Maximum Total Organic Carbon Limit for DWPF Melter Feed (U)

by
A. S. Choi
Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

DOE Contract No. **DE-AC09-89SR18035**

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P. O. Box 62, Oak Ridge, TN 37831; prices available from (423) 576-8401.

Available to the public from the National Technical Information Service. U. S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

708730

WSRC-TR-95-0119-TL (Revision 0)

March 13, 1995

MAXIMUM TOTAL ORGANIC CARBON LIMIT FOR DWPF MELTER FEED (U)

Distribution:

D. B. Amerine, 704-S
W. D. Kimball, 704-S
J. F. Ortaldo, 704-S
H. H. Elder, 704-S
M. J. Montini, 704-S
J. T. Carter, 704-25S
R. E. Edwards, 704-25S
M. Norton, 704-27S
D. C. Witt, 704-29S
J. E. Owen, 704-30S
D. C. Iverson, 704-30S
W. S. Odom, 704-30S
W. A. Mangiante, 992-1W

L. M. Papouchado, 773-A
E. W. Holtzscheiter, 773-A
M. J. Plodinec, 773-A
R. A. Jacobs, 704-T
N. H. Kuehn, 704-T
L. F. Landon, 704-T
C. T. Randall, 704-T
D. A. Crowley, 704-1T
J. R. Zamecnik, 704-1T
A. S. Choi, 704-1T (4)

TIM, 773-A (4)

INFORMATION ONLY

WESTINGHOUSE SAVANNAH RIVER COMPANY
INTER-OFFICE MEMORANDUM

WSRC-TR-95-0119-TL
(Revision 0)

March 13, 1995

Keywords: DWPF Melter, Total Organic Carbon, Off-Gas LFL, Cold Cap Model

Retention Period: Permanent

D. B. Amerine, Manager / DWPF
Westinghouse Savannah River Company

Attention: W. D. Kimball, 704-S

MAXIMUM TOTAL ORGANIC CARBON LIMIT FOR DWPF MELTER FEED (U)

The highest level of total organic carbon (TOC) that can be routinely allowed in DWPF melter feed was determined in this study to be about 24,000 ppm on an aqueous slurry basis. This maximum TOC limit is valid only when:

- The measured melter plenum temperature and the air purge to the backup film cooler (BUFC) are controlled and interlocked at 650 °C and 220 lb/hr, respectively, or above during feeding.
- The maximum peak magnitude of a melter off-gas surge is 3 times nominal with an average magnitude of 2.25 times nominal for the first 1 minute, and the total duration of a surge is up to 8 minutes.

If the peak magnitude of a surge is increased to 7 times nominal with an average magnitude of 4.75 times nominal during the first 1 minute as stated in the Basic Data Report (BDR), the maximum TOC limit is then reduced to about 17,000 ppm at the same melter plenum temperature and BUFC air purge rate as before. Based on discussions between SRTC and DWPF personnel, however, it was concluded that this 7X BDR surge scenario is overly conservative.

(Cont'd on the next page)

C. T. Randall, 704-T
Authorized Derivative Classifier

INFORMATION ONLY

This report describes the 4-stage cold cap and melter off-gas dynamics models as well as the bases and assumptions used to determine this TOC limit. The 4-stage cold cap model was validated earlier against the data obtained using the formic acid flowsheet feed. With a more oxidizing feed under the current nitric acid flowsheet, use of this model is believed to be conservative. Nevertheless, this conservatism still needs to be verified during the IDMS PX-7 run.

In addition, in view of recent DWPF melter startup data, the 3X off-gas surge criteria used in this study, including the 8 minute total surge duration and the first 1 minute surge at an average magnitude of 2.25 times nominal, appear to be conservative. However, this conservatism still needs to be verified by conducting a dynamic simulation study using recent melter startup data. SRTC recommends that DWPF review the adequacy of the 3X surge criteria used in this study based on their operating experience, and confirm adequate conservatism prior to implementing the maximum TOC limit of 24,000 ppm in the Process Requirements for melter feed preparation (PR-SO4).

EWHoltzscheiter
E. W. Holtzscheiter, Manager
SRTC-DWPT Section

DOCUMENT APPROVAL

Author, Process Modeling and Control, DWPT/SRTC

3/27/95
Date

Technical Reviewer, Process Cognizant Engineer, DWPF

3/27/95
Date

Manager, Process Modeling and Control, DWPT/SRTC

3/27/95
Date

Manager, Process Cognizant Engineering, DWPF

3/27/95
Date

WESTINGHOUSE SAVANNAH RIVER COMPANY
SAVANNAH RIVER TECHNOLOGY CENTER

WSRC-TR-95-0119
(Revision 0)

March 13, 1995

Keywords: DWPF Melter, Total Organic Carbon, Off-Gas LFL, Cold Cap Model

Retention Period: Permanent

MEMORANDUM

To: C. T. Randall, 704-T

From: A. S. Choi, 704-1T

MAXIMUM TOTAL ORGANIC CARBON LIMIT FOR DWPF MELTER FEED (U)

SUMMARY

DWPF recently decided to control the potential flammability of melter off-gas by limiting the total carbon content in the melter feed and maintaining adequate conditions for combustion in the melter plenum. With this new strategy, all the LFL analyzers and associated interlocks and alarms were removed from both the primary and backup melter off-gas systems.[1] Subsequently, D. Iverson of DWPF-T&E requested that SRTC determine the maximum allowable total organic carbon (TOC) content in the melter feed which can be implemented as part of the Process Requirements for melter feed preparation (PR-SO4).

The maximum TOC limit thus determined in this study was about 24,000 ppm on an aqueous slurry basis. At the TOC levels below this, the peak concentration of combustible components in the quenched off-gas will not exceed 60% of the LFL during off-gas surges of magnitudes up to 3 times nominal, provided that the melter plenum temperature and the air purge rate to the BUFC are monitored and

C. T. Randall, 704-T
Authorized Derivative Classifier

controlled above 650 °C and 220 lb/hr, respectively. Appropriate interlocks should discontinue the feeding when one or both of these conditions are not met. Both the magnitude and duration of an off-gas surge have a major impact on the maximum TOC limit, since they directly affect the melter plenum temperature and combustion. The 3X surge criteria used in this study assume a peak magnitude of 3 times nominal with an average magnitude of 2.25 times nominal during the first 1 minute and a total duration of 8 minutes. Although the data obtained during recent DWPF melter startup tests showed that the peak magnitude of a surge can be greater than 3 times nominal, the observed duration was considerably shorter, on the order of several seconds. The long surge duration assumed in this study has a greater impact on the plenum temperature than the peak magnitude, thus making the maximum TOC estimate conservative.

Two models were used to make the necessary calculations to determine the TOC limit. The 4-stage cold cap model was validated against the formic acid flowsheet data,[2] and used to calculate the compositions of glass and calcine gas. The calcine gas composition was then used in the melter off-gas dynamics model to predict the simultaneous transient responses by the off-gas system parameters during surges including flammability. This report describes these models briefly as well as the key bases and assumptions used.

INTRODUCTION

One of the critical design and operating requirements for the DWPF melter off-gas system is to maintain the concentration of combustible components in the melter off-gas at the discharge of the Quencher below 60% of its lower flammable limit (LFL) at off-gas flow rates 3 times nominal.[3] According to the NFPA Code 69,[4] this 60% LFL limit is applicable only when automatic instrumentation with safety interlocks is provided to control the concentration of combustible components. Therefore, the LFL analyzers were initially installed in both the primary and backup off-gas systems to monitor the concentration of combustible components directly, and were set to interlock off the feeding at 20% of the LFL anticipating a maximum 3-fold increase in combustibles concentration during off-gas surges.

However, in light of frequent calibration and general maintenance requirements, the usefulness of these LFL analyzers was questioned seriously when the actual LFL readings obtained during the startup tests were considerably lower than the 60% LFL limit due to high plenum temperature even during off-gas surges. The potential benefits of the LFL analyzers were also weighted against the tight space constraints in the canyon. DWPF eventually decided to control the potential off-gas flammability by limiting the total carbon level in the feed in conjunction with maintaining adequate conditions for combustion, thereby removing all the LFL analyzers and associated interlocks and alarms from both melter off-gas systems.[1]

With no LFL analyzers in place, it then became mandatory to monitor any operating variables that can contribute to the potential off-gas flammability and devise necessary safety interlocks in order to comply with the NFPA Code 69. It was determined during the ninth Scale Glass Melter campaign (SGM-9) that there are three key operating variables that impact the combustion of carbon compounds in the melter;[5] (1) carbon content in the feed, (2) melter plenum temperature, and (3) air supply to the melter. Based on an earlier study,[6] DWPF currently has a melter feed interlock at 220 lb/hr of BUFC air flow to ensure adequate air supply for combustion. The minimum effective melter plenum temperature was specified as 650 °C to ensure that the design melt rate is achieved, to keep the plenum space free of glass buildup, and to burn the hydrocarbons not consumed within the cold cap.[3] The data from pilot melter runs at TNX, however, showed that the combustion efficiency was still nearly complete at plenum temperatures around 450-550 °C.[5,7,8] Nevertheless, DWPF has decided to add a melter feed interlock at 650 °C measured plenum temperature to ensure adequate combustion even under the worst-case operating conditions, i.e., off-gas surges, and to make sure that the other potential benefits are not overlooked.

With the melter plenum temperature and the air purge rate to the BUFC set at their minima, the objective of this study was then to determine the maximum allowable TOC content in the melter feed to ensure that the 60% LFL limit is not exceeded under all operating conditions, including startup and shutdown.

OVERVIEW OF MODELS

Figure 1 shows the overall mass flow scheme used to model the physical and chemical events taking place inside the melter.[2] The slurry feed is first split into volatile and nonvolatile components prior to any calculations. The volatile components of the feed such as H_2O and light aromatic compounds are vaporized upon entering the melter, and fed to the plenum reactor, whereas the remaining nonvolatile feed components are fed to the cold cap reactor, where they are gradually heated, and undergo dehydration, decomposition and redox reactions, before the final oxide products are fused into the glass matrix. The calcine gases are fed to the plenum reactor and further react with the volatile feed components in the presence of excess air. During off-gas surges, the melter plenum temperature and pressure, the melter pressure control air flow, and the gas residence time all vary simultaneously. The efficiency of the plenum combustion is influenced by these dynamic conditions in the melter plenum, and the off-gas flammability downstream of the melter is entirely determined by this combustion efficiency and the availability of dilution air. In this section, an overview of the two models is given that were used to quantify the effects of the key melter operating variables on the efficiency of the melter reactions and the off-gas flammability.

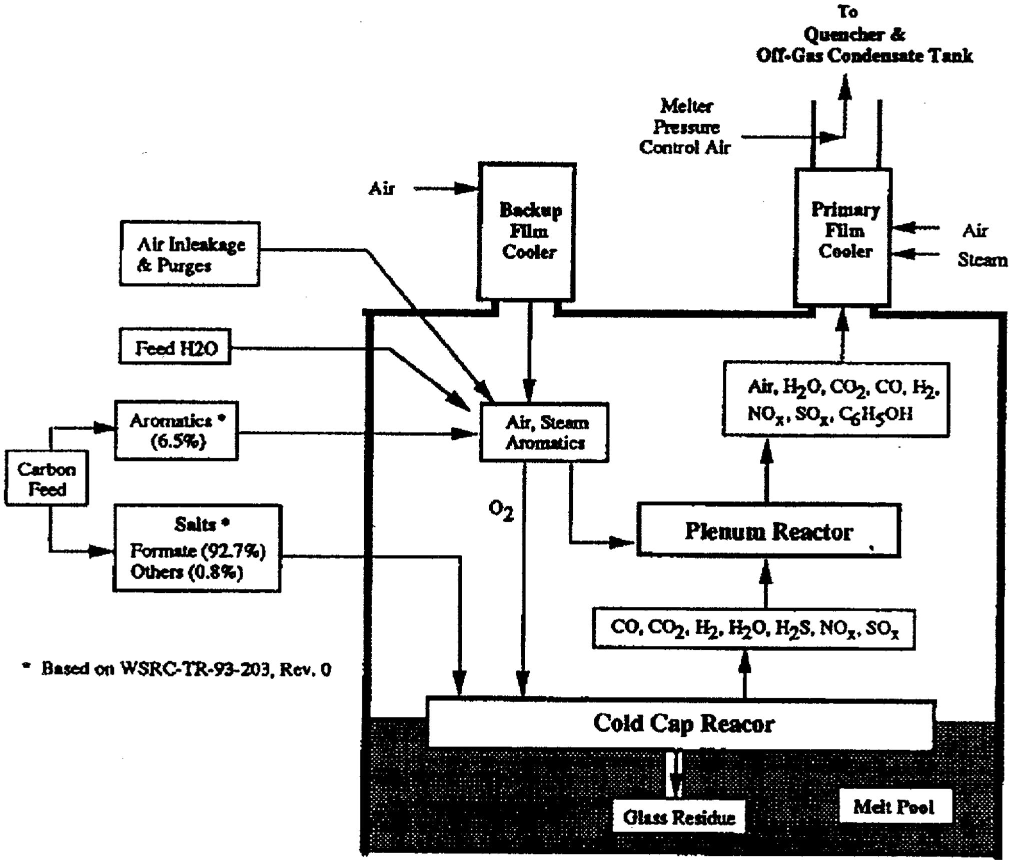


FIGURE 1. Schematic of Overall Carbon Flows during Melter Reactions.

4-Stage Cold Cap Model

A detailed modeling of the vitrification of the high level radioactive waste is quite complicated mainly due to:

- A very large number of elements and chemical species present in waste.
- Simultaneous physical and chemical changes occurring over a narrow region with a steep temperature gradient.
- Lack of physical, transport and kinetic data for the cold cap phenomena.

- Extensive solution nonideality existing in a waste glass melt.

- Complex spatial boundary of a cold cap.

The approach taken initially to overcome these difficulties was to assume that all the chemical events occurring in the cold cap were at thermodynamic equilibrium and to ignore the effects of chemical kinetics and transport resistances.[9,10] The resulting model, however, could not explain the experimentally observed glass redox ratio and calcine gas composition consistently. Some of the shortcomings of this early attempt were partially overcome in the 4-stage cold cap model which approximates the melting process as a continuous, multistage process consisting of a series of simple, recognizable physical and chemical events that are similar to those observed by differential scanning calorimetry and X-ray diffraction experiments.[11] The 4-stage cold cap model was validated earlier against the data obtained under the formic acid flowsheet conditions.[2] A detailed description of the model is given elsewhere,[2] and only its key features are highlighted next.

Model Structure

The 4-stage cold cap model assumes that the entire process of decomposing and melting the melter feed solids is carried out in the following four distinct stages:

Stage 1: Decomposition of formates, hydroxides and nitrates to oxides and gaseous products at 700 °C.

Stage 2: Decomposition of carbonates and sulfates (partial) to oxides and gaseous products at 900 °C. A first liquid form appears.

Stage 3: Formation of multiple oxides of a spinel type such as Fe_3O_4 and $NiFe_2O_4$ and a solid solution among them at 1,050 °C. Formation of $LiAlO_2$, $LiBO_2$, etc. by chance substitution in silicate phase.

Stage 4: Final fusion into glass matrix at 1,150 °C.

The equilibrium compositions of gas and solids products from each stage are then calculated to be the ones that minimize the total Gibbs free energy for that stage. Once the calculation for one stage is converged, the gas product is fed to the next stage above, while the solids product is fed to the next stage below, thus establishing a gas-solids countercurrent flow between adjacent stages. Once the equilibrium compositions are determined for all stages, the overall mass balance is checked for the entire system. The stage calculations are repeated until the overall mass balance is checked within a specified tolerance.

Model Database

The validity of the 4-stage cold cap model is determined strongly by how closely the actual melting process approaches the thermodynamic equilibrium conditions and also by the accuracy of the Gibbs free energy database used. Moreover, one of the key factors affecting the accuracy of the calculations is a reasonable treatment of the solution nonideality that exists among many solution phases appearing during the course of melting the waste/frit mixture. For systems higher than ternary, the theoretical treatment of the activity coefficients becomes exceedingly complicated. As stated earlier, typical feed streams to the high level waste glass melter have an enormous number of chemical constituents to be calcined and melted into glass, which makes a detailed theoretical treatment of the solution nonideality that could exist among those species beyond our reach at the present time.

For this reason, the Gibbs free energy database for complex liquids developed at the National Institute of Standards and Technology (NIST) are used in lieu of activity coefficients to partially account for the solution nonideality problem. The basis for the NIST free energy database was the assumption that the strong interactions present in the mixture result from the formation of complex liquids and solids with identifiable stoichiometry and Gibbs free energy of formation.[12] The NIST free energy database are fitted into a six-coefficient equation of the form:

$$\Delta G_f(T) = a / T + b + c\,T + d\,T^2 + e\,T^3 + f\,T \ln T, \quad \text{J/mole} \qquad (1)$$

Due to the limitations of the STGSOL software which the 4-stage cold cap model is based on,[13] the NIST free energy data were converted into a three-coefficient equation form. Currently, the NIST free energy database contains the data for 112 chemical compounds, and lacks the data for species containing several elements that are of interest to us such as B. For those species, the free energy of formation for pure compounds were used.[14]

Revised Melter Off-Gas Dynamics Model

A detailed modeling of the plenum combustion to predict the off-gas flammability is also quite complicated mainly due to:

- Complex fluid mixing pattern induced by several gas inlets.
- Complex radiative heat transfer in the plenum among lid heaters, refractory, and the dynamic melt surface, making the prediction of the gas temperature profile difficult.

- Uncertainties associated with the fate of aromatic compounds upon entering the melter.

- Difficulties in measuring the cold cap off-gas compositions to verify those calculated by the model.

In the global reaction scheme used by the early model,[10] heavy aromatic components of the feed were assumed to be decomposed into CO and H_2 without participating in the cold cap reactions. The oxidation of free aromatics, CO, and H_2 was then modeled by using the modified kinetic expressions from the literature and by approximating the plenum as a well-mixed reactor. The effects of process dynamics on the combustion efficiency and the off-gas flammability were not considered. No attempt was made to compare the calculated off-gas compositions to the experimental data.

A spreadsheet model, called MOG LEL model, was next developed using the empirical correlations for the overall efficiency of CO and H_2 oxidation.[2] The correlations were developed from the SGM-9 data by assuming predecomposition of heavy aromatic components into CO and H_2, as in the earlier model.[10] The composition of calcine gases was provided by the 4-stage cold cap model. In order to account for the effects of process dynamics, the melter off-gas dynamics model was first run to determine the worst-case system responses for combustion during off-gas surges such as the minimum gas temperature and dilution air flow, and they were subsequently used in the MOG LEL model to predict the combustion efficiency and the off-gas flammability. It was not surprising that the resulting predictions were sometimes very conservative since all the worst-case system responses were assumed to occur simultaneously. During this study, the melter off-gas dynamics model was revised to include the kinetics of CO and H_2 oxidation in the melter plenum, which enabled a simultaneous calculation of combustion kinetics and process dynamics, thereby increasing the accuracy of predictions and reducing the degree of conservatism in them.

Kinetics of CO and H_2 Oxidation

The kinetic expressions for CO and H_2 oxidation included in the melter off-gas dynamics model were also derived from the SGM-9 data by making the following assumptions:

- First-order reactions, i.e.,

$$-r_{CO} = k_{CO} C_{CO} \tag{2}$$

$$-r_{H_2} = k_{H_2} C_{H_2} \tag{3}$$

where $-r$'s are the reaction rates in lbmoles/ft^3/sec, k's the first-order rate constants in 1/sec, and C's the concentrations in lbmoles/ft^3.

- The melter plenum is a constantly-stirred tank reactor (CSTR). So,

$$k_{CO} = \frac{v_i C_{CO,i} X_{CO}}{v_o C_{CO} \tau} \tag{4}$$

$$k_{H_2} = \frac{v_i C_{H_2,i} X_{H_2}}{v_o C_{H_2} \tau} \tag{5}$$

where v's are the volumetric flow rates in ft^3/sec, X's the fractional conversions, τ the residence time in seconds, and the subscripts i and o denote the inlet and outlet, respectively.

- Constant density. So,

$$C_{CO} = C_{CO,i}(1-X_{CO}) \tag{6}$$

$$C_{H_2} = C_{H_2,i}(1-X_{H_2}) \tag{7}$$

- Predecomposition of aromatic compounds as follows:

$$C_6H_5OH + 2\ 1/2\ O_2 \dashrightarrow 6\ CO + 3\ H_2 \tag{8}$$

$$(C_6H_5)_2 + 6\ O_2 \dashrightarrow 12\ CO + 5\ H_2 \tag{9}$$

$$(C_6H_5)_2C_6H_4 + 9\ O_2 \dashrightarrow 18\ CO + 7\ H_2 \tag{10}$$

$$(C_6H_5)_2NH + 7\ O_2 \dashrightarrow 12\ CO + 5\ 1/2\ H_2 + NO_2 \tag{11}$$

$$C_6H_4NO_2(OH) + 2\ 1/2\ O_2 \dashrightarrow 6\ CO + 2\ 1/2\ H_2 + NO_2 \tag{12}$$

$$2\ C_6H_5C_6H_4OH + 11\ O_2 \dashrightarrow 24\ CO + 10\ H_2 \tag{13}$$

$$2\ C_6H_5B(OH)_2 + 2\ 1/2\ O_2 \dashrightarrow B_2O_3 + H_2O + 2\ C_6H_6 \tag{14}$$

$$2\ C_6H_5NH_2 + 6\ O_2 \dashrightarrow 12\ CO + 7\ H_2 + N_2 \tag{15}$$

$$2\ C_6H_5NHCHO + 6\ O_2 \dashrightarrow 14\ CO + 7\ H_2 + N_2 \tag{16}$$

$$2\,C_6H_5NO + 6\,O_2 \dashrightarrow 12\,CO + 5\,H_2 + 2\,NO \qquad (17)$$

$$2\,C_6H_5NO_2 + 6\,O_2 \dashrightarrow 12\,CO + 5\,H_2 + 2\,NO_2 \qquad (18)$$

$$C_6H_6 + 3\,O_2 \dashrightarrow 6\,CO + 3\,H_2 \qquad (19)$$

The use of the apparent first-order kinetics shown in Eqs. 2 and 3 are justified, since oxygen was present several times in excess of the stoichiometric requirement during the SGM-9 run.[5] The constant-density assumptions made in Eqs. 6 and 7 were based on the fact that the fuel concentrations were low at both the inlet and outlet of the plenum reactor.

The calculated values of k's at different temperatures are shown in Table 1. The logarithms of these rates were then plotted against 1/T in Figures 2 and 3 to obtain the first-order rate parameters, k_o and E_a:

$$k_{CO} = k_{o,CO}\exp(-E_{a,CO}/RT) \qquad (20)$$

$$k_{H_2} = k_{o,H_2}\exp(-E_{a,H_2}/RT) \qquad (21)$$

where k_o's are the preexponential factors in 1/sec, and E_a's the activation energies in Btu/lbmole. The values for these apparent first-order rate parameters thus determined are tabulated in Table 2.

TABLE 1. Apparent First-Order Rate Constants for CO and H_2 Oxidation

Case	Gas Temp (^oC)	k_{CO} (1/sec)	k_{H2} (1/sec)	Residence Time (sec)
1	479	0.4669	0.6203	6.8
2	393	0.2430	0.2530	7.4
3	395	0.2569	0.2688	8.2
4	484	0.5023	0.9923	6.5
5	515	1.2363	1.4706	6.8

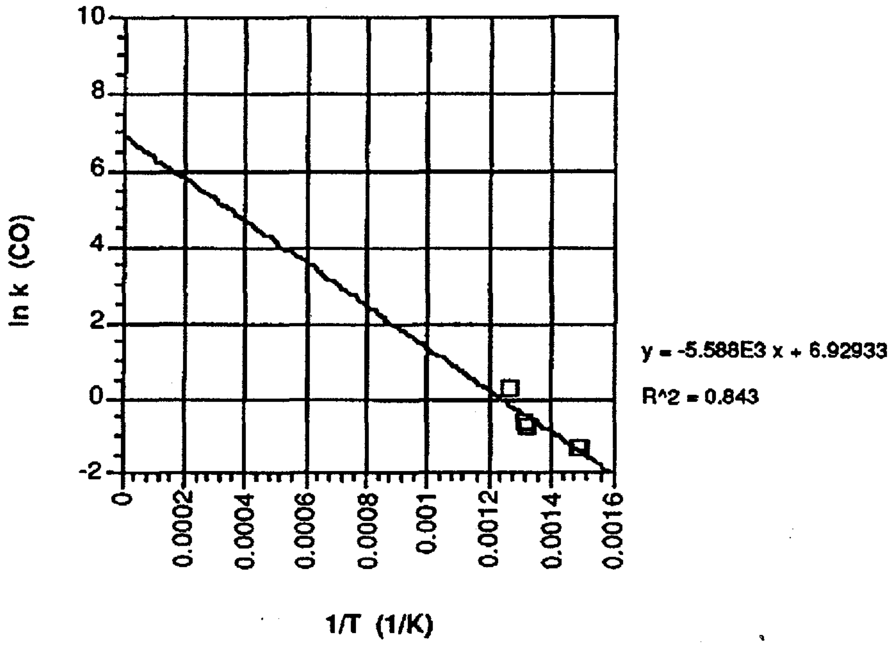


FIGURE 2. Rate Constants for CO Oxidation vs 1/T during SGM-9 Run

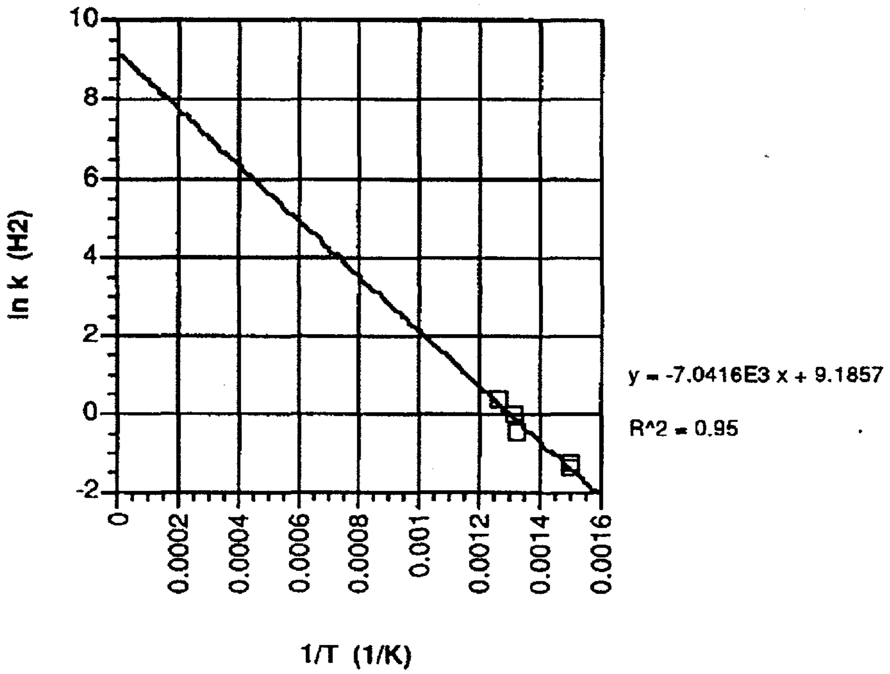


FIGURE 3. Rate Constants for H_2 Oxidation vs 1/T during SGM-9 Run

TABLE 2. Apparent First-Order Rate Parameters for CO and H_2 Oxidation during SGM-9 Run

	k_o (1/sec)	E_a (Btu/lbmole)
CO	1021.8	19974.3
H_2	9756.6	25170.2

Model Revision

The melter off-gas dynamics model has been used extensively in DWPF to study the dynamic responses by the entire melter off-gas system under many transient conditions such as off-gas surges, switchover and switchback between the primary and backup off-gas systems, initial startup and idling, feed tube flushing, etc.[15,16] All the controller hardwares and software logic currently used in the DWPF melter off-gas system are simulated by this model. A detailed description of the model is given elsewhere.[15,16] During this study, the apparent first-order rate parameters shown in Table 2 were added to this model along with the rate equations, Eqs. 2 and 3. Instantaneous dynamic responses by the system under various upset scenarios can now be reflected in the calculation of combustion kinetics As stated earlier, however, this revised model still needs the input from the 4-stage cold cap model in order to predict the off-gas flammability from a given feed composition.

BASES AND ASSUMPTIONS

The overall approach taken to determine the maximum TOC limit was first to fix the formate carbon level in the feed at the maximum set by the bounding redox condition and then to increase the aromatic carbon level until the calculated concentration of combustible components in the off-gas equals 60% of the LFL under the worst-case operating scenario. To do so, the following process bases and assumptions were used:

- The composition of the reference DWPF melter feed is represented by that given in Table 3, which was calculated using the Tanks 42/51 blend sludge and the blend salt, and has the following characteristics:[17]

- nitrates (N) = 0.485 molar
- formates (F) = 0.705 molar
- formate carbons = 6,367 ppm (aqueous slurry basis)
- aromatic carbons = 447 ppm (aqueous slurry basis)

- The nitrate level is fixed at 0.485 molar, and the formate level is increased to the maximum at F - N = 0.5 molar or F = 0.985 molar. The corresponding maximum formate carbon level is equal to 8,900 ppm.

- The measured melter plenum temperature is maintained at the minimum value of 650 °C, which is equivalent to an actual gas temperature of about 470 °C.[2]

- The air purge to the BUFC (FCV-3221B) is maintained at the minimum value of 220 lb/hr.[6]

- The worst-case operating scenario for potential flammability in the off-gas system is assumed to be when the total off-gas flow including the combustible components is increased to three times the nominal at the peak of an off-gas surge, as stated in the Basic Data Report.[3]

  This 3X off-gas surge is assumed to proceed as follows: At time zero, both condensable and noncondensable flows are increased from 1X to 3X nominal, then linearly decreased to 1.5X nominal during the first 1 minute, and further decreased linearly 1X nominal during the next 7 minutes.

- Under the conditions described above, the aromatic carbon content in the feed will be increased from nominal 447 ppm to a value where the calculated peak concentration of combustible components in the quenched off-gas becomes 60% of the LFL.

RESULTS AND DISCUSSION

To describe the vitrification chemistry for the melter feed composition given in Table 3, a total of 18 elements and 100 or so chemical species made of these elements were considered in the thermodynamic equilibrium calculations. Table 4 lists these elements and all the chemical species considered in each phase. Each one of the species included in the Invariant Condensed Phase was allowed to form a separate phase by itself. All the species in the Melt Phase have a letter "l" after their names, which denotes a liquid state, and so they all formed one liquid phase. The species in the Spinel Phase were allowed to form a solid solution, as discussed earlier.[2]

TABLE 3. DWPF Melter Feed Composition from Reference 9, WSRC-TR-93-203 (Rev. 0)

Formate/Nitrate Species	lb/hr
Ca(COOH)2	3.902E-02
Ca(NO3)2	2.607E+00
Co(COOH)2	2.045E-04
Co(NO3)2	0.000E+00
CsCOOH	2.135E-01
CsNO3	5.308E-04
Cu(COOH)2	1.548E+00
Cu(NO3)2	0.000E+00
KCOOH	9.477E+00
KNO3	3.146E-02
Mg(COOH)2	3.249E+00
Mg(NO3)2	0.000E+00
Mn(COOH)2	2.349E+00
Mn(NO3)2	0.000E+00
NH4COOH	0.000E+00
NH4NO3	2.438E-03
NaCOOH	6.296E+00
NaNO3	1.584E+01
Ni(COOH)2	4.172E-02
Ni(NO3)2	0.000E+00
Pb(NO3)2	4.217E-05
Pd(NO3)2	0.000E+00
Sr(COOH)2	1.789E-03
Sr(NO3)2	2.798E-02
UO2(COOH)2	7.923E-08
UO2(NO3)2	9.601E-05
Y(COOH)3	7.190E-04
Y(NO3)3	1.004E-02
Zn(COOH)2	6.100E-02
Zn(NO3)2	0.000E+00
Total_1 =	4.180E+01
COOH - NO3, M	2.196E-01
Total COOH salt	2.328E+01
Toal NO3 salt	1.852E+01

Organic Species	lb/hr
(C6H5)2	0.000E+00
(C6H5)2C6H4	6.362E-02
(C6H5)2NH	0.000E+00
C6H5B(OH)2	0.000E+00
C6H5C6H4OH	4.791E-02
C6H5NH2	1.612E-04
C6H5NHCHO	1.786E-01
C6H5NO	2.919E-03
C6H5NO2	5.923E-03
C6H5OH	4.956E-02
C6H6	0.000E+00
(CH3)2CHOH	0.000E+00
CH3OH	0.000E+00
Total_2 =	3.487E-01
stoichiometric O2 req'd to burn 100% organics =	4.544E+00

Total Feed	
(lb/hr) =	5.990E+02
(GPM) =	9.005E-01
Carbon Feeds	**lb/hr**
Formate	3.819E+00
Aromatic	2.681E-01
Misc	3.211E-02
Total Carbon	4.120E+00

Other Inorganic Species	lb/hr	Other Inorganic Species	lb/hr
Ag	1.245E-02	PbCO3	2.800E-04
Al2O3	1.028E+01	PbSO4	9.870E-02
B2O3	1.296E+01	PuO2	8.545E-03
Ba(OH)2	0.000E+00	Rh	1.751E-03
BaSO4	2.336E-01	Ru	8.130E-03
Ca(OH)2	0.000E+00	SiO2	1.260E+02
Ca3(PO4)2	2.407E+00	TcO2	2.888E-03
CaC2O4	6.364E-02	ThO2	1.343E-01
CaF2	1.646E-02	TiO2	7.645E-01
CaO	3.131E-03	U3O8	2.328E+00
CaSO4	5.472E-02	Zeolite	2.187E-03
Cr2O3	1.757E-01	ZnO	7.215E-02
Cs2O	2.480E-04	hyd H2O	6.326E+00
CuO	2.347E-02	H2O	3.337E+02
Fe2O3	2.373E+01		
H2C2O4	7.563E-02	Total_3 =	5.568E+02
H3BO3	8.076E+00		
Hg	2.412E-01		
K2O	1.125E-01		
Li2O	1.134E+01		
MgO	3.526E+00		
MnO2	2.026E+00		
MoO2	1.690E-03		
NH4OH	8.660E-02		
Na2O	1.114E+01		
Na2SO4	4.246E-01		
Na3PO4	1.020E-02		
NaCl	3.386E-02		
NaF	3.348E-02		
NiO	2.937E-01		

TABLE 4. Elements and Chemical Species Considered in 4-Stage Cold Cap Model

Element	Phase			Invariant Condensed Phase
	Gas	Melt	Spinel	
O	O_2	Al_2O_3 l	$CaFe_2O_4$	Al_2O_3
C	CO	$Al_6Si_2O_{13}$ l	$FeAl_2O_4$	CaO
H	CO_2	$CaFe_2O_4$ l	$MgFe_2O_4$	$CaSO_4$
N	N_2	CaO l	$CuFe_2O_4$	Cu
S	NO	Ca_2SiO_4 l	$NiFe_2O_4$	Cu_2O
Si	NO_2	$FeAl_2O_4$ l	$MgAl_2O_4$	CuO
Na	N_2O_5	Fe_2SiO_4 l	$MnAl_2O_4$	FeO
Li	N_2O	FeO l	$NiAl_2O_4$	Fe_2O_3
Fe	H_2	Fe_3O_4 l	Fe_3O_4	Fe_3O_4
Al	H_2O	K_2SiO_3 l	Fe_2O_3	FeS
Mn	SO_2	$KAlO_2$ l	FeO	K_2O
Ca	SO_3	K_2O l	MgO	Li_2O
Mg	H_2S	Li_2O l	CaO	MnO
Ni	NH_3	$LiAlO_2$ l	Al_2O_3	Mn_2O_3
K	$NaBO_2$ g	MgO l	NiO	Mn_3O_4
B	$LiBO_2$ g	$MgSiO_3$ l	CuO	MgO
Cu	KBO_2 g	Na_2O l		Na_2O
Cs	$CsBO_2$ g	Na_2SiO_3 l		Ni
	B_2O_3 g	$Na_2Si_2O_5$ l		NiO
		SiO_2 l		Ni_3S_2
		B_2O_3 l		SiO_2
		$CsBO_2$ l		Na_2SO_4
		KBO_2 l		$CsBO_2$
		$LiBO_2$ l		
		$NaBO_2$ l		

The equilibrium compositions of glass and calcine gas calculated by the 4-stage cold cap model are shown in Tables 5 and 6, respectively. From Table 5, the glass redox ratio, Fe(II) / Fe(total), is calculated to be 0.05. This value is well within the current redox limit of less than 0.1, and close to what would be expected from a melter feed having a (F - N) value of 0.22 molar.

On the other hand, in Table 6, the calculated concentrations of CO and H_2 in the calcine gas are shown to be zero, indicating that in the presence of excess oxygen generated by the decomposition of nitrates, 100% of CO and H_2 were oxidized to CO_2 and H_2O, respectively. This was a direct consequence of the thermodynamic equilibrium which assumes 100% efficiency. We expect that at 700 °C and with excess oxygen, the conversion of CO and H_2 would be quite high but not as high as 100% due to inherent inhomogeneity in transport resistances and gas-solids mixing in the cold cap. Unfortunately, no data are available at the present time that can be used to infer just how efficient these cold cap reactions can be under the current nitric acid flowsheet conditions.

Combustible species are generated in the cold cap by the following decomposition scheme shown for a bivalent metal formate:

$$M(COOH)_2 = MO + CO_2 + CO + H_2 \qquad (22)$$

With a more reducing feed under the formic acid flowsheet, i.e., F - N = 0.71 molar, the molar ratio of CO to CO_2 in the cold cap off-gas was measured earlier to be about 0.15 by turning off the lid heaters and maintaining the melter plenum temperature below 430 °C.[7] In this study, the calculated concentrations of CO and CO_2 in Table 6 were adjusted to match this molar ratio, and the concentration of H_2 was also adjusted to be 1/2 of the molar sum of CO and CO_2, as indicated by Eq. 22. In doing so, the oxidizing effects of the nitrates were totally ignored, thereby making the concentration of combustible components fed to the plenum reactor conservatively high.

The results of subsequent calculations made using the revised melter off-gas dynamics model are shown in Figures 4 and 5. At a TOC level of 24,000 ppm in the feed, Figure 4 shows that the peak concentration of combustible components in the quenched off-gas is just under 60% of the LFL during a 3X off-gas surge. When 8,900 ppm of formate carbon is subtracted from this TOC, the remaining aromatic carbon level is 15,100 ppm, which is equivalent to 76% aromatic carbon removal across the Salt and Chemical Processing Cells.

Figure 5 also shows that the minimum melter pressure control air flow is about 380 lb/hr, as the melter pressure is varied between -4 and -6 "wc. The minimum gas temperature in the melter plenum during the 3X surge is shown in Figure 4 to

TABLE 5. **Glass Compositions Calculated using 4-Stage Cold Cap Model with DWPF Melter Feed Given in Table 1. (gmoles/hr)**

Silicate Phase:

SiO_2 l	773.131	Na_2SiO_3 l	146.151
$LiBO_2$ l	225.587	$LiAlO_2$ l	91.440
K_2SiO_3 l	24.866	MgO l	23.215
Li_2O l	13.486	Ca_2SiO_4 l	6.947
Fe_3O_4 l	4.599	$CaFe_2O_4$ l	2.921
KBO_2 l	2.612	FeO l	2.060

Spinel Phase:

$MgFe_2O_4$	29.366	Fe_2O_3	27.186

Invariant Condensed Phase:

Mn_3O_4	5.977	Cu_2O	2.287
NiO	1.910	$CaSO_4$	1.527

TABLE 6. **Comparison of Cold Cap Off-Gas Compositions for DWPF Melter Feed Given in Table 1.**

	Calculated by 4-stage cold cap model		Adjusted for plenum combustion
	(mole %)	(wt%)	(wt%)
H_2O	56.30	37.85	25.30
CO_2	25.19	41.35	43.44
CO	0.00	0.00	4.09
H_2	0.00	0.00	1.08
O_2	9.78	11.68	18.22
N_2	8.73	9.12	7.87
Total	100.00	100.00	100.00

FIGURE 4. 3X OFF-GAS SURGE WITH MIN BUFC AIR & PLENUM TEMP (TOC = 24,000 ppm)

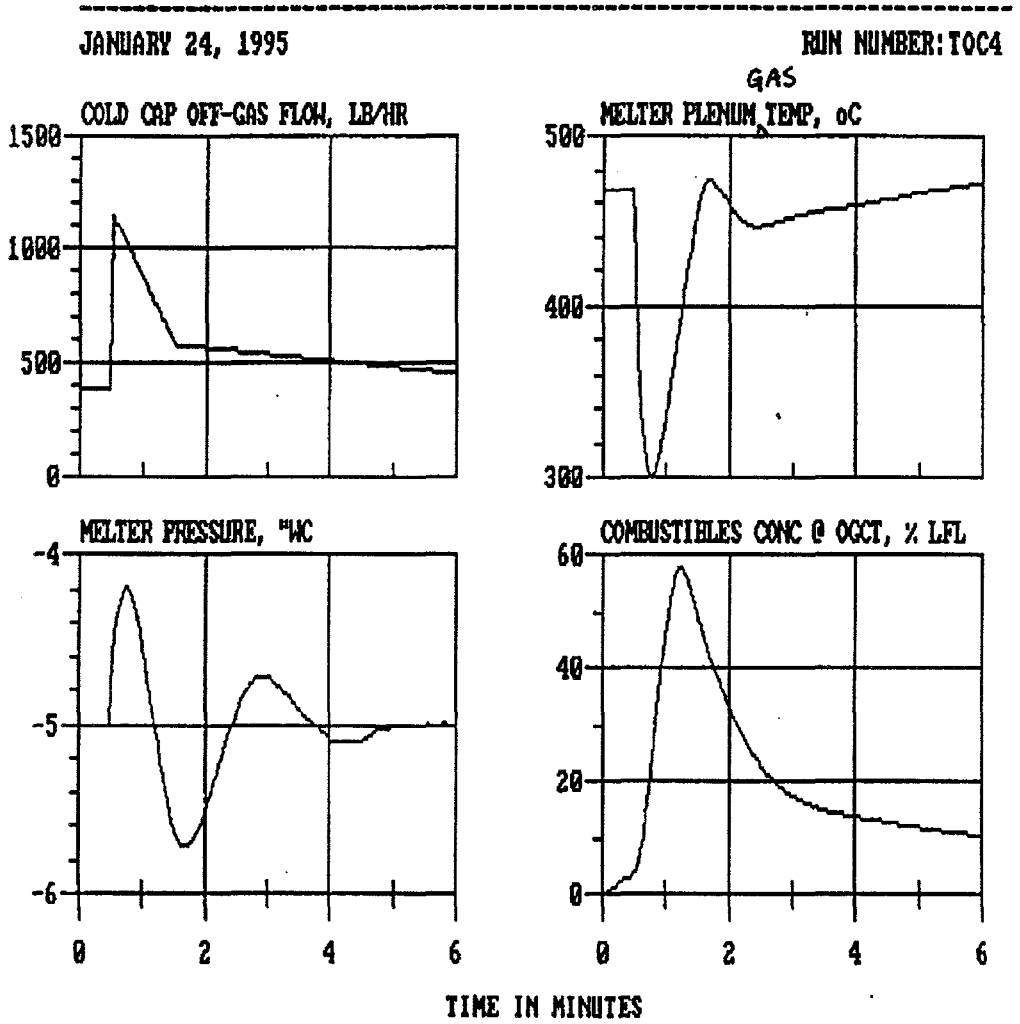
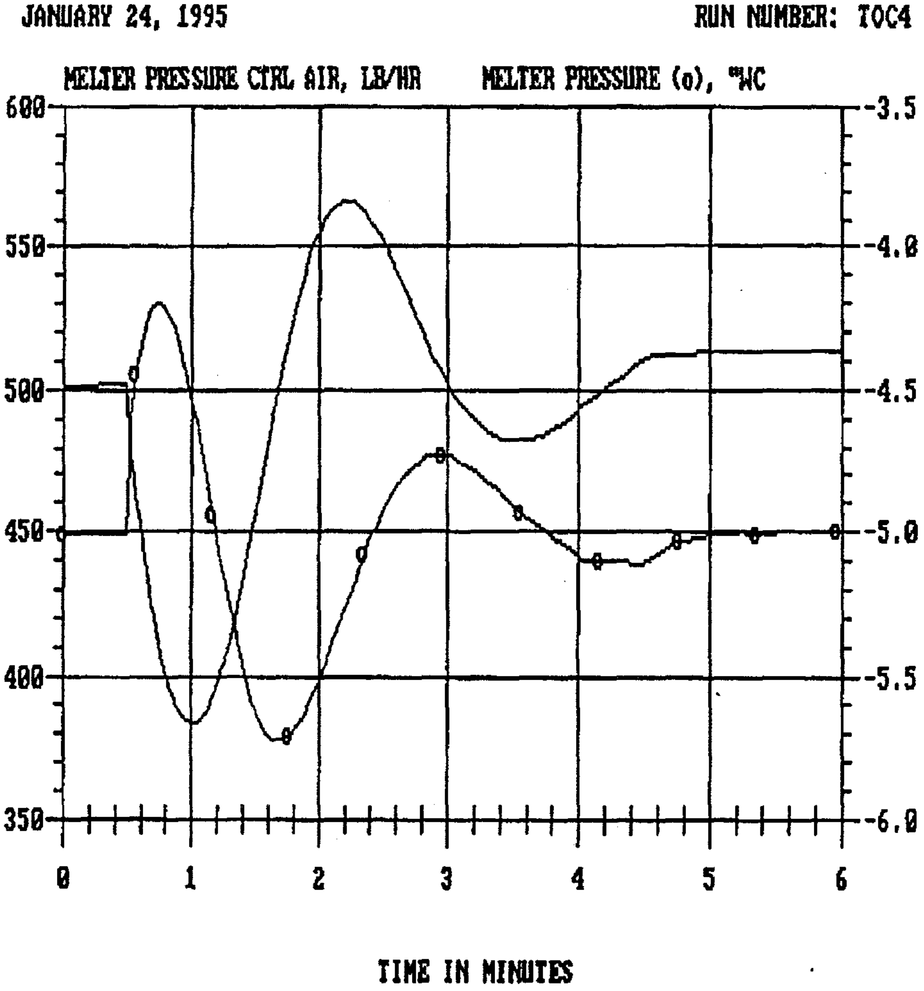


FIGURE 5. 3X OFF-GAS SURGE WITH MIN BUFC AIR & PLENUM TEMP (TOC = 24,000 ppm)



be about 300 °C. These minimum control air flow and plenum gas temperature were then used in the MOG LEL model and, as expected, the calculated peak concentration of combustible components reached 60% of the LFL at a much lower TOC level of about 13,000 ppm or 93.5% aromatic carbon removal. This confirms that use of the MOG LEL model is indeed very conservative.

RECOMMENDATIONS

Both the magnitude and duration of an off-gas surge have a major impact on the maximum TOC limit and off-gas flammability. In this study, the 3X off-gas surge was assumed to have a total duration of 8 minutes with an average flow of 2.25 times nominal during the first 1 minute. Although the data obtained during recent DWPF melter startup tests showed that the peak magnitude of a surge can be greater than 3 times nominal, the observed duration was considerably shorter, only on the order of several seconds. Therefore, a dynamic simulation study is strongly recommended to update the off-gas surge criteria defined in the Basic Data Report using the startup data. The revised melter off-gas dynamics model should be a tool for doing so. The conservatism in the 3X surge criteria assumed in this study should then be verified against the updated surge basis.

The conservatism imposed on the 4-stage cold cap model results (Table 6) should be validated against the data obtained from carefully controlled experiments with the nitric acid flowsheet feed. We recommend to do so during the IDMS PX-7 run. In the meantime, the TOC level of 24,000 ppm determined in this study is believed to be conservative enough to be included in the Process Requirements for melter feed preparation (PR-SO4), provided that both the measured melter plenum temperature and the air purge rate to the BUFC are controlled and interlocked at 650 °C and 220 lb/hr, respectively, or above.

The concept of complex liquid formation by NIST in the treatment of solution nonideality is worth further investigation, and efforts should be given to the improvement and expansion of its Gibbs free energy database. The assumption that all aromatic species are predecomposed to CO and H_2 in the presence of O_2 in the plenum must be modified so that the reducing effects of heavy aromatic species on the glass redox can be reflected properly. To do this, the Gibbs free energy database must be expanded to include heavy organic species. The apparent first-order rate parameters determined in this study for the oxidation of CO and H_2 also need to be verified and substantiated with additional data taken under a wider range of temperatures and combustibles concentrations. Finally, an explicit melter combustion model which includes fluid dynamics, radiative heat transfer and detailed chemical kinetics appears to be worth pursuing, if funding permits.

REFERENCES

1. Letter from W. D. Kimball to E. W. Holtzscheiter, "Removal of the DWPF Off-Gas LEL Analyzers (U)," **OPS-DTO-940016,** September 12, 1994.

2. Choi, A. S., "Prediction of Melter Off-Gas Explosiveness," **WSRC-TR-90-346 (Rev. 0)**, January 22, 1992.

3. Basic Data Report, **DPSP-80-1033,** Volume 1, April 1985.

4. NFPA 69, *Standard on Explosion Prevention Systems*, National Fire Protection Association, Inc., February 10, 1992.

5. Choi, A. S., et al, "Summary of Campaigns SGM-9 and SGM-10 of the DWPF Scale Glass Melter," **DPST-88-626,** December 15, 1988.

6. Choi, A. S., "Minimum Air Flow for the DWPF Melter Backup Film Cooler (U)," **WSRC-TR-92-376,** July 31, 1992.

7. Crow, K. R., and Sabatino, D. M., "SCM-2 Acid Hydrolysis Run - Sampling Results," **DPST-84-659,** July 30, 1984.

8. Crow, K. R., "SCM-2 Off-Gas Results for Sludge-Precipitate Feed," **DPST-85-575**, August 5, 1985.

9. Diemer, Jr., R. B., "DWPF Glass Melter Chemical Reaction Model," **SD-0000058,** Engineering Department, Louviers, June 20, 1983.

10. Diemer, Jr., R. B., "DWPF Glass Melter Chemistry with Acid Hydrolysis Feed," **DL-0000142,** Engineering Department, Louviers, June 17, 1985.

11. Bickford, D. F., Bowan, B. W., and Hrma, P., "Control of Radioactive Waste Glass Melters - Part 1 & 2", **DP-MS-86-217-AI & II**, October 12, 1987.

12. Plante, E. R., Bonnell, D. W., and Hastie, J. W., "Experimental and Theoretical Determination of Oxide Glass Vapor Pressures and Activities," **Advances in the Fusion of Glass,** Am. Cer. Soc., pp 26.1-26.18 (1988).

13. Flynn, H. E., Morris, A. E., and Carter, D., "Staged Thermodynamic Model of Glass Fusion Based on SOLGASMIX-PV," **Advances in the Fusion of Glass**, Am. Cer. Soc., pp 28.1-28.14 (1988).

14. Barin, I., and Knacke, O., **Thermodynamic Properties of Inorganic Substances**, Springer Verlag, New York, NY (1973).

15. Choi, A. S., "Computer Simulation of DWPF Melter Vacuum/Pressure Protection Design Change Proposal (DCP-J-S 93267) - Phase I," **WSRC-TR-93-556**, December 20, 1993.

16. Choi, A. S., "Phase II Computer Simulation of DWPF Melter Vacuum/ Pressure Protection Design Change Proposal (DCP-J-S 93267) (U)," **WSRC-TR-94-0154**, March 11, 1994.

17. Choi, A. S., "Material Balance Tables for the DWPF Coupled Feed Flowsheet with Batch One Sludge (U)," **WSRC-TR-93-203 (Rev. 0), August 19, 1993.**