	7.778	12.031	9.931	10.911	12.803	8.980	10.860	10.482	18-20

(a) Goles and Nakaoka 1989.

TABLE 7.5. Rheology Measurements for Simulant Down Curve

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
n	0.845	0.838	0.841	0.842	0.900	0.839	0.852	0.863	0.874	0.798
K	0.021	0.023	0.016	0.022	0.015	0.022	0.021	0.016	0.016	0.028
Tauy, Pa	0.918	1.276	0.435	1.102	0.483	1.063	1.450	0.628	1.352	0.918
Apparent Viscosity, cP										
183 sec-1	14.540	16.758	9.555	15.667	11.674	15.284	17.655	11.246	15.932	14.740
383 sec-1	10.890	12.012	7:520	11.459	9.655	11.191	12.508	8.704	11.315	10.774
468 sec-1	10.194	11.130	7.114	10.668	9.260	10.420	11.565	8.215	10.480	10.006

TABLE 7.6. Rheology Measurements for Formated Simulant

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	PSCM-23(a)
n	0.775	0.875	0.905	0.793	0.864	0.858	0.853	0.799	0.780	0.787	--
K	0.024	0.011	0.008	0.017	0.017	0.014	0.011	0.016	0.018	0.022	--
Tauy, Pa	0.821	0.435	0.821	0.531	0.966	0.725	0.435	0.580	0.580	0.869	2.7
Apparent Viscosity, cP											
183 sec-1	11.761	8.121	9.591	8.780	13.611	10.884	7.513	8.879	8.922	12.117	29
383 sec-1	8.302	6.373	6.901	6.432	10.057	8.129	5.744	6.438	6.403	8.562	20
468 sec-1	7.641	6.037	6.421	5.975	9.396	7.611	5.404	5.969	5.917	7.886	18

(a) Goles and Nakaoka 1989.

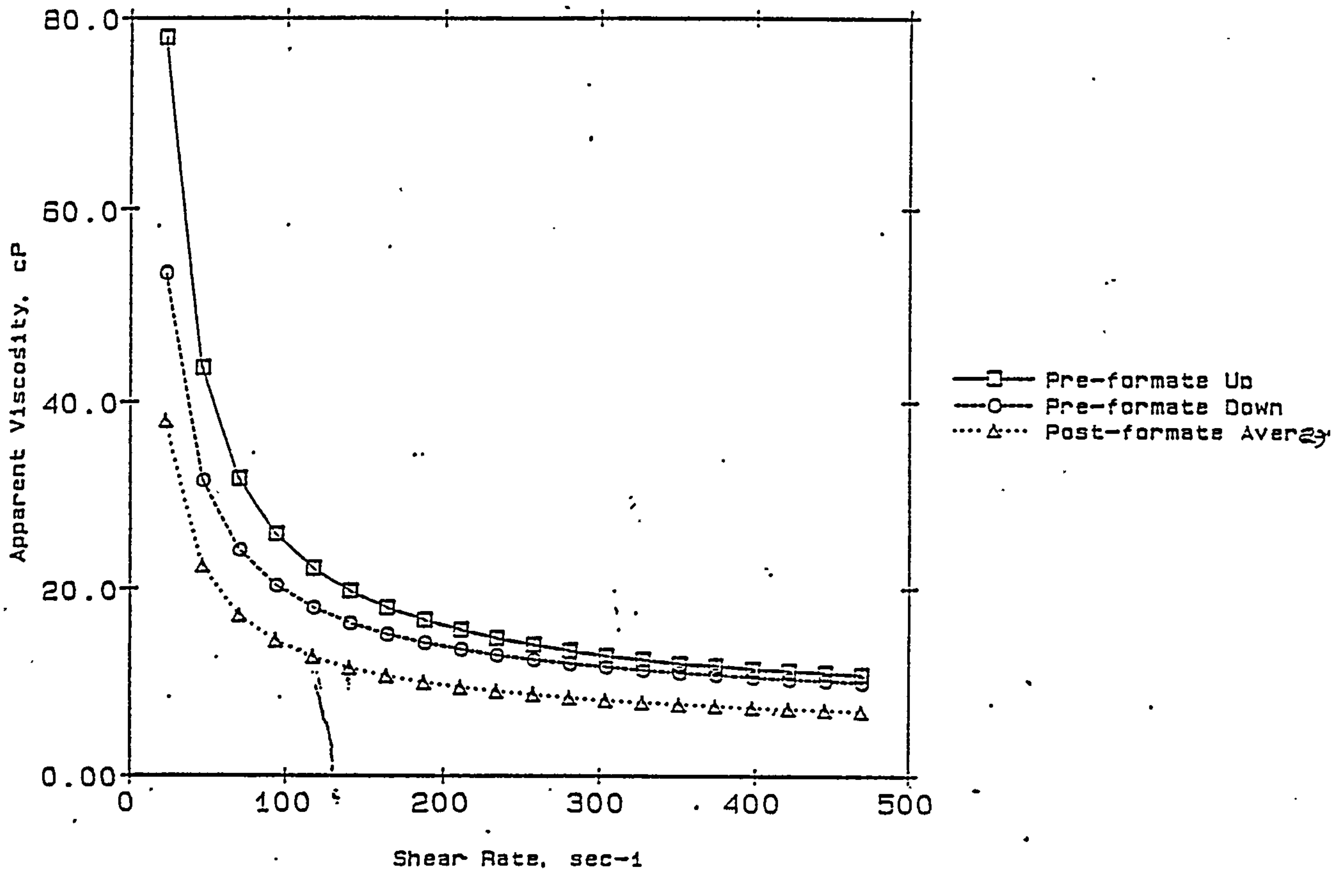

FIGURE 7.2. Comparison of Apparent Viscosity as a Function of Shear Rate for Initial and Formated Simulants

ranged from 20 to 7 centipoise (cP) in the shear rate range of 183 to 468 sec^{-1}. The yield stress ranged from 0.435 to 2.17 Pa. The apparent viscosity decreased after formic acid addition, ranging from 13.6 to 5.4 cP in the shear rate range of 183 to 468 sec^{-1}. The maximum yield stress was lower for formated simulant, the range being from 0.435 to 0.966 Pa. Rheological properties were fairly consistent over the range of formic acid added (16-31 ml/L) and nitrate and carbonate contents. The initial and formated simulants' apparent viscosity and yield stress were lower by a factor of 2-3 compared with PSCM-23 data (Goles and Nakaoka 1989).

7.2.3 Density, % Total Solids, % Total Oxide, and Total Oxide/L

Table 7.7 lists the density, wt% solids, wt% TO and g WO/L for each test simulant. The stock feed batch was prepared per column 5, Table C.1 of the

TABLE 7.7. Physical Properties of Test Simulants[a]

Density	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Preformate	1.12	1.15	1.13	1.14	1.12	1.13	1.13	1.13	1.14	1.13
Formated	1.12	1.12	1.11	1.12	1.12	1.11	1.13	1.11	1.12	1.11
Frit	1.29	1.29	1.27	1.29	1.30	1.30	1.29	1.29	1.30	1.29

Percent Total Solids	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Preformate	16.20	18.43	14.65	17.95	15.66	15.52	17.97	14.58	18.11	16.14
Formated	16.34	17.99	15.72	17.89	15.91	15.59	17.98	15.96	18.34	16.10
Adjusted	14.90	15.86	14.32	15.22	(b)	14.46	15.92	14.54	16.12	15.11
Frit	35.77	36.43	35.31	35.36	51.20	36.64	35.91	35.06	36.84	36.08

Percent Total Oxide	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Preformate	12.26	12.71	12.42	12.78	12.06	12.03	12.61	12.37	12.69	12.22
Formated	12.37	12.61	12.44	12.90	12.15	12.04	12.42	12.20	12.62	12.07
Adjusted	11.08	11.06	11.36	10.73	(b)	11.15	10.99	11.26	11.09	11.35
Frit	32.83	32.45	32.85	31.75	35.46	34.21	32.07	32.26	32.93	33.12

Total Oxide/L	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Preformate	137.68	145.57	140.12	145.58	135.00	135.41	142.76	139.95	144.86	137.75
Formated	137.58	143.73	138.64	147.19	121.50	134.61	141.44	136.88	143.37	135.29
Adjusted	123.76	124.34	126.17	120.15	(b)	123.41	123.74	124.62	124.13	126.37
Frit,	424.64	418.54	418.18	408.02	463.46	445.36	453.49	414.54	426.88	426.81

	Run 11				Run 12				Run 13			
ml 90 wt% Formic Acid/L	0	23	32	53	0	54	90	151	0	24	38	55
Density, g/ml	1.13	1.10	1.12	1.13	1.08	1.12	1.09	1.13	1.08	1.13	1.07	1.09
Percent Total Solids	15.7	16.2	17.5	15.4	14.8	14.8	13.2	12.7	14.4	14.4	11.1	3.8
Percent Total Oxide	11.3	11.5	12.5	11.5	10.3	11.8	10.5	9.6	11.2	11.1	8.7	10.7
Total Oxide/L	128	126	140	130	112	132	113	108	121	126	92	117

(a) Data for formated samples was collected prior to the adjustment of the WO/L for frit addition.
(b) Based on TO/L target of 125 g/L, no adjustment required.

Test Plan which prescribes a target value of 150 gWO/L.[a] The designed target value was 125 gWO/L. Because this was not discovered until after initial runs were completed, Runs 1-10 were conducted with a simulant averaging 140 WO/L to maintain consistency for the perceived statistical analyses. The simulant oxide content was adjusted to 125 gWO/L after formating, prior to addition of frit. For Runs 11-13, the simulant was adjusted to 125 gWO/L prior to formating. No trends related to formic acid addition or carbonate and nitrate addition were observed in these measured values.

7.3 CHEMISTRY OF THE HWVP FORMATING STEP

Addition of formic acid to HWVP feed results in two types of reactions: neutralization and redox. The feed chemistry as it relates to these two types of reactions is described prior to further discussion of results.

7.3.1 Redox Reactions

Formic acid is a fairly strong reducing agent. A generalized redox reaction with formic acid is

$$HCOOH + 2\ M^{+3} \rightarrow CO_2 + 2\ H^+ + 2\ M^{+2}.$$

The redox chemistry of the simulant prepared for this study includes the reduction of NO_3^-, Fe^{+3}, Cr^{+6}, Mo^{+6}, and Mn^{+4} by formic acid. Identification of these components as active participants in redox reactions is based on theoretical considerations (thermodynamic favorability of the redox reaction) and experimental data (detection of reduced species). Other potentially active redox species in HWVP feed include nitrite and organics.

Observations pertinent to this discussion are 1) ammonia [both as $NH_4^+(aq)$ and $NH_3(g)$] was detected in formated simulants; 2) $NO_2(g)$ was not visually observed; 3) the solubility of the chromium and molybdenum species decreased significantly after formating, and 4) the solubility of manganese

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(a) Prior to frit addition the measured TO/L is referred to as waste oxide (WO)/L. After frit addition, the WO plus glass forming oxides in the frit are referred to as TO/L.

species increased significantly after formating. Changes in solubility that may be attributed to changes in the redox state of Cr^{+6}, Mo^{+6}, and Mn^{+4} as a function of formic acid addition are discussed in Section 7.4.

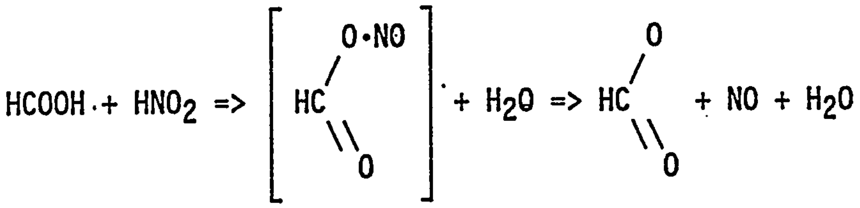
For the feed simulant used in this study, Fe^{+3} and NO_3^- are of primary interest because their concentration in the simulant is greater than ten times that of the other potential redox participants. The reaction between formic acid and nitric acid has been studied by Healy, Longstaff, and Bradley. These systems involved high nitrate and acid content relative to the simulant used for this study. However, general trends are thought to be relevant and are therefore summarized below.

Healy observed that at nitric acid concentrations (1-4 M), nitric oxide (NO) rather than nitrogen dioxide (NO_2) was the major product. The gas composition for the reaction was 36% NO, 4% NO_2, and 60% CO_2. For the HWVP simulant the concentration of nitrate would be considered low. The nitrate concentration in the test simulants ranged from 0.13 to 0.87 M. The reaction between nitric acid and formic acid for low acid concentrations may be defined as

$$4\ HNO_3 + 6\ HCOOH \rightarrow 4\ NO + 6\ CO_2 + 8\ H_2O.$$

Nitric oxide (NO) is oxidized in the presence of oxygen to nitrogen dioxide. However, the rate of this reaction is strongly concentration dependent, becoming in the order of minutes at low concentrations. Therefore, the lack of NO_2 detection during formating does not necessarily indicate the absence of NO.

It has been suggested that the rate determining step for the reaction between HNO_3 and HCOOH involves nitrous acid as an intermediate. Longstaff and Singer reported that at low acidity the reaction rate was first order with respect to nitrous acid (HNO_2) and formic acid. The rate-determining step was postulated to be a bimolecular reaction between formic acid and nitrous acid in <2.5 M nitric acid. Healy suggested that the mechanism may involve the free radical, the formate ion (HCO_2^-), via the reaction



The reactions between nitrate and formic acid addressed in the current study are listed below. Two gaseous products of nitrate reduction are considered: nitric oxide and ammonia. These reactions are based on the predicted formation of NO as supported by the studies summarized above and the detection of ammonia during the current study. The free energy of reaction is given for the formation of two types of gaseous products in both basic and acidic medias. Free energies of formation used to calculate the free energy of reaction are given in Table 7.8.

Media	Balance Redox Equation	G^o_R kcal/mole
Product - NO		
acid	$6\ HCOOH\ (aq) + 4\ HNO_3 \rightarrow 6\ CO_2 + 4\ NO + 8\ H_2O(l)$	-53
base	$6\ HCOO^-\ (aq) + 4\ NO_3^- + 2H_2O \rightarrow 6\ CO_2 + 4\ NO + 10\ OH^-$	-58
Product - $NH3/NH_4^+$		
acid	$4\ HCOOH\ (aq) + HNO_3 + H^+ \rightarrow 4\ CO_2 + NH_4^+(aq) + 3\ H_2O(l)$	-50
base	$4\ HCOO^-\ (aq) + NO_3^- + 2H_2O \rightarrow 4\ CO_2 + NH_3(aq) + 5\ OH^-$	-60

All four of these reactions are thermodynamically favorable as indicated by their negative free energies. Based on the equivalency of the free energy values, no one media or product appears to be favored. (Note that this does not address the activation energy of the two competing reactions). The significant difference lies in the stoichiometry. To produce ammonia, the mole ratio of formic acid to nitrate is 4, compared with 1.5 required for production of NO. As is discussed in Section 7.5, the threshold for obtaining a detectable conversion of ferric ion to ferrous ion is between these two stoichiometric values, $HCOOH/NO_3 = 3$. Extracted from this observation is the

TABLE 7.8. Free Energy of Formation

Substance	Free Energy Formation, kcal/mole HCOOH
HCOOH(aq)	-85.1
HCO_2^-	-80
CO_2	-94.26
HNO3	-26.5
NO_3^-	-26.5
NO	+20.7
NH_3	-6.37
NH_4^+	-19
H_2O	-56.56
OH^-	-37.6
H^+	0

hypothesis that the extent of nitrate reduction can be correlated to the off gas composition. And that in turn, the extent of nitrate reduction can be related to the formic acid requirements.

7.3.2 Hydrolysis Chemistry

It is recommended in this study that the formic acid requirements be correlated to redox reactions rather than neutralization reactions. Therefore, the neutralization chemistry discussed in this section is limited to the solubilization of feed components, as a basis for explaining the observed distribution of elements between supernate and solid phases. Measured distributions are discussed in Section 7.4.

Based on the solubility equilibria constants and solubilities measured in the laboratory, the cations of the HWVP feed are present primarily as insoluble hydroxide salts prior to formating with the following exceptions: 1) sodium, which exists as a soluble species, 2) lanthanum and neodydeum, which were added as insoluble fluorides, 3) barium, which was added as an insoluble sulfate and 4) manganese, which is believed to exist as the insoluble oxide, MnO_2, as it was added. Although copper and magnesium were added as sulfates during the simulant preparation, their respective hydroxides are much less soluble and would be expected to form under alkaline conditions.

The relative solubility of the hydroxide salts is reflected by their respective solubility constants. Table 7.9 lists the hydroxide solubility

TABLE 7.9. Solubility Constants for HWVP Feed Components

Hydroxide	Solubility Constants (25°C)	Reference
$Zr(OH)_4$	1.3E-56	Baes
	1.1E-54	Elinson
$Fe(OH)_3$	4E-38	Latimer
$Al(OH)_3$	1.9E-33	Latimer
	3.16E-34	Baes
$Cr(OH)_3$	6.7E-31	Latimer
	1E-31	Baes
$Pd(OH)_3$	E-24	Latimer
$La(OH)_3$	E-20	Latimer
	2.0E-22	Baes
$Nd(OH)_3$	E-20	Latimer
	4.0E-24	Baes
$Ce(OH)_3$	E-20	Latimer
	7.9E-23	Baes
$Pr(OH)_3$	E-20	Latimer
	3.2E-23	Baes
$Sm(OH)_3$	E-20	Latimer
	3.2E-26	Baes
$Cu(OH)_2$	5.6E-20	Latimer
	4.4E-20	Baes
$Y(OH)_3$	3.2E-25	Baes
$Fe(OH)_2$	1.6E-15	Latimer
	7.08E-16	Baes
$Mn(OH)_2$	7.1E-15	Latimer
	1.6E-13	Baes
$Cd(OH)_2$	1.2E-14	Latimer
$Ni(OH)_2$	1.6E-14	Latimer
	6.3E-18	Baes
$Mg(OH)_2$	5.5E-12	Latimer
	6.9E-12	Baes
$Ca(OH)_2$	7.9E-6	Latimer
$Sr(OH)_2 \cdot 8H_2O$	3.2E-4	Latimer
$Ba(OH)_2 \cdot 8H_2O$	5E-3	Latimer
NaOH	>1	Estimated
RbOH	>1	Estimated
CsOH	>1	Estimated

constants for a majority of the feed constituents. These constants may be used for relative comparison; however, these constants are dependent on the temperature, ionic strength, and species concentration. Kinetics also affects the dissolution process.

During titration of the feed with formic acid, dissolution of the hydroxides occurs when the hydroxide concentration becomes lower than that required to satisfy the equilibrium constant. With the exception of Zr, Fe, and possibly Cr and Al, all of the hydroxides are predicted to be neutralized by formic acid as the pH decreases to approximately 4. The extent to which these neutralization reactions occurred in the test simulant was measured by determining the concentration of the cation in the supernate as a function of formic acid addition and pH. These results are discussed further in Section 7.4. The proposed neutralization reactions are:(a)

$CsOH + HCOOH \rightarrow CsCOOH + H_2O$

$RbOH + HCOOH \rightarrow RbCOOH + H_2O$

$NaOH + HCOOH \rightarrow NaCOOH + H_2O$

$Sr(OH)_2 + 2\ HCOOH \rightarrow Sr(COOH)_2 + 2\ H_2O$

$Na_2CO_3 + 2\ HCOOH \rightarrow 2\ Na(COOH) + H_2CO_3$(b)

$Ca(OH)_2 + 2\ HCOOH \rightarrow Ca(COOH)_2 + 2\ H_2O$

$Mg(OH)_2 + 2\ HCOOH \rightarrow Mg(COOH)_2 + 2\ H_2O$

$Ni(OH)_2 + 2\ HCOOH \rightarrow Ni(COOH)_2 + 2\ H_2O$

$Cd(OH)_2 + 2\ HCOOH \rightarrow Cd(COOH)_2 + 2\ H_2O$

$Y(OH)_3 + 3\ HCOOH \rightarrow Y(COOH)_3 + 3\ H_2O$

$Cu(OH)_2 + 2\ HCOOH \rightarrow Cu(COOH)_2 + 2\ H_2O$

$Sm(OH)_3 + 3\ HCOOH \rightarrow Sm(COOH)_3 + 3\ H_2O$

$Pr(OH)_3 + 3\ HCOOH \rightarrow Pr(COOH)_3 + 3\ H_2O$

$Ce(OH)_3 + 3\ HCOOH \rightarrow Ce(COOH)_3 + 3\ H_2O$

(a) Notation, $M(COOH)_R$, refers to either aqueous or insoluble salt.

(b) Carbonic acid decomposes into its anhydride and water in an acidic environment or with the addition of heat via the reaction

$$H_2CO_3 \rightarrow H_2O + CO_2(g).$$

CO_2 is only very slightly soluble in water and is released from solution.

$Pd(OH)_3 + 3\ HCOOH \rightarrow Pd(COOH)_3 + 3\ H_2O$

$Al(OH)_3 + 3HCOOH \rightarrow Al(COOH)_3 + 3H_2O$ [dissolution at pH < 5]

$Cr(OH)_3 + 3\ HCOOH \rightarrow Cr(COOH)_3 + 3\ H_2O$ [excessive (151 ml/L) formic acid addition, only]

$Fe(OH)_3 + 3HCOOH \rightarrow Fe(COOH)_3 + 3H_2O$ [excessive (151 ml/L) formic acid addition, only].

Similar reactions are given by Farnsworth (1987). Farnsworth did not include calcium, palladium, and cadmium. Farnsworth did include manganese, lanthanum, and neodyneum. Neodyneum and lanthanum are not included as these cations are believed to exist as the highly insoluble fluorides which they were added. Manganese was added as insoluble MnO_4 and would precipitate as $Mn(OH)_2$ only after reduction, $Mn^{+4} \rightarrow Mn^{+2}$. Based on experimental data reported in Section 7.4, chromium and ferric hydroxide solubilize only after excessive amounts of formic acid (151 ml/L) are added.

The neutralization reactions presented above represent a simplistic view of the actual hydrolysis chemistry of the feed. In reality the hydrolysis products exists both as aqueous species (hydrated oxides) and as solids (hydroxide salts). Equilibria between these species may be expressed by the following equations.(a)

Aqueous Cation, M^{+z}, to a Soluble Hydrated Oxide

$$xM^{+z} + yH_2O \longleftrightarrow Mx(OH)_y^{(xz-y)+} + yH^+ \qquad K_{xy} = \frac{[Mx(OH)_y^{(xz-y)+}][H^+]^y}{[M^{+z}]^x}$$

Hydroxide Salt, $M(OH)_z$, to a Soluble Hydrated Oxide

$$xM(OH)_z\ (s) + H^+ \longleftrightarrow M_x(OH)_y^{(xz-y)+} + H_2O \qquad K_{sxy} = \frac{[M_x(OH)_y^{(xz-y)+}]}{[H^+]_{xz-y}}$$

(a) As a first approximation the formation constant, K, is assumed to be equal to the formation quotient, Q. This implies that the activity coefficients for the reacting species are equal to one.

Solubilization of a hydroxide salt can also be represented as:

$$xM(OH)_z\ (s) \longleftrightarrow M_x(OH)_y{}^{(xz-y)+} + (xz-y)OH^-$$

$$K^b{}_{sxy} = [M_x(OH)_y{}^{(xz-y)+}][OH^-]^{(xz-y)}$$

$K^b{}_{sxy}$ is related to K_{sxy} by the dissociation product of water, K_w:

$$K_w = [H^+][OH^-]$$

$$K^b{}_{sxy} = K_{sxy}K_w{}^{xz-y}$$

Formation constants (K_{xy}) for hydrated oxides are listed in Table 7.10. Solubility constants ($K^b{}_{sxy}$) for hydroxide are listed in Table 7.11.

7.4 SOLUBILITY MEASUREMENTS

For Runs 12 and 13, in addition to the total simulant composition, the fraction of soluble species was determined by compositional analysis of the supernate. Table 7.12 lists the composition of the simulant and soluble fractions for these tests.

The significant changes in solubility as a function of formic acid addition are described below and summarized in Table 7.13. These results are compared with those reported by Goles and Nakaoka (1989) for the PSCM-23 run. Differences in solubility behavior for Run 12, Run 13 and PSCM-23 are explained by differences in the pH after reflux (post reflux). A potential reaction scenario for chromium behavior during the formating step is also given.

7.4.1 Ions that Increase in Solubility After Formating

The increase in solubility of aluminum, calcium, strontium, magnesium, and cadmium is attributed to neutralization of their respective hydroxide salts by formic acid. This was observed during Run 12 and the PSCM-23 run. For Run 13 the carbonate loading was approximately 13 times greater than in Run 12. During Run 13 formic acid was consumed by neutralization of the

TABLE 7.10. Formation Constants for Hydrated Oxides in HWVP Feed(a)

Hydrated Oxide	Log Kxy	Hydrated Oxide	Log Kxy
$AlOH_2^+$	-4.97	$MgOH^+$	-11.44
$Al(OH)_2^+$	-9.3	$Mg(OH)_4^{+4}$	-39.71
$Al(OH)_3(aq)$	-15.0	$MnOH^+$	-10.59
$Al(OH)_4^-$	-23.0	$Mn(OH)_2$	(-22)
$Al_2(OH)_2^{+4}$	-7.7	$Mn(OH)_3^-$	(35)
$Al_3(OH)_4^{+5}$	-13.94	$Mn(OH)_4^{-2}$	-48.3
$Al_3(OH)_4(OH)_{24}^{+7}$	3.7	$Mn_2(OH)_3^+$	-23.9
$Al_4(OH)_8^{+8}$	6.0	$HMoO_4^-$	3.89
$CdOH^+$	-10.08	H_2MoO_4	7.50
$Cd(OH)_2$	-20.35	$Mo_7O_{24}^{-5}$	57.74
$Cd(OH)_3^-$	<-33.3	$Mo_7O_{23}(OH)^{-5}$	62.14
$Cd(OH)_4^{-2}$	-47.35	$Mo_7O_{22}(OH)_2^{-4}$	65.68
$Cd_2(OH)^{+3}$	-9.39	$Mo_7O_{21}(OH)_3^{-3}$	68.21
$Cd_4(OH)_4^{+4}$	-32.85	$Mo_{19}O_{59}$	65.68
$CrOH^{+2}$	-4.0	$NiOH^+$	-9.86
$Cr(OH)_2^+$	-9.7	$Ni(OH)_2$	-19
$Cr(OH)_3$	-18	$Ni(OH)_3^-$	-30
$Cr(OH)_4^-$	-27.4	$Ni(OH)_4^{-2}$	<-44
$Cr_2(OH)_2(OH)_2^{+4}$	-5.1	Ni_2OH^{+3}	-10.7
$Cr_3(OH)_4^{+5}$	-8.2	$Ni_4(OH)_4^{+4}$	-27.7
$CuOH^+$	<-8	$ZrOH_3^+$	0.3
$Cu(OH)_2$	(<-17.3)	$Zr(OH)_2^{+2}$	(-1.7)
$Cu(OH)_3^-$	(<-27.8)	$Zr(OH)_3^+$	(-5.1)
$Cu(OH)_{24}^{-2}$	-39.6	$Zr(OH)_4$ (aq)	-9.7
$Cu_2(OH)_2^{+2}$	-10.36	$Zr(OH)_5^-$	-16.0
$FeOH^+$	-9.5	$Zr_2(OH)_4^{+8}$	0.61
$Fe(OH)_2$	-20.6	$Zr_3(OH)_5^{+7}$	3.7
$Fe(OH)_3^-$	-31	$Zr_4(OH)_8^{+8}$	-2.19
$Fe(OH)_2$	-20.6	$FeOH^{+2}$	-31
		$Fe(OH)^{2+}$	-5.67
		$Fe(OH)_3$	<-12
		$Fe(OH)_4^-$	-21.6
		$Fe_2(OH)_2^{+4}$	-2.95
		$Fe_3(OH)_4^{+5}$	-6.3

(a) Values extracted from Baes, 1986.

carbonate and not available for neutralization of the hydroxide salts. Therefore, the solubility changes which result from neutralization of the hydroxides are negligible for Run 13. The potential impact of end point pH during formating is discussed further in Section 7.6.

TABLE 7.11. Solubility Constants for Hydroxide Salts in HWVP Feed(a)

Hydroxide Salt	Log K_{sxy}
α-$Al(OH)_3$	8.5
$Ce(OH)_3$	19.9
β-$Cd(OH)_2$	13.65
$Cr(OH)_3$	12
$Cu(OH)_2$	8.64
CuO	7.62
$Fe(OH)_2$	12.85
α-FeO(OH)	0.5
$La(OH)_3$	20.3
$Mb(OH)_2$	16.84
$Mn(OH)_2$	15.2
MoO_3	-12.06
$Ni(OH)_2$	10.8
$Nd(OH)_3$	18.6
$Pr(OH)_3$	19.5
$Sm(OH)_3$	16.5
$Y(OH)_3$	17.5
ZrO_2	-1.9

(a) Values extracted from Baes 1986.

Manganese solubility increased during the addition of formic acid in Run 12 and PSCM-23. The increase in solubility may be attributed to the reduction of the insoluble MnO_2 (species as added to simulant) to Mn^{+2} by formic acid. In an acid environment (Run 12 and PSCM-23) this species would be soluble. In an alkaline environment (Run 13), $Mn(OH)_2$ would be precipitated. Significantly less manganese was soluble in Run 13 formated simulant.

The dissolution of $Fe(OH)_3$ (~20%) was observed at relatively high post reflux acidity, after an excessive amount of formic acid addition (151 ml/L) in Run 12. The pH after formic acid addition was 3.09; after reflux the pH

TABLE 7.12. Solubility Data for Runs 12 and 13

Element[a]	Run 12 (low carbonate), g/L							
	Preformate		1.17 Moles Formic Acid/L		1.95 Moles Formic Acid/L		3.27 Moles Formic Acid/L	
	Total	Supernate	Total	Supernate	Total	Supernate	Total	Supernate
Al	5.995	0.031	6.893	0.006	6.782	0.005	6.61	1.8
B	0.045	0.011	0.079	0.013	0.078	0.014	0.068	0.036
Ba	.447	0	0.52	0	0.511	0	0.467	0.001
Ca	0.501	0.002	0.576	0.002	0.599	0.003	0.559	0.496
Cd	2.64		3.11	0.002	3.04		2.82	1.83
Ce	0.698		0.802		0.788		0.798	0.004
Cr	0.501	0.126	0.576		0.566		0.559	0.248
Cu	0.392	0.001	0.441	0.015	0.444	0.001	0.445	0.012
Fe	25.9	0.004	29.9	0.001	29.3	0.001	29.2	6.5
La	1.45		1.03		1.01		2.68	0.04
Mg	0.392		0.006	0.463	0.444	0.011	0.433	0.33
Mn	0.807		0.927	0	0.91		0.855	0.396
Mo	1.09	0.71	1.25	0.36	1.23	0.29	1.19	0.017
Na	10.8	10.4	12.4	11.5	12.87	11.21	2.2	12.5
Nd	3.34		3.88		3.84		3.78	0.037
Ni	2.23		2.81		2.57		2.61	0.28
P	0.327	0.02	0.339	0.02	0.333	0.02	0.34	0.02
Ru	0.654		0.78	0.05	0.777	0.07	0.798	0.6
SO_3	1.41		1.06		1.03		0.456	
Si	2.3	0.01	2.66	0.003	2.64	0.006	2.50	0.027
Sr	0.294	0.001	0.35	0.001	0.344	0.001	0.331	0.195
Y	0.229		0.26		0.255		0.251	0.105
Zr	14.8	0.002	16.4	0.178	16.4	0.154	16.0	0.012
NO_3	9.61	26.1	2.22			9.35		
pH[b]	8.68[d]		3.98		3.56		3.09	
pH[c]			9.70		9.67		4.23	

TABLE 7.12. (contd)

Element[a]	Run 13 (high carbonate), g/L							
	Preformate		0.53 Moles Formic Acid/L		0.82 Moles Formic Acid/L		1.19 Moles Formic Acid/L	
	Total	Supernate	Total	Supernate	Total	Supernate	Total	Supernate
Al	0.078	6.015	5.835	0.049	9.99	0.05	0.026	6.67
B	0.24	0.058	0.074	0.27	0.078	0.281	0.306	0.066
Ba	0.001	0.458	0.45	0.004	0.737	0.005	0.034	0.508
Ca	0.006	0.445	0.430	0.012	0.71	0.014	0.081	0.488
Cd	0.001	2.565	2.526	0.003	4.12	0.001	0.003	2.84
Ce		0.786	0.767	x	1.29	x	x	0.87
Cr	0.238	0.479	0.494	0.002	0.77	x	x	0.53
Cu	0.001	0.402	0.395	0.002	0.64	0.002	0.001	0.44
Fe	0.013	25.95	26.150	0.042	43.8	0.028	0.027	28.45
La		1.145	0.599	x	1.035	x	x	1.11
Mg		0.35	0.352	0.014	0.58	0.03	0.153	0.41
Mn	0.001	0.786	0.772	0.001	1.265	0.001	0.002	0.87
Mo	0.923	1.065	1.08	0.829	1.76	1.06	0.431	1.19
Na	18.2	18.6	19.1	19	27.9	28.9	20.9	21.1
Nd	0.003	3.5	3.43	0.010	5.66	0.006	0.006	3.83
Ni	0.003	2.	2.25	0.005	3.8	0.002	0.003	2.56
P		0.25	x	0.35	x	x	x	x
Ru		0.64	0.62	x	1.04	x	0.021	0.72
SO_3	0.95		x	1.08	x	1.47	1.2	x
Si	0.088	2.23	2.17	0.151	3.585	0.13	0.142	2.59
Sr	0.004	0.305	0.3	0.011	0.405	0.016	0.092	0.332
y		0.222	0.215	x	0.368	x	x	0.243
Zr	0.008	14.7	14.0	0.035	24.4	0.023	0.02	16.1
NO_3		6.9	6.76	x	5.22	0.05	x	x
pH[b]	7.80[d]		x	6.80	x	5.20	5.20	x
pH[c]			x	8.80	x	8.90	9.10	x

(a) Fluoride data not reproducible. Pd, Pr, Rb, Rh, Sm, and CO_3 not measured. Blanks represent concentrations below detection limit.
(b) Minimum pH at indicated formic acid addition.
(c) pH after 2 hr reflux.
(d) Initial pH measured at 95°C (corrected for temperature).

TABLE 7.13. Comparison of Solubility Behavior for Run 12, Run 13 and PSCM-23

Element	% Soluble Prior to and After Formating/Reflux Step Run 12 (pH 4.2)[(a)]	Run 13 (pH 9.0)	PSCM-23 (pH 4.2)
Neutralization			
Al	<1% to 10%	<1% throughout	<1% to 9%
Ca	<1% to 31%	<1% throughout	<1% to 95%
Cd	<1% to 23%	<1% throughout	not measured
Mg	<1% to 26%	<1% to 5.5%	<5% to 100%
Sr	<1% to 21%	<1% throughout	<5% to 59%
Redox			
Mn	<1% to 16%	<1% throughout	<1% to 70%
Cr	6% to <4% to 16%	26% to <1%	20% to 10%
Mo	16% to 0.5%	50% to 6%	30% to 45%

(a) pH of feed after formic acid addition and 2-h reflux.

was 4.23. In all other cases for Runs 12 and 13 the post reflux pH was ~9 and >99% of Fe^{+3} was present as a solid.

7.4.2 Ions that Decrease in Solubility After Formating

During Run 13 the solubility of molybdenum steadily decreased from 50% to 6% and the solubility of chromium decreased from 26% to below detection limit (<4%). This same behavior was reported for samples collected during the PSCM-23 run (Goles and Nakoaka 1989) and is believed to be associated with changes in redox states.

During Run 12, the solubility of molybdenum also decreased from 17% to 1%. For this same test, the concentration of chromium in the supernate phase decreased from 7% to <4% down to a pH 3.6. As the formic acid loading increased from 90 ml/L to 151 ml/L the pH decreased to 3.1 and chromium ion solubility increased. This increase in solubility is most likely due to the solubilization of the $Cr(OH)_3$ hydroxide in the presence of excess acid. A reaction scenario for chromium is described below.

7.4.3 Proposed Reaction Scenario for Chromium

The following reactions describe the proposed scenario for chromium ion behavior during the feed preparation steps:

$$2\ Cr^{+3} + 3\ NO_3^- + 3\ H_2O \rightarrow 2\ Cr^{+6} + 3\ NO_2^- + 6\ OH^- \quad (1)$$

$$2\ Cr^{+6} + 3\ HCOOH \rightarrow 2\ Cr^{+3} + 3\ CO_2 + 6\ H^+ \quad (2)$$

$$Cr^{+3} + 3\ OH^- \rightarrow Cr(OH)_3\ \text{(solid)} \quad (3)$$

$$Cr(OH)_3 + 3\ H^+ \rightarrow Cr^{+3} + 3\ H_2O\ \text{(excess formic acid).} \quad (4)$$

Evaluation of the data which support this scenario are presented below.

These data are derived from Run 13 samples of initial simulant and formated simulant with 24 ml 90 wt% formic acid/L (0.53 moles formic acid/L).

Initial Simulant - Twenty-six percent of the chromium is soluble as the Cr^{+6} species.

- 0.0024 moles out of a total 0.0092 moles chromium (26%) was soluble in the simulant.
- The initial pH of this simulant was 7.8, being buffered by a high bicarbonate loading. The initial pH of simulants without carbonate ranged from 9-10. In an alkaline environment, the remaining chromium as Cr^{+3} would precipitate as the hydroxide.
- Chromium (+6) was the predominant, soluble chromium species in the alkaline supernate. Colormetric analysis for Cr^{+6} concentration agreed within 2% of the ICP analysis for chromium in the supernate.
- Chromium was added to the simulant in the +3 valence state. Oxidation of chromium (+3) to Cr (+6) may have resulted from the presence of nitrate (Equation 1); a thermodynamically favorable reaction.

Formated Simulant - Cr^{+6} is reduced by formic acid and precipitates as $Cr(OH)_3$.

- After addition of 24 ml 90 wt% formic acid/L simulant (0.53 moles formic acid/L), the concentration of chromium in the supernate decreased to below the ICP detection limit for chromium (0.00038 moles/L). This may be attributed to the reduction of Cr^{+6} to Cr^{+3} (Equation 2) and subsequent precipitation of the Cr^{+3} as a hydroxide (K_{sp} = 6.7 E-31) (Equation 3).

- The moles of Cr^{+6} reduced is but a small fraction of the total amount of formic acid added. Considering that three moles of formic acid react with two moles of Cr^{+6} to produce Cr^{+3}, the fraction of formic acid consumed is 0.002 * 1.5/0.53 = 0.57%.
- In the presence of excess acid (151 ml 90 wt% formic acid/L, the hydroxide would dissolve (Equation 4) (Run 12).

7.5 FORMIC ACID REQUIREMENTS

The formic acid requirements are discussed in terms of dependency on carbonate, nitrate, and initial Fe^{+3} feed content.

Carbonate decomposes to CO_2 as the feed is acidified with formic acid and as the feed is heated to 1000 °C for vitrification. The % decomposition as a function of process step is not known. This decomposition reaction is

$$H_2CO_3 \text{ ----> } H_2O + CO_2.$$

Unlike formic acid, the carbon in carbonate and CO_2 is in its maximum oxidation state, +4. Therefore, neither the CO_3^{-2} nor the CO_2 would be expected to act as reducing agents during formic acid addition or in the vitrification step. The endpoint pH after formating high carbonate simulants was less acidic. The relationship between acidity and the process step at which redox occurs is discussed further in Section 7.6.

A glass Fe^{+2}/Fe^{+3} ratio of 0.08 was measured for both Runs 6 (high carbonate) and 8 (low carbonate) at equivalent formic acid and nitrate loadings. This finding suggested that redox participants such as nitrate, should provide the primary criteria for formic acid adjustments. After evaluation of subsequent runs, a threshold for obtaining an acceptable glass Fe^{+2}/Fe^{+3} ratio was defined independent of carbonate concentrations in the range of 8 to 59 g/L.

The nitrate ion content in the feed is a significant factor in the determination of the formic acid requirement for glass redox adjustments. The significance of the $HCOOH/HNO_3$ ratio is attributed to the consumption of formic acid through the reduction of the nitrate ion to produce ammonia and/or nitrogen oxide/nitrogen dioxide/nitrous oxide and carbon dioxide.

This reaction may take place during the formating and/or the melting step(s). Ammonia was observed during the current studies and reported as an off gas component from the melter for the PSCM-23 run (Goles and Nakaoka 1989). Release of NO_x, N_2O, and CO_2 during formating has been measured previously (Wiemers 1987).

In Figure 7.3 the glass Fe^{+2}/Fe^{+3} ratio is plotted as a function of $HCOOH/NO_3$ for Runs 1-13. A detectable glass redox is measured after the mole ratio, $HCOOH/NO_3$, is greater than 3.

Addition of the 32 data points collected by Farnsworth (1987) suggests two relationships: 1) glass redox is dependent on Fe^{+3} initial/NO_3 and 2) for reference feed, $Fe^{+3}/NO < 4$, a minimum requirement for redox adjustments is $HCOOH/NO_3 = 3$. Detectable Fe^{+2}/Fe^{+3} (≥ 0.005) ratios were measured for all samples with $HCOOH/NO_3 \geq 3$. Farnsworth's data is plotted with data from this study in Figure 7.4. The collated data is listed in Table 7.14.

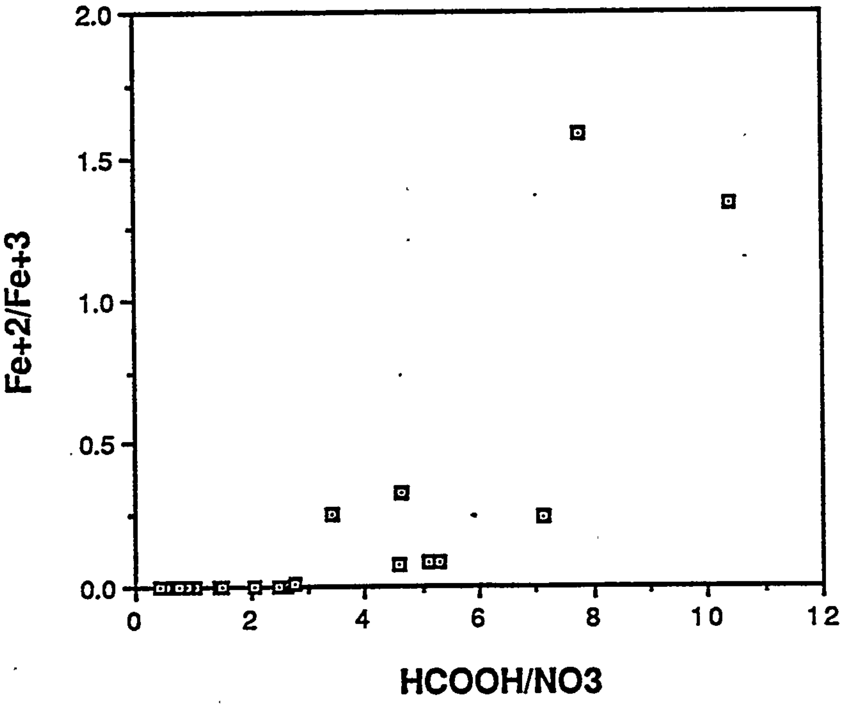


FIGURE 7.3. Dependence of Glass Redox on $HCOOH/NO_3$

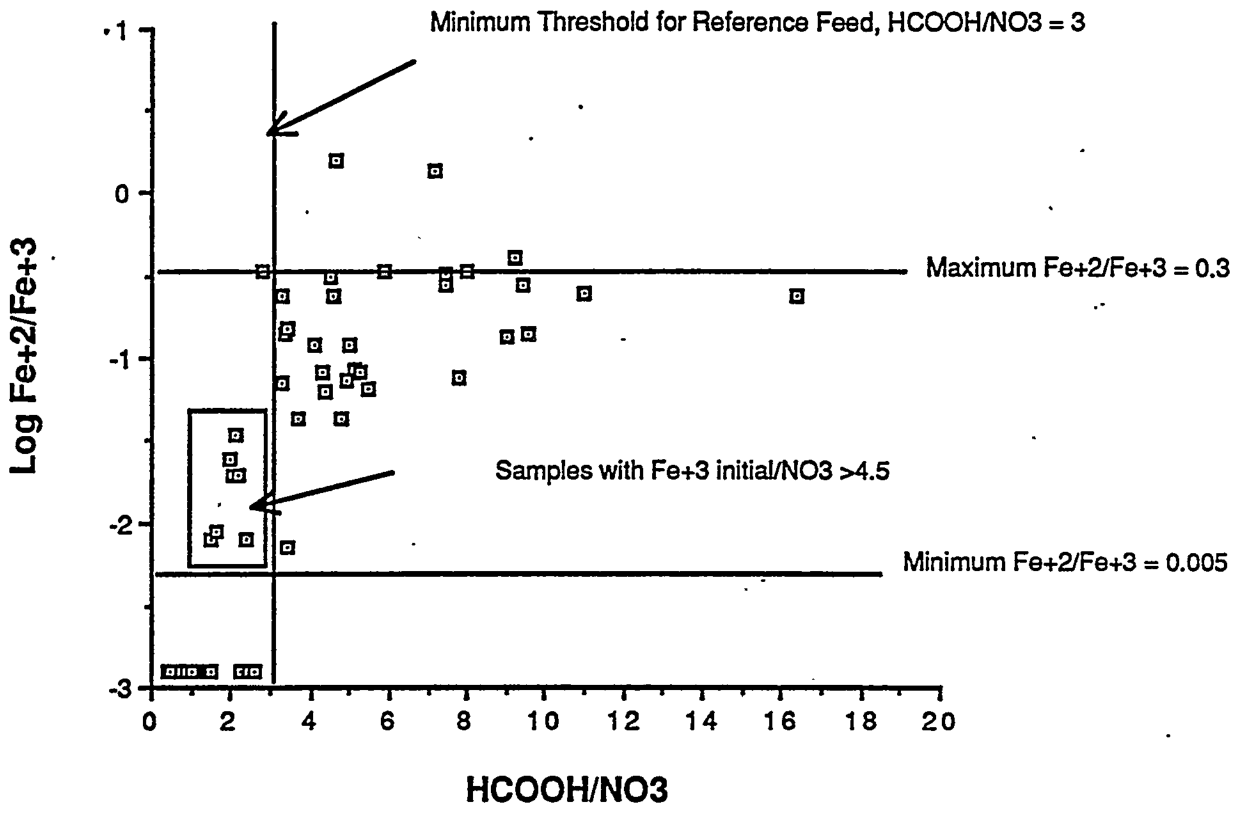


FIGURE 7.4. Threshold for $HCOOH/NO_3$ and Fe^{+2}/Fe^{+3} Relationship

In the presence of high iron ($Fe/NO_3 > 4$) the formic acid requirements for acceptable glass redox were less, $HCOOH/NO_3 = 1.5$ to 2.5. It is speculated that the variation in the formic acid requirements may be attributed to differences in the ratio of nitrate redox reaction products, NO, NO_2, N_2O and NH_3.

The scatter of data observed after the threshold may be attributed to differences between laboratory formating procedures, vitrification conditions, and secondary reactions which become more significant once the $HCOOH/NO_3$ threshold is met. For example, Farnsworth's simulants also contained varying amounts of the organic, oxalic acid.

Based on the observed threshold for the reference feed, $HCOOH/NO_3 = 3$, the formic acid requirements for the target low, nominal, and high nitrate

TABLE 7.14. HCOOH/NO_3 Threshold Support Data

Sample	ml HCOOH/L	HCOOH, M	NO_3, M	$Fe^{(+3)}$, M	FA/NO_3	Fe/NO_3	Fe^{+2}/Fe^{+3}	Fe^{+2}, M
Farnsworth 1987								
NCAW-84	14	0.30	0.14	0.94	2.17	6.72	0.020	0.018
NCAW-84	24	0.52	0.14	0.94	3.72	6.72	0.043	0.039
NCAW-84	48	1.04	0.14	0.94	7.44	6.72	0.272	0.201
NCAW-86	12	0.26	0.17	0.55	1.51	3.16	0.008	0.004
NCAW-86	26	0.56	0.17	0.55	3.26	3.16	0.235	0.104
NCAW-86	36	0.78	0.17	0.55	4.52	3.16	0.312	0.130
Hi Fe	10	0.22	0.11	1.15	2.05	10.88	0.020	0.023
Hi Fe	24	0.52	0.11	1.15	4.91	10.88	0.074	0.079
Hi Fe	44	0.95	0.11	1.15	9.01	10.88	0.136	0.138
Hi Fe	80	1.74	0.11	1.15	16.38	10.88	0.235	0.219
Lo Fe	24	0.52	0.23	0.22	2.24	0.96	0.003	0.001
Lo Fe	36	0.78	0.23	0.22	3.35	0.96	0.141	0.028
Lo Fe	44	0.95	0.23	0.22	4.10	0.96	0.121	0.024
Lo Fe	80	1.74	0.23	0.22	7.45	0.96	0.319	0.054
Hi Al	12	0.26	0.16	0.86	1.65	5.42	0.009	0.008
Hi Al	24	0.52	0.16	0.86	3.30	5.42	0.071	0.057
Hi Al	32	0.69	0.16	0.86	4.39	5.42	0.064	0.052
Hi Al	40	0.87	0.16	0.86	5.49	5.42	0.067	0.054
Hi Al	80	1.74	0.16	0.86	10.99	5.42	0.252	0.172
Lo Al	10	0.22	0.10	1.05	2.15	10.44	0.035	0.036
Lo Al	20	0.43	0.10	1.05	4.30	10.44	0.083	0.081
Lo Al	44	0.95	0.10	1.05	9.45	10.44	0.281	0.231
Hi Na	12	0.26	0.19	0.85	1.38	4.51	0.002	0.002
Hi Na	30	0.65	0.19	0.85	3.44	4.51	0.152	0.113
Hi Na	51	1.11	0.19	0.85	5.88	4.51	0.334	0.214
Hi Na	80	1.74	0.19	0.85	9.19	4.51	0.406	0.246
Lo Na	12	0.26	0.11	1.01	2.39	9.28	0.008	0.008
Lo Na	24	0.52	0.11	1.01	4.78	9.28	0.044	0.043
Lo Na	48	1.04	0.11	1.01	9.56	9.28	0.141	0.125
Hi Zr	8	0.17	0.09	0.58	2.00	6.63	0.025	0.014
Hi Zr	20	0.43	0.09	0.58	4.99	6.63	0.119	0.061
Hi Zr	32	0.69	0.09	0.58	7.98	6.63	0.335	0.145
Data from Current Study								
Run 1	22	0.47	0.46	0.50	1.02	1.09	<0.005	0.001
Run 2	31	0.67	0.74	0.50	0.90	0.68	<0.005	0.001
Run 3	16	0.34	0.13	0.50	2.62	3.85	<0.005	0.001
Run 4	16	0.35	0.69	0.50	0.50	0.73	<0.005	0.001
Run 5	15	0.32	0.13	0.50	2.47	3.85	<0.005	0.001
Run 6	32	0.69	0.13	0.50	5.29	3.85	0.082	0.038
Run 7	31	0.67	0.88	0.50	0.76	0.57	<0.005	0.001
Run 8	31	0.66	0.13	0.50	5.11	3.85	0.087	0.040
Run 9	16	0.35	0.87	0.50	0.40	0.58	<0.005	0.001
Run 10	22	0.48	0.33	0.50	1.44	1.52	<0.005	0.001
Run 11	23	0.50	0.34	0.50	1.49	1.49	<0.005	0.002
Run 11	32	0.69	0.34	0.50	2.07	1.49	<0.005	0.002
Run 11	53	1.15	0.34	0.50	3.43	1.49	0.248	0.098
Run 12	54	1.17	0.42	0.51	2.78	1.21	0.007	0.004
Run 12	90	1.95	0.42	0.51	4.63	1.21	0.330	0.127
Run 12	151	3.28	0.42	0.51	7.76	1.21	1.580	0.314
Run 13	24	0.53	0.12	0.48	4.58	4.16	0.077	0.034
Run 13	38	0.82	0.12	0.48	7.14	4.16	0.240	0.093
Run 13	55	1.19	0.12	0.48	10.34	4.16	1.340	0.275

loadings are listed in Table 7.15. For feed with the estimated maximum nitrate loading, approximately five times the nominal amount of formic acid would be required. To minimize the volume of formic acid required for redox adjustments, sugar may be added as an additional source of reduced carbon. Current design is based on a maximum of 30 ml 90 wt% formic acid per liter of feed.

It is estimated that a significant amount (~50%) of nitrate may be converted to nitrite via radiolysis reactions. The $HCOOH/NO_2^-$ requirement is expected to be less because NO_2^- is in a lower oxidation state than NO_3^-. Differences in kinetics and reaction mechanisms could result in differences in gas composition and release rates. Characterization and formating of actual DST waste currently being conducted at PNL will provide an estimate of the waste nitrite and nitrate content. Glass redox adjustments will also be evaluated. However, supplemental data collected from cold simulants containing nitrite and off gas compositional data is required to support this single data point.

7.6 MASS BALANCE

Development of a predictive model for glass redox (Fe^{+2}/Fe^{+3}) as a function of the amount of formic acid added and feed composition necessitates the spanning of two different chemistry systems: 1) formating during which

TABLE 7.15. Formic Acid Requirements Based on Reference Nitrate Loadings[(a)]

Level	Nitrate Concentration		Formic Acid Requirements, ml (90 wt%)/L	
	g NO_3/100 g WO	moles NO_3/L	$HCOOH/NO_3 = 3$	$HCOOH/NO_3 = 4$
Low	3	0.07	9	12
Nominal	9	0.20	27	37
High	36	0.78	108	143

(a) Current plans for HWVP are to add a maximum of 30 ml HCOOH/L. Additional reductant requirements will be met by adding sugar.

the formic acid is added and 2) vitrification, the product from which the Fe^{+2}/Fe^{+3} is measured. The presence of oxidized (e.g., CO_2) and reduced (e.g., NO_2, NH_3) species in the off gas suggests that redox reactions take place in both systems.

To establish a relationship between the products of both systems, a preliminary mass balance spreadsheet was developed for Runs 12 and 13 (refer to Table 7.16). Corresponding flowsheets are shown in Figures 7.5 and 7.6. The analytical data available for this flowsheet development are the initial concentration of nitrate and ferric ion in the simulant; the amount of formic acid added; the concentration of nitrate after formic acid addition and reflux (i.e., prior to vitrification); and the Fe^{+2}/Fe^{+3} ratio in the vitrified sample. Off gases shown for the formating step in Figures 7.6 and 7.7 (H_2, CO_2, N_2O and NO_x) were reported by Wiemers (1987). NH_3 was observed in formated simulants prepared in the current study. Goles and Nakaoka (1989) reported H_2, CO_2, CO, SO_x, NO_x, and NH_3 in the off gas of the melter.

The amount of reduced carbon (formate or formic acid) leaving the formating step was estimated based on the amount of nitrate reduced (assuming NH3 to be the end product):(a)

Reduced Carbon ("HCOOH") to melter = HCOOH added - [4 * nitrate reacted].

Both of these runs satisfied the requirements, $HCOOH/NO_3 \geq 3$ and $Fe/NO_3 < 4$, prescribed for obtaining a $Fe^{+2}/Fe^{+3} \geq 0.005$. Comparison of the run data indicates that the amount of nitrate reduced during the formating step is greater for low carbonate, high nitrate sample. For example, at approximately equivalent $HCOOH/NO_3$(~4.6), the moles of nitrate consumed per mole of formic acid added during formating was 0.20 for Sample 2, Run 12 compared with 0.0075 for Sample 1, Run 13. This effect may be due 1) a concentration effect on the reaction equilibrium imposed by the higher nitrate concentration (0.42 M for Run 12 versus 0.115 M for Run 13) and/or

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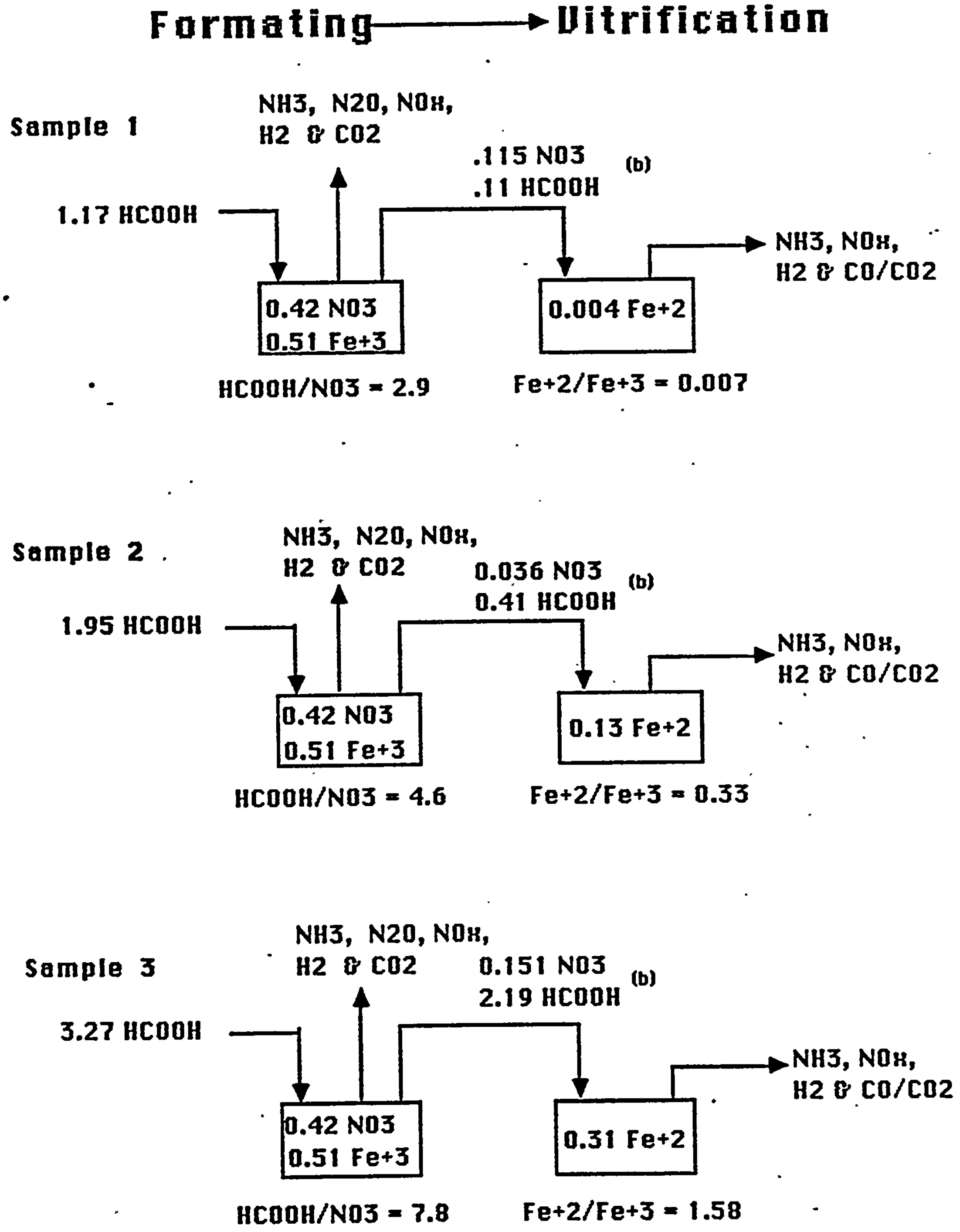
(a) Assuming the nitrate reduction product as NH_3 maximizes the estimate of carbon utilization in the formating step. The amount of ammonia produced was not quantified in this study.

TABLE 7.16. Mass Balance Spreadsheet

Run 12 (Low Carbonate Loading)	Preformate	Sample 1	Sample 2	Sample 3
NO_3 initial, M	0.42			
NO_3 remaining, M(a)		0.155	0.036	0.151
Total NO_3 consumed, M(a,b)		0.265	0.384	0.269
HCOOH added, M		1.17	1.95	3.27
HCOOH remaining, M(a,c)		0.11	0.41	2.19
HCOOH consumed, M(a,b)		1.06	1.54	1.08
Fe^{+3} initial, M	0.51			
Glass Fe^{+2}, M		0.004	0.13	0.31
$HCOOH/NO_3$		2.8	4.6	7.8
Glass Fe^{+2}/Fe^{+3}		0.007	0.33	1.58
Percent Efficiency for Nitrate Reduction in Formating Step				
NO_3 consumed/HCOOH added		23	20	8.2
Percent Efficiency for Fe^{+3} Reduction				
Fe^{+2} produced/HCOOH added		0.3	6.7	9
Run 13 (high carbonate loading)				
NO_3 initial, M	0.115			
NO_3 remaining, M(a)		0.111	0.057	0.002
Total NO_3 consumed, M(a,b)		0.004	0.058	0.113
HCOOH added, M		0.53	0.82	1.19
HCOOH remaining, M(a,c)		0.51	0.59	0.74
HCOOH consumed, M(a,b)		0.02	0.23	0.45
Fe^{+3} initial, M	0.48			
Glass Fe^{+2}, M		0.034	0.093	0.28
$HCOOH/NO_3$		4.7	7.1	10.3
Glass Fe^{+2}/Fe^{+3}		0.077	0.24	1.34
Percent Efficiency for Nitrate Reduction in Formating Step				
NO_3 consumed/HCOOH added		0.75	7.1	9.5
Percent Efficiency for Fe^{+3} Reduction				
Fe^{+2} produced/HCOOH added		6.4	11.3	24

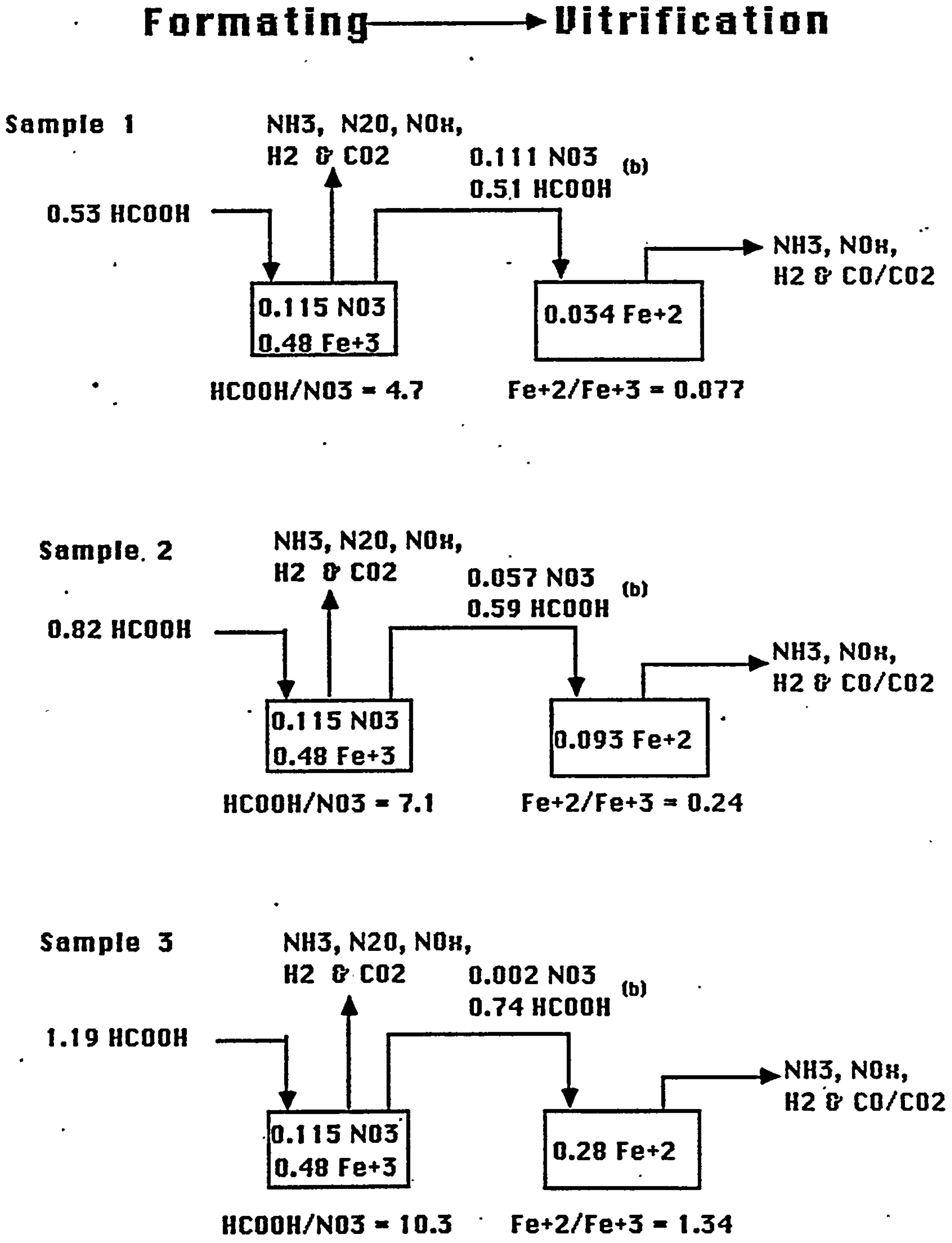
(a) Refers to formating step, only.
(b) Calculated by difference.
(c) Estimation based on nitrate consumption. Assumes NH_3 product.



(a) Amounts expressed in moles/L.

(b) Estimation based on nitrate consumption. Assumes NH3 as end product which minimizes carbon to melter.

FIGURE 7.5. Preliminary Mass Balance Flowsheet for Run 12



(a) Amounts expressed in moles/L.

(b) Estimation based on nitrate consumption. Assumes NH3 as end product which minimizes carbo to melter.

FIGURE 7.6. Preliminary Mass Balance Flowsheet for Run 13

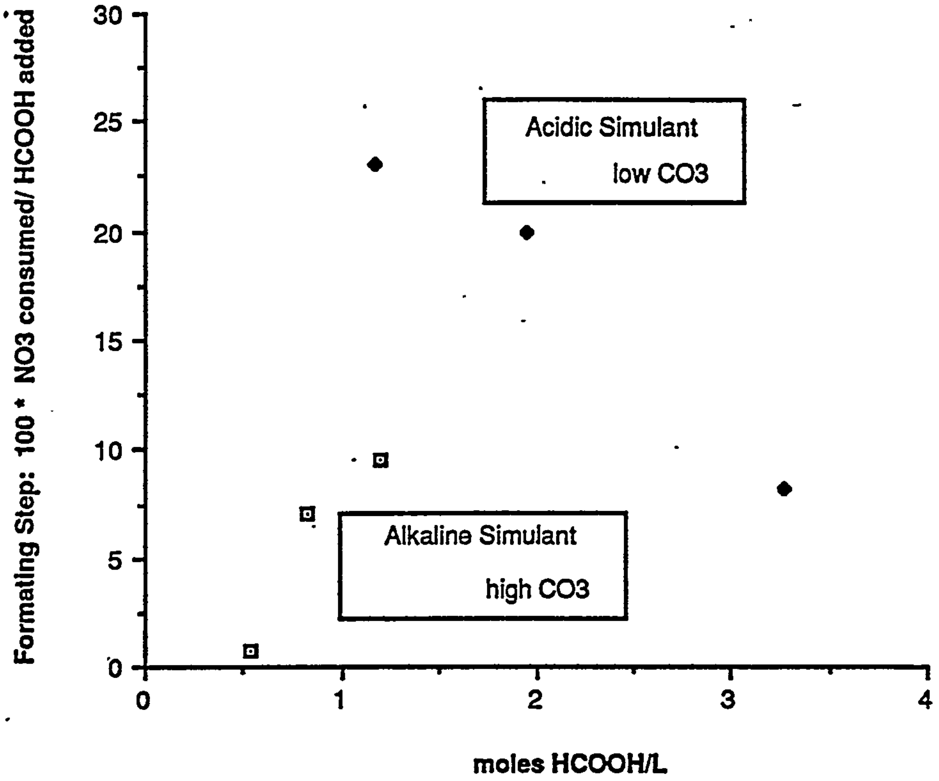


FIGURE 7.7. Nitrate Reduction Efficiency During Formating

2) the higher acidity of the low carbonate run (minimum pH for Run 12: 364; Run 13: 5-7). As discussed in Section 7.3.1 and Wiemers (1987) the redox potentials for reactions of interest are pH dependent. Figure 7.7 illustrates graphically the dependence of nitrate reduction during formating on carbonate concentration. It is speculated that to satisfy the threshold for Fe^{+3} reduction >0.5% ($HCOOH/NO_3$ = 3), the remaining nitrate is consumed during vitrification.

At equivalent $HCOOH/NO_3$, the amount of Fe^{+2} present in the vitrified sample per mole of formic acid added during formating (% efficiency for Fe^{+3} reduction), is independent of the carbonate and nitrate content. For example, at approximately equivalent $HCOOH/NO_3$, the % efficiency for Fe^{+3} reduction is 6.7 for Sample 2, Run 12 and 6.4 for Sample 1, Run 13. Also, for Sample 3, Run 12, the % efficiency for Fe^{+3} reduction is 9 which is reasonably close 11.3 for Sample 2, Run 13. Run 12 had low carbonate loading, while Run 13 has high carbonate loading. Figure 7.8 illustrates graphically

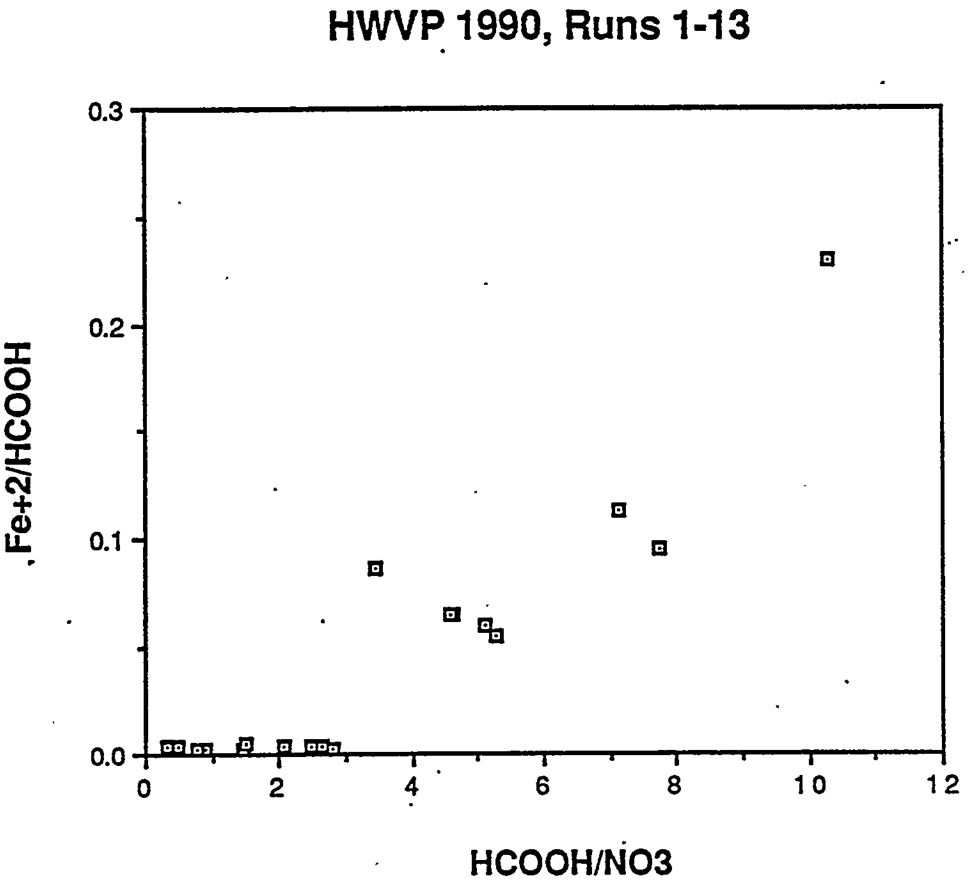


FIGURE 7.8. Relationship Between Ferrous Ion, Nitrate, and Formic Acid

the threshold value, $HCOOH/NO_3 = 3$ discussed previously and the fairly linear relationship between the moles of Fe^{+2} produced per mole of formic acid added as a function of $HCOOH/NO_3$. Data from Runs 1-13 is included in Figure 7.8.

The following scenario describing the relationship between the formic acid, nitrate, ferric ion, and carbonate is based on the above observations. The reduction of nitrate and ferric ion by formic acid are two competing reactions. At the loadings specified for the reference feed composition ($Fe^{+3}/NO_3 \leq 4$), the relationship, $HCOOH/NO_3 = 3$, must be satisfied before an equilibrium is reached yielding ≥0.5% of the ferric ion reduced to ferrous ion in the vitrified sample. The extent to which nitrate is reduced during formating (rather than during vitrification) depends on the pH; which is dependent on the carbonate content. The % nitrate reduction during formating ranged from 4 to 98%. Because the threshold for $HCOOH/NO_3$ is independent of the carbonate concentration, it is assumed that the same amount of nitrate is reduced independent of which step, vitrification or formating, the reduction reaction takes place. The implications of this suggestion for HWVP design relate to the most favorable step for release of the product gases.

8.0 HWVP APPLICATION

It has been demonstrated that nitrate content of pretreated NCAW does affect the glass redox adjustment requirements. In a nitrite- and organic-free feed simulant, where $Fe^{+3}/NO_3 \leq 4$, three moles of formic acid are required per mole of nitrate to obtain an acceptable reduction of Fe^{+3} ($\geq$0.5%). The effect of additional active redox participants on formic acid requirements remains to be established.

Secondary effects related to feed composition and laboratory vitrification conditions likely affect glass redox as implied by the data scatter in Figure 7.4. Quantitative relationships are not fully defined without further considering the SRAT and melter metals chemistry.

The formic acid requirement for glass redox adjustment was independent of carbonate feed content. However, carbonate may affect the HWVP operations from another perspective. Preliminary data (two data sets) suggests that by buffering the pH in the alkaline range, high carbonate loading results in less reduction of nitrate (i.e., less gas release) occurs during formating. With low carbonate loading and the resultant lower feed acidity, a larger amount of nitrate is reduced during formating. The impact of preferential release of gases may affect feed preparation steps and criteria.

Design considerations related to several qualitative observations recorded during this study are listed below. These observations are discussed in detail in Section 6.0.

- Ammonia was an end product of nitrate reduction by formic acid. The release rate of noxious (NH_3, NO_x, SO_x, and CO) and explosive (H_2, CO and NH_3 as NH_4NO_3) gases from the SRAT and melter need to be further defined to assess environmental emissions and potential hazards.

- The effect of magnetic solids in the formated feed on subsequent processing steps requires further consideration.

- An apparent dilatant melter feed resulted from feed formated to the level required for obtaining an acceptable Fe^{+2}/Fe^{+3} value in high nitrate feed. Addition of sugar for supplemental reductant capacity would minimize the formic acid requirements. However, the rheology of feed to which sugar is added to minimize formic acid requirements should be considered.

9.0 QUALITY ASSURANCE

Work authorized by this test plan was conducted in accordance with Impact Level II requirements as identified in Quality Assurance Plan No. WTC-006, latest revision for the HWVP. Test Plan, HWVP-89-1VJ0010300A was developed to support testing activities. All laboratory data, general observations, and details of the activities performed per this test plan were recorded in laboratory record books BNS #50597 and 53567.

ICP and Fe^{+2}/Fe^{+3} analyses was completed in accordance with guidance provided in SOW number M43108A. TIC and TC analyses was to be completed in accordance with guidance provided in SOW number M43108B and IC analyses per SOW number M43108C and M43108A.

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