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Melter Off-gas Flammability Analysis

by

Frank G. Smith, III and Alexander S. Choi

Westinghouse Savannah River Co.
Savannah River Technology Center
Aiken, South Carolina 29808

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Dr. F. G. Smith, III and Dr. A. S. Choi
Westinghouse Savannah River Co.
Savannah River Technology Center
Aiken, SC 29808
e-mail: frank02.smith@srs.gov

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Abstract
Models have been developed to assess off-gas flammability in waste glass melters. The models explicitly describe the effects of key melter operating variables such as total organic carbon in the feed, melter air purge and vapor space temperature on off-gas flammability. The first of two coupled models developed for the flammability assessment describes heterogeneous gas-liquid-solid reactions occurring in the cold cap and melt pool. This model predicts both glass and calcine gas compositions from a given feed chemistry using thermodynamic equilibrium. The resulting calcine gas composition becomes the input to the second model, which describes the homogeneous gas-phase combustion reactions in the melter gas plenum, and calculates time-dependent combustion efficiencies of the two major flammable gases, CO and H_2, using a global oxidation kinetics scheme. Once validated against pilot melter data, these models were used to simulate a series of safety scenarios to assess the effects of sugar over-batching and melter operating modes on off-gas flammability. The two operating modes considered were normal and transient operation induced by an off-gas surge. Results determined maximum sugar levels that can be tolerated under normal and upset conditions.

INTRODUCTION

The objective of this work was to develop predictive models to assess offgas flammability for a low activity radioactive waste melter. The models had to be comprehensive enough to explicitly describe the effects of key melter operating variables such as total organic carbon (TOC) in the feed, melter air purge and vapor space temperature. Once validated against pilot melter data, these models were used to simulate a series of safety scenarios involving over-batching of sugar, used as a reducing agent, and off-gas surges. The overall scope of the work was broken down into two parts, each focusing on a physically distinct region in the melter. The first of the two models describes heterogeneous gas-liquid-solid reactions occurring in the cold cap and melt pool, and predicts both glass and calcine gas compositions for a given feed chemistry using thermodynamic equilibrium. The resulting calcine gas composition then is input to the second model, which describes homogeneous gas-phase combustion reactions in the plenum above the melt line using a global kinetics scheme.

A schematic representation of the melter system is shown in Figure 1. The slurry feeding the melter is about 50% water and 50% solids in the form of metal salts. Sugar is added to the feed as a reducing agent. Within the melter, the water is volatilized and the metal salts react to form oxides releasing calcine gases. Sugar and other organic material in the feed are burned to produce primarily H_2, CO, CO_2, CH_4 and water vapor. The metal oxides form the glass product while the gases pass through the offgas treatment system and are vented out the facility stack. Air that is added to the melter and leaks into the melter forms part of the offgas stream. Leaving the melter, the offgas passes through a film cooler where air is added to reduce the gas temperature. Just beyond the film cooler, the offgas mixes with an air stream that is modulated to control the pressure in the melter. The combined gas then passes through a wet scrubber that removes particulates in the offgas and condenses most of the steam. Beyond the scrubber, the offgas passes through additional treatment equipment and is finally vented to the atmosphere. To ensure plant safety the gases leaving the scrubber must be nonflammable.

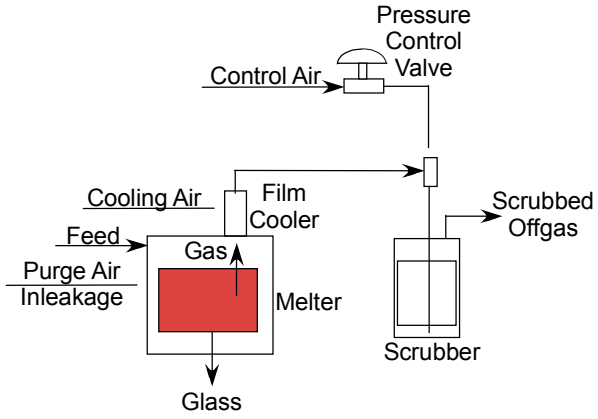

Figure 1. Schematic representation of melter offgas system.

MODELING APPROACH

Melter chemistry modeling is defined as the modeling of chemical phenomena occurring inside the melter, including decomposition, calcination and redox reactions in the cold cap and degassing and homogenization in the melt pool primarily via redox reactions. Gaseous products from the cold cap further react with air in the vapor space of the melter plenum. Detailed first-principles modeling of the cold cap and vapor space chemistry in a slurry-fed melter is extremely difficult even with the use of state-of-the-art computing technology. Solely from the combustion standpoint, there are a variety of nonvolatile organic species in the feed that form many different byproducts, both flammable and non-flammable, while decomposing in the cold cap. Presently, the fate of all those organic species in both the cold cap and vapor space is not completely known, and kinetic data for most of the reactions involved are not available. Perhaps, the biggest obstacle to successful modeling of melter chemistry is the complexity of the vitrification chemistry. A very large number of waste components and glass-forming chemicals undergo simultaneous physical and chemical changes in the cold cap that has a steep temperature gradient of over 600 ^{o}C over a several-inch thickness and a spatial domain that is highly dynamic and difficult even to define. Numerous intermediate phases, both liquid and solid, are formed before the final fusion into the glass matrix takes place, and little or no attempt has been made to measure physical and/or transport properties of calcine gases in these phases. As a result, sufficient data does not exist for mechanistic modeling of the cold cap. Regarding combustion modeling, the heat transfer and fluid mixing in the vapor space is sufficiently complicated that a full solution to the transport equations of reacting flows based on first principles is not practical.

Nonetheless, by using simplifying assumptions supported by experimental data, successful melter chemistry and dynamic off-gas models have been developed and used to establish safety bases and to control key melter operating variables (Choi, 1996). The gradual nature of the melting process can be approximated as a multi-stage countercurrent equilibrium process, ignoring the effects of chemical kinetics and transport resistances within the cold cap and melt. One of the key technical safety requirements used to control off-gas flammability is the TOC content of the feed. The TOC content of the melter feeds in this study is increased by the addition of sugar to control glass redox. Hydrocarbon species are decomposed in the cold cap to produce flammable gases such as CO, H_2 and light hydrocarbons, and the degree to which these flammable gases react in the melter plenum directly impacts the off-gas flammability potential downstream.

Off-gas flammability is determined not only by the TOC content of feed but by other operating variables affecting the combustion efficiency in the melter such as vapor space temperature and the rate of air purge. Besides those operating variables that can be monitored and controlled, off-gas flammability is also impacted by the unpredictable, therefore, uncontrollable process/system upsets such as off-gas surges, unintentional melter overfeeding, equipment malfunction and even an earthquake. The work described in this paper addresses these issues by developing models of the cold cap and plenum combustion validated using experimental data and by introducing appropriate conservatism into the flammability assessment.

The FACT/Sage commercial software package (Pelton and Wu, 1999) was used to provide a database of oxides, solids, and gases appropriate for modeling melter cold cap chemistry. Three FACT/Sage data sets (Slag A, Slag C and Spinel) were used in the cold cap model. Slag A contains magnesium, iron, calcium, sodium and potassium as oxides, sulfates, chlorides and fluorides along with alumina, silica and titanium oxide. Slag C includes sodium, calcium and magnesium as sulfates and hydroxides, boron oxide and some of the same species present in Slag A. The Spinel phase contains oxides of iron, zinc and aluminum. In addition to these solid phases, a condensed phase containing another 42 solid species was created. The solid species in the condensed phase were selected based on results from preliminary FACT/Sage calculations using the entire database. To complete the cold cap model, 20 ideal gases were used to form the gas phase. Since it is the most stable gaseous hydrocarbon, methane alone is used to represent hydrocarbons in the gas phase.

Chem/Sage was selected as the software to develop a multi-stage equilibrium reactor model of the cold cap because of its compatibility with FACT/Sage. The conceptual model, illustrated in Figure 2, is that Stages 1 and 2 represent hydrocarbon reactions in the upper part of the cold cap as a combination of pyrolysis and partial combustion. Similarly, Stages 3 and 4 represents hydrocarbon reactions at a higher temperature lower in the cold cap. At nominal sugar levels, the hydrocarbons fed to Stage 4 will burn to completion. Stage 3 is included to empirically account for non-ideal effects. The feed distribution to the model stages was adjusted to conservatively predict experimental data.

Off-gas data from pilot melter experiments conducted at the Vitreous State Laboratory at Catholic University (e.g. Matlack and Pegg., 2003) was used to validate the models. To isolate cold cap reaction products, in some of these experiments the melter was intentionally overfed to achieve low offgas temperatures and suppress combustion. Data showed that the rate of off-gas generation was greatly

reduced under flooded conditions most likely because of an excessive water layer either slowing down reactions or suppressing the release of gases. However, we assume that, even under such severe conditions, the relative composition of dry calcine gases will still reflect the true cold cap conditions. Therefore, the cold cap model was tuned to produce conservative target values for the molar ratios of CO/CO_2 and $H_2/(CO+CO_2)$, that bounded essentially all the data. An example of the model comparison to experimental data for CO is shown in Figure 3. While there is a wide variation in the data, the model provides a conservative prediction.

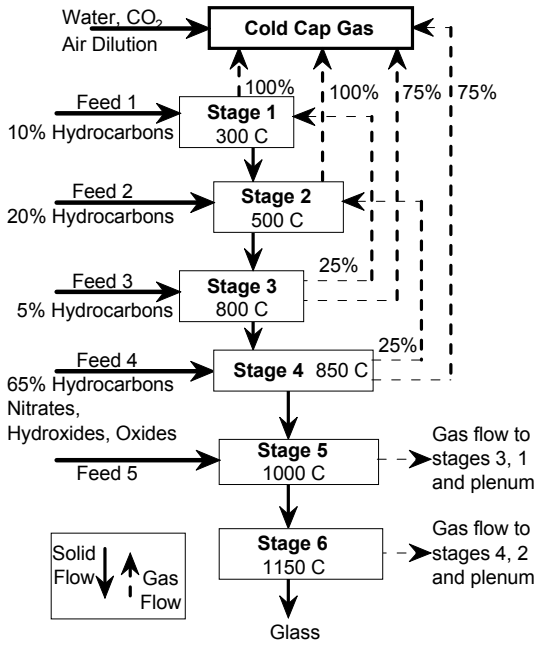

Figure 2. Six stage FACT/Sage cold cap model.

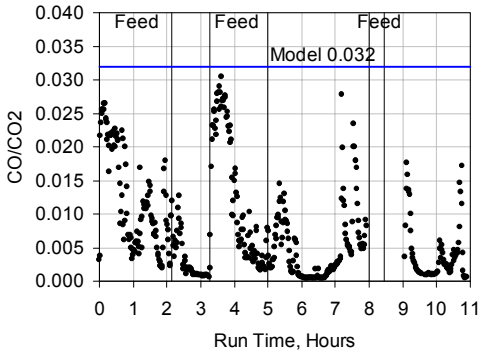

Figure 3. Example of cold cap model validation.

The CHEMKIN software was used to model combustion reactions in the melter plenum because of its flexibility and an extensive database of gas-phase reaction parameters. First-order global kinetic parameters for CO and H_2 oxidation in the melter plenum, derived from and validated against pilot melter data (Choi, 2000), were modified and used in a perfectly stirred reactor model of the melter plenum. The resulting global kinetic parameters, modified to match one set of experimental data, over-predicted the measured concentrations of CO and H_2 during a second run by 5 and 29%, respectively indicating the conservatism in the model. The reactor model further assumes that oxygen is present in sufficient excess of the stoichiometric amount required to burn all flammable gases entering the plenum reactor and the density in the melter plenum is constant.

At constant density, the fractional conversion of CO and H_2 are given by the equations:

$$X_{CO} = \frac{k_{CO}\,\tau}{1+k_{CO}\,\tau} \text{ and } X_{H_2} = \frac{k_{H_2}\,\tau}{1+k_{H_2}\,\tau}$$

where X is the fractional conversion and τ the gas residence time in seconds. The first-order rate constants, k_{H2} and k_{CO}, are expressed in the Arrhenius form as:

$$k_{CO} = k_{o,CO}\exp\left(\frac{-E_{a,CO}}{RT}\right) \text{ and } k_{H_2} = k_{o,H_2}\exp\left(\frac{-E_{a,H_2}}{RT}\right)$$

where k_o's are the preexponential factors in 1/sec, E_a's the activation energies in cal/gmole, R the universal gas constant in cal/gmole/K, and T the mean gas temperature in degrees Kelvin. Kinetic parameters were derived from off-gas data taken during several pilot melter runs at different scales.

SIMULATION RESULTS

The validated LAW melter combustion model was run to simulate several accident scenarios involving over-batching of sugar and off-gas surges. Specifically, these safety case studies were conducted in stages. In Stage 1, the effects of sugar over-batching up to 4X nominal and the melter operating modes on the off-gas flammability were assessed independently in order to determine the maximum sugar levels that can be tolerated under normal and upset conditions at the given baseline fixed melter air purge of 101 scfm. The two operating modes considered were normal and transient operation induced by an off-gas surge. The peak intensity of off-gas surge was set at 7X/3X, representing 7X nominal condensable (steam generated from free H_2O in feed) and 3X nominal non-condensable (calcine gas) flows, respectively. In Stage 2, the effect of varying air purge on the off-gas flammability was assessed under conditions of simultaneous sugar over-batching and off-gas surge at melter plenum temperatures of the nominal 400 ^oC and the projected minimum of 300 ^oC. Finally, in Stage 3, the degree of sugar over-batching that would result in 25% of the Composite Lower Flammability Limit (CLFL) at the

scrubber exit was determined under the conservative operating scenario of 7X/3X off-gas surge and at the minimum air purge and minimum melter plenum temperature. Since the projected list of flammable gases in the noncondensable LAW melter exhaust includes H_2, CO, and CH_4 representing the HC species, the resulting flammability potential of each case was calculated in terms of percent of the composite LFL:

$$\%\ CLFL = \frac{100}{\left(\frac{[H_2]}{LFL_{H_2}} + \frac{[CO]}{LFL_{CO}} + \frac{[CH_4]}{LFL_{CH_4}}\right)}$$

where the concentrations are given in volume percent, and the LFL's for H_2, CO and CH_4 are given as 4, 12.5 and 5 volume percent, respectively.

Figure 4 shows an example of the variation in calcine gas composition predicted by the cold cap model for one particular waste feed composition with different levels of sugar addition. While the production of CO_2 is roughly linear in sugar, most of the gases show a nonlinear relationship to the sugar level. Ammonia and nitrous oxides are produced from nitrate and nitrite salts in the waste feed. As the amount of sugar added to the feed increases, ammonia is preferentially formed.

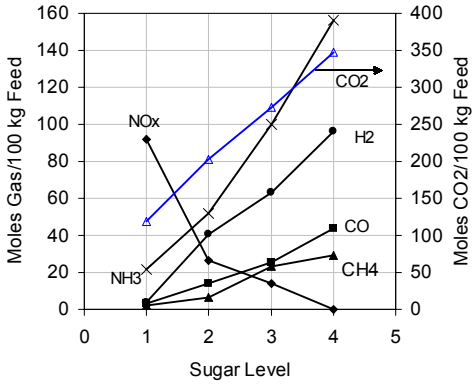

Figure 4. Cold cap offgas composition as a function of sugar addition.

Figure 5 shows results from a typical transient off-gas simulation including the effects of a gas surge. The surge was assumed to consist of 7 times the nominal condensable (steam) and 3 times the nominal non-condensable gas flows. The composition of non-condensable flow was assumed to remain constant throughout the duration of surge. The condensable flow is 100% steam due to free water in the feed. Due to limitations of the CHEMKIN software, these two flows were combined into one stream for simulation purposes, and the resulting time-profile of the combined surge is shown in Figure 3. During the first 20 seconds, both the off-gas flow and plenum gas temperature remain at their respective steady state values. The off-gas flow then ramps up by a factor of ~5 to near 900 g/sec during the next 22 seconds. The off-gas flow contains steam by over 50 wt% and enters the plenum at near the boiling point of water. Therefore, the surge quickly cools the plenum, and the minimum plenum gas temperature near the peak of surge is shown to be only 456 K or 183 ^oC, which is too low for combustion reactions to proceed at an appreciable rate. This sudden drop in gas temperature coupled with a sharp increase in flammable gas flows pushes the concentration of flammable gases at the scrubber exit from the initial value of near 5% of the CLFL to a peak value of near 20% of the CLFL, when melter air inleakage is not counted as part of the combustion and dilution air. When melter air inleakage is included, the entire flammability profile is reduced by roughly 50%, which shows how significant the impact of melter air inleakage is on the overall flammability assessment.

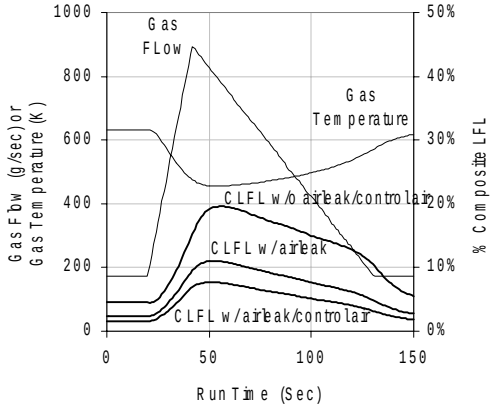

Figure 5. 7X/3X Off-Gas Surge with Nominal Sugar @ 400 ^oC Plenum Temp.

SUMMARY AND CONCLUSION

As noted above, the safety case studies were conducted in three stages. A total of 16 cases were run during Stage 1 at the indicated melter plenum temperature of 400 ^oC and by not counting the melter pressure control air as a dilution source. Some of the highlights from the Stage 1 case study include:

- Without taking credit for the melter air inleakage in the combustion and dilution air, the maximum sugar level that can be tolerated under a minimum 50% excess combustion air requirement would be 1.6 times nominal.
- If the minimum excess combustion air requirement is reduced to 20%, the maximum tolerable sugar level in the absence of melter air inleakage would increase to 1.8 times the nominal.

- If the baseline melter air inleakage of 300 scfm is included as part of the combustion and dilution air, the maximum sugar level that can be tolerated under the minimum 50% excess combustion air requirement would be 3.9 times the nominal.
- For the transient operating mode induced by off-gas surges at the nominal sugar level, the peak concentration of flammable gases at the scrubber exit was predicted to be 20% of the CLFL without taking credit for melter air inleakage. When the melter air inleakage was included as part of the combustion and dilution air, the peak concentration of flammable gases at the scrubber exit decreased from 20 to 11% of the CLFL.

A total of 19 additional cases were run during Stage 2 case study by setting the sugar level either at 1X or 2X nominal and the melter plenum temperature either at 300 or 400 ^{o}C, while varying the air purges. Some of the highlights from the Stage 2 case study include:

- The potential for off-gas flammability was remote in all nominal sugar cases considered, regardless of operating mode and plenum temperature and air purge variations.
- In the event of 7X/3X off-gas surges, the peak concentration of flammable gases at the scrubber exit was predicted to be 55% of the CLFL for the 2X nominal sugar case under the least conservative operating scenario of including both melter air inleakage and pressure control air, at the higher plenum temperature of 400 ^{o}C.

The Stage 3 case study was made iteratively under the conservative operating scenario of 7X/3X off-gas surges at the minimum plenum temperature of 300 ^{o}C with no melter pressure control air. Some of the highlights from the Stage 3 case study include:

- It would take 12% over-batching of sugar for the flammable gas concentration in the scrubber vent to reach 25% of the CLFL at the peak of the 7X/3X off-gas surge. Transient variation in melter air inleakage is accounted for in this calculation.
- If 100% of the baseline melter air inleakage rate of 300 scfm is included in the combustion and dilution air, the flammability potential of the scrubber vent would decrease to 19% of the CLFL at the peak of the 7X/3X off-gas surges.
- If no melter air inleakage is included in the combustion and dilution air, the flammability potential of the scrubber vent would increase to 33% of the CLFL at the peak of the 7X/3X off-gas surges.

In conclusion, predictive models were developed to describe solid phase and gas phase melter chemistry. However, experimental data were insufficient to claim that model validation was complete. To overcome this shortcoming, several layers of conservatism were built into both models. This includes tailoring the multistage structure of the cold cap model such that the predicted calcine gas compositions are bounding, particularly with respect to H_2 and CO. Furthermore, methane combustion in the plenum was arbitrarily suppressed so that the predicted off-gas composition exiting the melter would be more flammable. In the end, however, it was the excellent overall agreement shown between model predictions and measured data for both flammable and non-flammable gases that support the use of these models as a tool for assessing melter offgas flammability potential.

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