Methods of Off-Gas Flammability Control for DWPF Melter Off-Gas System at Savannah River Site

by

A. S. Choi
Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808
D. C. Iverson

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ABSTRACT

Several key operating variables affecting off-gas flammability in a slurry-fed radioactive waste glass melter are discussed, and the methods used to prevent potential off-gas flammability are presented. Two models have played a central role in developing such methods. The first model attempts to describe the chemical events occurring during the calcining and melting steps using a multistage thermodynamic equilibrium approach, and it calculates the compositions of glass and calcine gases. Volatile feed components and calcine gases are fed to the second model which then predicts the process dynamics of the entire melter off-gas system including off-gas flammability under both steady state and various transient operating conditions. Results of recent simulation runs are also compared with available data.

I. INTRODUCTION

In February 1996, the Defense Waste Processing Facility (DWPF) at the U.S. Department of Energy's Savannah River Site commenced its first radioactive operation to convert over 300 million liters of high level nuclear waste into a stable borosilicate glass matrix for a long-term storage in a geological repository. At the heart of the DWPF operation are the joule-heated melter which converts a 50 wt% slurry feed containing pretreated waste and glass-forming frit into glass and calcine gases and the off-gas treatment system which removes semivolatile contaminants such as cesium and mercury from the off-gas using a series of filters and scrubbers (see Figure 1). One of the critical safety requirements for the melter off-gas system is to maintain the concentration of flammable gases in the off-gas downstream of the Quencher below 60% of the lower flammable limit (LFL) under all operating conditions, while keeping the entire system under moderate vacuum.

The original DWPF design for the melter off-gas flammability control was to monitor the concentration of flammable gases using the LFL analyzers and to interlock off the feeding when readings exceeded a preset limit. However, it was shown during cold run tests that even after frequent calibration and maintenance these analyzers still were not very reliable. Furthermore, in the event of a sudden off-gas surge which could lead to a significant buildup of flammable gases in the off-gas system, these LFL analyzers were not considered to be an effective means to prevent off-gas flammability, since the duration of surges is typically much shorter than the time delay for the response of these analyzers.

As a result, DWPF recently decided to remove all the LFL analyzers and associated interlocks and alarms, and instead control off-gas flammability by limiting the total carbon content allowable in the feed in conjunction with maintaining adequate conditions for combustion in the melter. This approach is consistent with the NFPA Code 69 which requires that all operating variables that can contribute to potential off-gas flammability be monitored, and necessary safety interlocks and operating procedures to control those variables be devised. This paper describes comprehensive methods currently in place at the DWPF to control and interlock these variables.

II. VARIABLES AFFECTING FLAMMABILITY

It was confirmed during a pilot melter run that the melter off-gas flammability is largely determined by the following operating variables:

- Carbon content in feed.
- Melter vapor space temperature.
- Air flows for combustion and dilution.

One key operating variable not included in this list is the melter feed rate. Sustainable feed rates are dictated by the thermal capacity of the melter, and careful control of the feed rate is essential to maintaining a stable cold cap with enough venting holes, which is in turn essential to achieving high melt rates consistently. Nevertheless, cold cap instabilities can still occur during the slurry feeding, resulting in surges in the off-gas flow, and it is during these upset periods when abnormally high concentrations
of flammable gases can be vented into the off-gas system. Therefore, in order to avoid potential off-gas flammability under all operating conditions, the operating windows for these variables should be set such that the concentration of flammable gases remains below the LFL throughout the duration of these surges. So, the problem of off-gas flammability control is dynamic in nature, and must be solved simultaneously with other process constraints and requirements which are discussed briefly next.

A. Carbon Content

The primary sources of carbon in the reference DWPF melter feed are the formate and aromatic carbons at 6,400 and 500 ppm, respectively, for a total organic carbon (TOC) level of 6,900 ppm on an aqueous slurry basis. The current redox criterion limits the formate content in the feed as follows:

\[ \text{molar formate (F)} - \text{molar nitrate (N)} \leq R \quad (1) \]

where R is a constant which takes a value of 0.5 at the nominal copper level, and can be greater than 1 at lower copper levels. Eq. (1) shows that the maximum formate carbon limit is set by the concentration of nitrate as well as the value of R. It must be ensured that the maximum formate carbon limit thus set does not push the TOC level high enough to cause potential off-gas flammability.

B. Feed Rate

With all other operating variables fixed, increasing the feed rate has more negative impact on the off-gas flammability than increasing the TOC level alone, since the former not only increases the rate of the TOC being fed but lowers the melter vapor space temperature due to increased lid heat demand to vaporize and superheat the excess water. Therefore, within the highest sustainable feed rate dictated by the thermal capacity of a melter, the maximum allowable feed rate without potential off-gas flammability would decrease with increasing TOC level. The reference feed rate to maintain the DWPF design glass production rate of 228 lb/hr is 0.9 gallons per minute at 44 to 45 wt% total solids.

C. Melter Vapor Space Temperature

Dome heaters are used to maintain the melter vapor space temperature high enough to; (1) evaporate the feed water, (2) supplement the joule heat in melting the cold cap, (3) keep the vapor space free of glass buildup, and (4) burn combustible gases that are not consumed in the cold cap. The melter feeding will be interlocked off when the temperature measured in the vapor space thermwells falls below 650 °C. Due to thermal radiation shine on the thermwells, the actual gas temperature at the measured vapor space temperature of 650 °C is estimated to be only...
about 470 °C using the available correlation. So, during an off-gas surge, the gas temperature can drop to a very low value, and a sharply reduced combustion efficiency could lead to potential off-gas flammability.

D. Combustion / Dilution Air

Air for the oxidation of combustible gases in the melter is supplied primarily through the backup film cooler (BUFC). Feeding will be interlocked off when the BUFC air flow falls below 250 lb/hr. This minimum air flow rate is equivalent to 1.5 times the stoichiometric air flow required to oxidize 3 times the nominal combustible gas flow, thereby ensuring no shortage of oxygen for combustion practically under all operating conditions.

During normal operation, the combustion efficiency in the melter is nearly 100%, and little or no dilution air is required. However, in the event of a large off-gas surge, a reduced combustion efficiency coupled with a surge in the combustible gas flow could push the concentration of combustible gases downstream of the Quencher above the LFL. The dilution air is supplied through the primary film cooler, and its rate is set such that the concentration of combustible gases in the noncondensable off-gas is maintained below 60% of the LFL under these abnormal conditions. The dilution air also cools the off-gas, and helps transport off-gas entrainments to the Quencher. The melter pressure control air flow normally at 500 lb/hr and any air inleakages to the system are not considered as dilution sources.

E. Off-Gas Surges

Surges can occur when boiling water falls through the vent holes or cracks in the cold cap and comes in contact with the hot glass surface, or when calcine gases accumulating under the cold cap due to a lack of vent holes suddenly burst out to release its pressure, thereby sending partially fused feed materials into the melter vapor space. These cold cap instabilities are characteristic of slurry-fed melters, and are known to be related to many design and operating parameters including the size of a melter, melter vapor space temperature and feed rate and composition. It is practically impossible to predetermine the frequency and characteristics of surges such as peak intensity and duration from a given set of design and operating conditions.

As a result, representative surge patterns have been constructed from the data obtained during pilot melter runs, and subsequently used in the design calculations. The design basis surge pattern for the melter pressure control is a 7 times normal off-gas flow at the peak with a 8-minute total duration. For the off-gas flammability control, a 3 times normal off-gas flow at the peak with the same 8-minute duration is assumed. Recent DWPF cold run data showed that the peak intensity of a surge can be greater than 7 times normal, but the observed surge durations were all on the order of 10 seconds. In general, a longer surge duration has a greater impact on the melter vapor space temperature than a higher peak intensity, thus making the design basis surge patterns conservative.

III. OVERVIEW OF MODELS

The task of predicting melter off-gas flammability from a given set of operating conditions requires accurate information on; (1) the composition of combustible gases produced in the cold cap, (2) the oxidation kinetics of combustible gases and other volatile feed components in the melter vapor space, and (3) the dynamic behavior of the entire melter off-gas system during off-gas surges. Two models were used to accomplish this task and further to define the operating windows for the variables affecting off-gas flammability.

A. Cold Cap Model

A multistage thermodynamic reaction model, called 4-Stage Cold Cap Model, was developed earlier by assuming that all the chemical events occurring in the cold cap are at thermodynamic equilibrium. In doing so, the effects of chemical kinetics and transport resistances are ignored. Instead, the cold cap model approximates the decomposition and melting steps as a continuous, multistage countercurrent process consisting of a series of simple, recognizable physical and chemical events similar to those observed by differential scanning calorimetry and X-ray diffraction experiments.

1. Model Structure. The decomposition and melting of the feed solids are assumed to proceed in four distinct equilibrium stages:

- **Stage 1**: Decomposition of formates and hydroxides to oxides and gases at 700 °C.
- **Stage 2**: Decomposition of carbonates, nitrates and sulfates to oxides and gases at 900 °C. A first liquid phase appears.
- **Stage 3**: Formation of multiple oxides of spinel type such as NiFe₂O₄ and solid solutions at 1,050 °C. Formation of LiAlO₂, etc. by chance substitution.
- **Stage 4**: Final fusion into glass matrix at 1,150 °C.

The equilibrium compositions of the gas and solids products from each stage are calculated by minimizing the total Gibbs free energy for that stage. Once calculations are 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.
2. Free Energy Database. Once equilibrium conditions are assumed in all stages, the validity of the 4-stage cold cap model is then determined largely by the accuracy of the Gibbs free energies for those species assumed and by a reasonable treatment of the solution nonideality that exists among many phases appearing during the course of melting the waste and frit mixture. Due to an enormous number of chemical constituents in the waste feed, a detailed theoretical treatment of solution nonideality is virtually impossible at the present time.

As a result, the Gibbs free energy database for complex liquids which was developed at the National Institute of Standards and Technology (NIST) was used in lieu of activity coefficients to partially handle the solution nonideality problem. The concept of complex liquids is based on the assumption that the strong interactions present in the mixture result from the formation of complex liquids and solids with identifiable local stoichiometry and Gibbs free energy of formation.$^7$ The NIST free energy equations are fitted into a six-coefficient equation of the form:

$$
\Delta G_f(T) = a + bT + cT^2 + dT^3 + eT^4 + fT \ln T
$$

(2)

where $T$ is in K, and $\Delta G_f$ is in Joule/mole. Currently, the NIST database contains the free energy data for 112 species. For those species missing in the NIST database, the free energy of formation for pure compounds from the literature is used.$^6$

3. Software. The 4-stage cold cap model was built using STGSOL, a multistage equilibrium software developed at the University of Missouri-Rolla with financial supports from the U. S. Department of Energy, the U. S. Bureau of Mines, and Savannah River Laboratory.$^7$ STGSOL is based on the SOLGASMIX algorithm for minimizing the total free energy of a system in order to calculate equilibrium compositions.

4. Model Validation. The cold cap model was validated using the data from the SCM-2 melter runs.$^{10,11}$ The significance of these runs was that efforts were made to directly measure the concentrations of CO, CO$_2$ and H$_2$ in the cold cap off-gas by turning off the lid heaters before the off-gas was sampled from the condensate tank, thereby minimizing the chance for further oxidation in the melter vapor space. Table 1 shows a reasonably good agreement between the measured and calculated iron redox ratio in glass and the off-gas composition for the feeds containing only the formate carbons.

However, for the feeds containing aromatic carbon residues from the precipitate hydrolysis process as well as formate carbons, Table 1 shows that the model tends to overpredict the oxidation efficiency, as indicated by the lower concentrations of CO and H$_2$ than those measured.

This occurred primarily due to the assumption that the aromatic carbon residues are instantaneously decomposed to CO and H$_2$ upon entering the cold cap due to low decomposition temperatures, thereby participating in the cold cap equilibrium reactions instantly. In doing so, the aromatic carbon species consume O$_2$, leaving the glass more reducing, as evidenced by both the data and the model results.

Therefore, in an effort to make the cold cap model conservative from the off-gas flammability standpoint, the decomposition products of the aromatic carbon residues are no longer allowed to participate in the cold cap reactions, except to consume available O$_2$ to show their reducing effects on glass. Instead, they will undergo oxidation reactions in the melter vapor space along with the equilibrium products of formate decomposition in the presence of excess oxygen, before exiting the melter.

<table>
<thead>
<tr>
<th>Carbon Type</th>
<th>Exp't</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formate-only</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$^{+2}$/Fe$^{+3}$</td>
<td>0.24</td>
<td>0.35</td>
</tr>
<tr>
<td>CO</td>
<td>7.7</td>
<td>8.64</td>
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<tr>
<td>CO$_2$</td>
<td>92.0</td>
<td>85.9</td>
</tr>
<tr>
<td>H$_2$</td>
<td>N/A</td>
<td>2.30</td>
</tr>
<tr>
<td>Formate &amp; Aromatic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$^{+2}$/Fe$^{+3}$</td>
<td>0.55</td>
<td>0.59</td>
</tr>
<tr>
<td>CO</td>
<td>18.5</td>
<td>8.52</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>116.0</td>
<td>100.05</td>
</tr>
<tr>
<td>H$_2$</td>
<td>3.00</td>
<td>2.72</td>
</tr>
</tbody>
</table>

B. Melter Off-Gas Dynamics Model

The primary goal of this model is to predict the dynamic responses of the entire melter off-gas system under various transient conditions such as off-gas surges. It does so by solving time-dependent overall mass and energy balance equations simultaneously along with those describing the dynamics of the DCS controllers and the control valves. It simulates virtually all the hardware in the system and DCS software logic. In order to keep track of combustible gases, the model also includes the global oxidation kinetics in the melter vapor space so that the off-gas flammability can be predicted as a function of concentrations, residence time, and temperature. The global oxidation kinetics scheme was adopted, since the complex patterns of fluid mixing and heat transfer in the melter vapor space makes even a reasonable prediction of the gas temperature profile extremely difficult.
1. **Global Oxidation Kinetics.**

As stated earlier, all the aromatic carbon species in the feed are predecomposed mainly to CO and H₂, and the subsequent oxidation to CO₂ and H₂O is assumed to follow the apparent first-order kinetics in the presence of abundant oxygen supply several times in excess of the stoichiometric requirement:

\[-r_{CO} = k_{CO} \cdot C_{CO}\]

\[-r_{H_2} = k_{H_2} \cdot C_{H_2}\]

where \(r\)'s are the reaction rates in lbmole/ft³/sec, \(C\)'s the concentrations in lbmole/ft³, and \(k\)'s the first-order rate constants in 1/sec of the form:

\[k = k_o \cdot \exp(-E_a/RT)\]

where \(k_o\) is the preexponential factor in 1/sec, and \(E_a\) the activation energy in Btu/lbmole. In Table 2, the apparent first-order rate parameters used in the model are shown. These rate parameters were derived using the off-gas data from a pilot melter run, during which the melter feed was spiked with progressively higher levels of TOC, and the impact of varying the air flow and melter vapor space temperature was also examined.² It was assumed that the melter vapor space is a constantly-stirred tank reactor at a constant density, since the fuel concentrations were very low at both the inlet and outlet of the vapor space reactor.

**TABLE 2. Apparent First-Order Rate Parameters for CO and H₂ Oxidation from SGM-9 Data.**

<table>
<thead>
<tr>
<th></th>
<th>(k_o)</th>
<th>(E_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1/sec)</td>
<td>(Btu/lbmole)</td>
</tr>
<tr>
<td>CO</td>
<td>1021.8</td>
<td>19974.3</td>
</tr>
<tr>
<td>H₂</td>
<td>9756.6</td>
<td>25170.2</td>
</tr>
</tbody>
</table>

2. **Model Scope.** The model is primarily used to check the operability of the melter off-gas system under abnormal conditions by simulating various types of transient operating conditions such as surges, switchover and switchback between the primary and backup off-gas systems, startup and shutdown, melter idling, feed tube flushing, etc. The model is also used to develop and test the DCS software protection logic by simulating various types of hardware failure modes such as transmitter or valve failures. Since the actual unit operations in the melter off-gas system are modeled directly in conjunction with the actions of controllers and valves, this model is also used to help fine tune controllers and optimize their performance in real time. Use of this model for off-gas flammability control will be discussed later in this paper.

Currently, there are 22 Proportional-Integral (PI) control loops in the model that control various pressures, temperatures and flow rates. The actions of some of these controllers and control valves have a direct impact on the temperature and the gas residence time in the melter vapor space, thus impacting the overall combustion efficiency in the melter and the off-gas flammability downstream. The model performs the gas dynamics calculations by keeping tracking of both condensable and noncondensable flows such as CO, H₂ and C₆H₆ throughout the system.

3. **Software.** The melter off-gas dynamics model is written in FORTRAN, and built on Bechtel's Dynamic Analysis Program (DAP) for I/O and its library of programs to calculate valve dynamics, pipe flows, etc.

4. **Model Validation.** The model was validated in two steps. The model was first calibrated by matching calculated pressure and temperature profiles throughout the primary melter off-gas system (Figure 1) with those measured when the melter was idling. The calibrated model was then validated by comparing the calculated results at 3 different feed rates with the steady state data collected at the same feed rates. Although not shown in this paper, the agreement was excellent. Furthermore, as the model predicted, the LFL readings for the off-gas samples taken at the Off-Gas Condensate Tank (OGCT) were all near zero during normal operation with no surge, indicating a complete combustion in the melter. The LFL analyzers were taken out soon after the start of the cold runs, and it is unfortunate that no LFL data exist for abnormal conditions.

The dynamic elements of the model were validated next by simulating the flushing of the feed tubes which is routinely done just prior to the start of feeding and right after the termination of feeding. Since the flush H₂O line near the 3-way valve is pressurized to 78 psig, compared to vacuum in the melter, it is expected that the flush H₂O will enter the melter on a pulsation mode with decreasing intensity due to the action of the flow controller. As a result, the flush H₂O flow profile shown in Figure 2 was devised based on assumed stroke times for the valve and dead time for the flow control loop and by adjusting the peak height of the first pulse to match the calculated peak melter pressure with that measured. The overall agreement between calculated and measured profiles of key process variables is shown to be quite good. One of the difficulties in validating the model under short transient conditions as in typical off-gas surges lasting just several seconds, the actual cooldown of the melter vapor space is not reflected correctly by the indicated temperatures due to the thermal inertia of thermowells. So, there is no means to validate calculated transient temperatures.
IV. OPERATING LIMITS FOR TOC & FEED RATE

As stated earlier, the feeding to the DWPF melter is interlocked off when the melter vapor space temperature and the BUFC air flow drop below 650 °C and 250 lb/hr, respectively. The feeding is also interlocked off when the total air supply to the melter drops below 850 lb/hr, including the air flow to the BUFC, to provide necessary air for the off-gas cooling and the TV cameras and seal pot purging. In this section, the results of recent model simulation runs are presented which were used to set the maximum allowable TOC limits in the feed at different feed rates based on these minimum temperature and air flow limits.

A. Simulation Bases and Procedures

On an equal mass basis, the aromatic carbon residues from precipitate processing has a more negative impact on the off-gas flammability than formate carbons. So, the aromatic carbon level in the reference feed was increased from 500 to 3,000 ppm by assuming a 95% efficiency in aromatic carbon removal during the feed preparation step. The maximum allowable TOC limits were then calculated by gradually increasing the formate carbon level from the reference value of 6,400 ppm until the calculated peak concentration of combustible gases exceeded 60% of the LFL in the OGCT during the course of a 3 times nominal off-gas surge. The calculations were repeated by varying the feed rates from 0.7 to 1.5 GPM at 0.1 GPM increments. The melter vapor space temperature remained at 650 °C at the onset of a 3 times nominal off-gas surge. The 3 times nominal off-gas surge is assumed to proceed as follows: At time zero, the flow rates of both condensable and noncondensable gases generated from the feed are increased from 1X to 3X normal instantly, then decreased linearly to 1.5X normal during the first one minute, and further decreased linearly to 1X normal during the next seven minutes.

B. Simulation Results

The results of the 3X surge simulation at the reference feed rate of 0.9 GPM are shown in Figure 3, and the maximum TOC level thus determined is 24,500 ppm. The gas temperature in the melter vapor space is shown to drop to a minimum of about 300 °C, and this temperature drop combined with a 3-fold increase in the combustibles...
flow and a shorter residence time caused the concentration of combustible gases peak at 60% of the LFL. The maximum TOC limits thus calculated are plotted next in Figure 4 against the product of feed rate and specific gravity, and the following correlation was derived:

$$\text{max TOC} = -4,860 + 45,180 \times \text{FR} \times \text{SpG}$$

$$- 108,200 \times \ln(\text{FR} \times \text{SpG})$$  (6)

where TOC is the total organic carbon in ppm, FR is the feed rate in GPM, and SpG is the specific gravity of the feed. Once the TOC level and the specific gravity are measured for each batch of feed, the following correlation can be used to estimate the maximum allowable feed rate:

$$\text{max FR} = 0.756 - 5.4 \times 10^{-6} \times \text{TOC} \times \text{SpG}$$

$$+ 1,185.5 \times \ln(\text{TOC} \times \text{SpG}) / (\text{TOC} \times \text{SpG})$$  (7)

where FR is the feed rate in GPM, and TOC is in ppm. If one desires to estimate the maximum feed rate of TOC regardless of the feed slurry characteristics, the following correlation can be used:

$$y = 4.517543 \times 10^{-4} - 1.081835 \times 10^{-6} \times tM - 4.858744 \times 10^{-3}$$

$$R^2 = 0.9995$$

**FIGURE 3.** 3X Surge Simulation Results at TOC = 24,500 ppm & Feed Rate = 0.9 GPM.

**FIGURE 4.** Calculated Maximum TOC level vs. Feed Rate * Specific Gravity
max TOC feed rate = 9.55 + 4.78E−4*(TOC/SpG) 
− 2.5E+3*Ln(TOC/SpG)/(TOC/SpG) (8)

where max TOC feed rate is in lb/hr, and TOC is in ppm. Eq. (8) is used to convert measured TOC concentrations into the maximum allowable TOC feed rate once the specific gravity is known. This shows the importance of specific gravities in the dynamic simulations of off-gas surges, since they generally relate the slurry feed rate to the relative ratio of condensable to noncondensable flows.

V. CONCLUSIONS

It was shown that mathematical models can be used successfully to define the operating windows for the key process variables affecting off-gas flammability, thereby excluding a potential for forming flammable gas mixtures in the off-gas system without actually measuring their concentrations.

ACKNOWLEDGMENTS

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