Flammability Control in a Nuclear Waste Vitrification System

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ABSTRACT

The Defense Waste Processing Facility at the Savannah River Site processes high-level radioactive waste from the processing of nuclear materials that contains dissolved and precipitated metals and radionuclides. Vitrification of this waste into borosilicate glass for ultimate disposal at a geologic repository involves chemically modifying the waste to make it compatible with the glass melter system. Pretreatment steps include removal of excess aluminum by dissolution and washing, and processing with formic and nitric acids to: 1) adjust the reduction-oxidation (redox) potential in the glass melter to reduce radionuclide volatility and improve melt rate; 2) adjust feed rheology; and 3) reduce by steam stripping the amount of mercury that must be processed in the melter. Elimination of formic acid in pretreatment has been studied to eliminate the production of hydrogen in the pretreatment systems, which requires nuclear grade monitoring equipment. An alternative reductant, glycolic acid, has been studied as a substitute for formic acid. However, in the melter, the potential for greater formation of flammable gases exists with glycolic acid. Melter flammability is difficult to control because flammable mixtures can be formed during surges in offgases that both increase the amount of flammable species and decrease the temperature in the vapor space of the melter. A flammable surge can exceed the 60% of the LFL with no way to mitigate it. Therefore, careful control of the melter feed composition based on scaled melter surge testing is required. The results of engineering scale melter tests with the formic-nitric flowsheet and the use of these data in the melter flammability model are presented.

INTRODUCTION & BACKGROUND

Defense Waste Processing Facility

The Department of Energy's Defense Waste Processing Facility (DWPF) at the Savannah River Site in South Carolina processes high-level radioactive waste (HLW) into glass for disposal in an off-site geologic repository. The DWPF began treating radioactive waste in 1996. Ultimately, the DWPF will immobilize the HLW portion of approximately $1.40\text{x}10^5$ m^3 (37 million gallons, Mgal) that is currently stored in underground tanks.

Most of the high level waste is a complex mixture of chemical and radionuclide wastes generated during the processing of reactor fuel and irradiated targets. Approximately $1.14\text{x}10^4$ m^3 (3 Mgal) of the $1.40\text{x}10^5$ m^3 (37 Mgal) of waste are sludge waste and $1.29\text{x}10^5$ (34 Mgal) are salt waste. The insoluble sludge, in the form of metal hydroxides, results from the neutralization of the acidic processing wastes. Neutralization to around pH 12 is required to prevent corrosion of the carbon-steel waste tanks. The sludge settles to the bottom of the waste tanks and contains insoluble radioactive elements including strontium, plutonium, americium, and curium. The salt waste, which is soluble in the liquid, forms a supernate layer that contains most of the soluble radioactive element cesium.[1]

Pretreatment Processes

A simplified diagram of the DWPF treatment system is shown in Figure 1. The sludge waste is transferred into the pretreatment vessel, or Sludge Receipt Adjustment Tank (SRAT), where it is partially acidified with nitric acid, then treated with formic acid and concentrated; this chemical process is referred to as the formic-nitric flowsheet. This treatment chemically reduces the HgO to elemental Hg°, improves the rheology of the slurry, and adjusts the reduction-oxidation (redox) potential of the slurry. The redox potential of the slurry depends on the balance of oxidants (nitrate, oxidized manganese) and reductants (organic antifoaming agent, formate, oxalate, coal). The redox adjustment is needed to optimize the melting of the sludge. The pH of the solution is typically 4-9 at the end of processing, so only a portion of the formic acid is undissociated acid; the remainder is present as the anion of a salt.

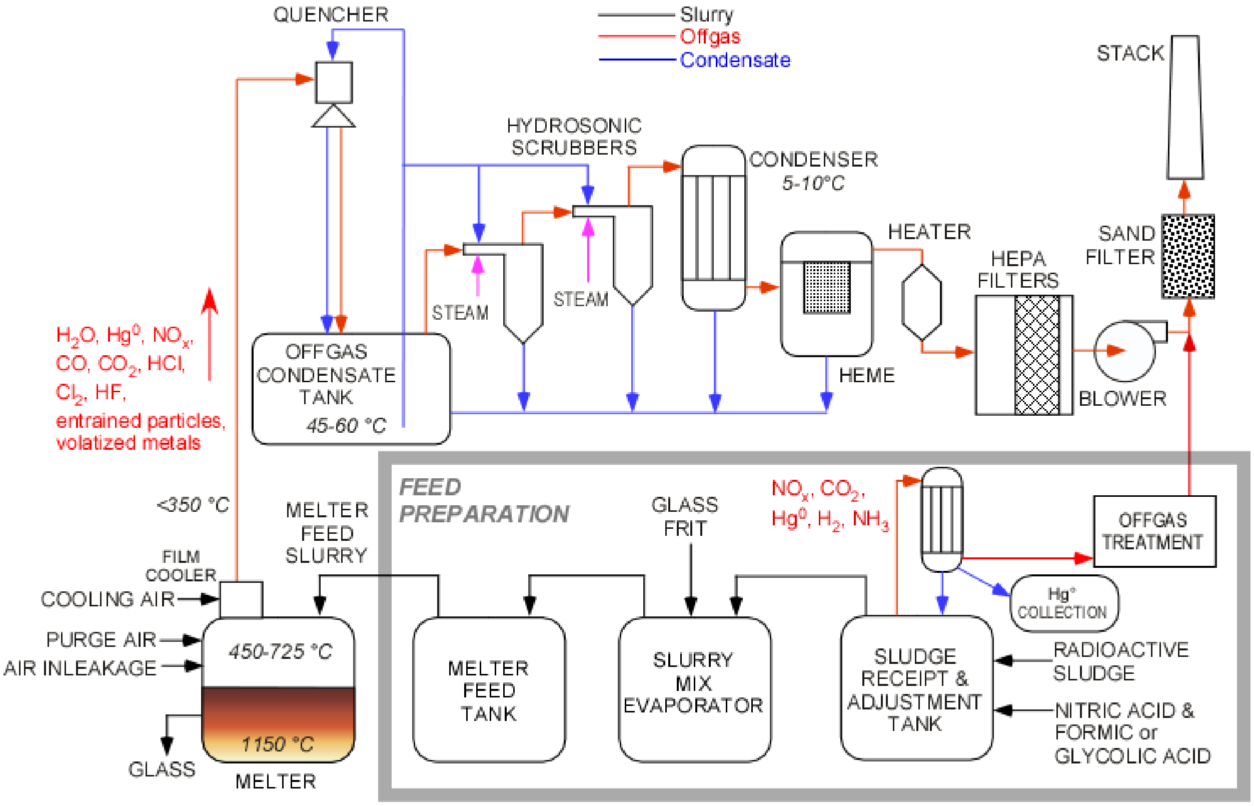


Figure 1 Flow Diagram of the DWPF Radioactive Waste Treatment System

Gaseous byproducts formed in the pretreatment process are CO_2 from carbonate decomposition and oxidation of formic acid, NO_x from reduction nitrite and nitrate by formic acid, hydrogen from catalytic decomposition of formic acid, and traces of ammonia from catalytic reduction of nitrate. The catalytic reactions are catalyzed by small amounts of rhodium, ruthenium, palladium, and silver that are present in the sludge as fission products. Due to its flammability, hydrogen measurement and control systems are required to guarantee safe operation. Because this is a nuclear facility, the reliability and redundancy of these measurement systems is significantly greater than would be needed in non-radioactive operations. Remote maintenance is both difficult and expensive.

The product in the SRAT vessel is then transferred to the Slurry Mix Evaporator (SME) where a borosilicate glass frit is added, followed by additional water removal to concentrate the product. The SME product is verified to be acceptable before it is transferred into the Melter Feed Tank (MFT). The melter feed material in the MFT is then fed to the melter where the HLW glass product is made.

Vitrification Process

The glass melter is a joule-heated slurry fed melter that melts glass at 1100-1150 °C. The slurry of HLW and borosilicate glass frit is fed via a feed tube onto the top of the glass surface in the melter. The melter is equipped with Inconel™ resistance heaters in the vapor space to assist in vaporization of the water in the slurry feed and to combust offgases evolved from the slurry. The melter is purged with air and the offgas passes through a film cooler designed to minimize particulate build up in the offgas line and to cool the offgas from 450-725 °C to less than 350 °C. The melter is equipped with two bubblers that inject argon gas below the surface of the glass to promote mixing. The melting process produces offgas that is primarily water with smaller amounts of N_2, NO_x (NO, NO_2, N_2O), CO, CO_2, and H_2, and trace amounts of HF, HCl, and Cl_2. The blower maintains the entire system under vacuum to minimize leakage of radioactive contamination into the process building.

After passing through the film cooler, the gas is then scrubbed in the quencher. The quencher is an ejector-venturi scrubber that reduces the gas temperature below the dew point, disengages most of the water vapor from the non-condensables, scrubs entrained solids, and allows semi-volatile salts (sulfates, nitrates, chlorides, borates) to coalesce. The quencher uses offgas condensate as the motive fluid. The offgas and condensate leaving the quencher enter the offgas condensate tank (OGCT) where the liquid and vapor disengage. The condensate is maintained at 40°C by a cooler.

The offgas from the OGCT is then passed through a series of two hydrosonic scrubbers, or HSS (Hydro-Sonic Systems, Linden TX), which remove sub-micron and micron-sized particles. The HSS removes particulates by combining water and steam with the offgas in a region of turbulent mixing. The droplets of liquid formed are separated from the vapor in a cyclone separator. The condensate and condensed steam are returned to the OGCT.

The offgas leaving the SAS is passed through a 5-10 °C chilled water heat exchanger designed to separate the condensables from the offgas and reduce elemental mercury to its dew point. The separated condensables are returned to the OGCT. A demister and high efficiency mist eliminator (HEME) with atomized water sprays remove suspended liquid droplets from the non-condensable gases. The offgas is heated 10°C above its dew point to prevent condensation in the high efficiency particulate air (HEPA) filters. The final treatment is a sand bed filter common to radioactive treatment plants. All condensates generated during this waste processing are recycled back to the waste tank farm.

Melter Offgas System Flammability Control

Control of flammability in the melter offgas system must also be considered. Potential flammability in the offgas is due to incomplete reaction of the reductants and oxidants and incomplete combustion in the melter vapor space. The primary flammable species formed are H_2 and CO, with smaller amounts of methane and potentially other organic species. The flammability concern is in the equipment downstream of the melter where much of the water has been condensed. The flammability limit maintained is the Lower Flammable Limit (LFL) as specified by National Fire Protection Association 69 Standard on Explosion Prevention Systems:[2]

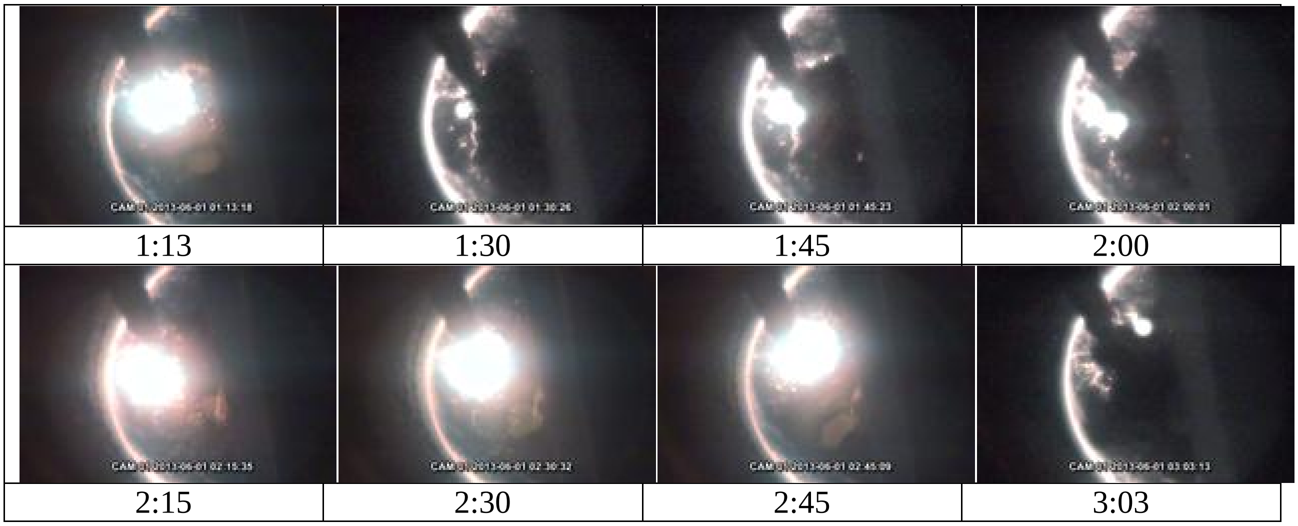
> *The combustible concentration shall be maintained at or below 25 percent of the LFL, unless the following conditions apply: Where automatic instrumentation with safety*

> *interlocks is provided, the combustible concentration shall be permitted to be maintained at or below 60 percent of the LFL.*

DWPF has chosen to implement this requirement in a different way that meets the intentions of the NFPA standard. Monitoring of the LFL with automatic controls cannot be performed because of the fast dynamic nature of the system. Surges in offgas flow can cause the formation of flammable mixtures so quickly that no automatic interlock, such as shutting off the feed or increasing the air purge, can be used to mitigate the flammable mixture; also, the additional air purge that would be needed would be outside the operating capability of the melter offgas system. Therefore, the method chosen to maintain the melter offgas system below 60% of the LFL is to maintain the melter feed composition such that the offgas composition cannot exceed 60% of the Lower Flammable Limit.

The melter feed contains both oxidants (nitrates, oxidized manganese) and reductants (formate, oxalate, coal, organic antifoam agent). The redox balance of these oxidants and reductants determines the proportion of the oxidized iron that is in the +2 reduced state versus the more oxidized +3 state. This Fe redox balance is indicative of foaming due to MnO_2 reduction to MnO to form O_2, and volatility of radioactive species such as technetium. The target redox Fe^{2+}/• Fe is 0.09 to 0.33. The bubbling of argon into the glass also affects the redox by raising it by about 0.10 due to stripping of oxygen from the melt.

The melting process is very dynamic because an aqueous slurry of material is fed onto the top of molten glass at 1150 °C. The feeding process produces a “cold cap”, which is a layer of un-melted and partially melted feed. The target cold cap coverage is typically 90%, which achieves a balance between the melting rate and the need to maintain the vapor space temperature above a minimum level. This cold cap resembles the surface of an active volcano, with vent holes periodically opening in the cold cap cover. A series of photos from a small-scale test melter are shown in Figure 2.



1:13	1:30	1:45	2:00
2:15	2:30	2:45	3:03

Figure 2 Cold Cap Photos versus Time

This dynamic behavior periodically results in surges in both condensable water and non-condensable reaction products. Surges can last from several seconds to several minutes. Condensable water surges cause the temperature of the vapor space in the melter to decrease, resulting in less combustion of the H_2 and CO produced from the cold cap, and thus more flammable gases entering the offgas system. The non-condensable surges include H_2, CO, CO_2, N_2, and NO_x, thus also increasing the concentration of flammable H_2 and CO in the offgas system. Both condensable and non-condensable surges also decrease the residence time in the melter vapor space, resulting in less combustion.

Flammability control is currently achieved by administratively controlling the following parameters:

1. Maximum total organic carbon = 18,900 mg/kg
2. Minimum total melter air purge = 234 scfm
3. Minimum melter vapor space temperature = 460°C

RESULTS & MODELING

The combination of a chemical thermodynamic cold cap model, a vapor space kinetics model, and a melter process system dynamic simulation program are used to predict the production of flammable offgases during process surges.

The dynamic model has been validated against actual process pressure, flow, and temperature data. The cold cap and vapor space models both must be calibrated and validated against actual process data using a melter that is of similar design compared to the actual DWPF melter.

Four-Stage Cold Cap Model

The cold cap model describes the chemistry of melting of the melter feed. The purpose of this model is to calculate the concentration of flammable gases produced from the calcination and fusion of the non-volatile feed components and the composition of the resulting glass that are internally consistent in terms of the overall oxygen balance. The model utilizes the STGSOL Version 2.5 software, a steady state, multistage, countercurrent chemical equilibrium software package developed at the Missouri University of Science and Technology using the SOLGASMIX algorithm[3] and the Gibbs energy database for complex liquids developed by NIST.[4]

It is assumed that all chemical species present in the cold cap are in thermodynamic equilibrium with one another, thus ignoring such effects as chemical kinetics and transport resistances within various phases that form among a very large number of waste components and glass-forming frit. To better represent the gradual nature of the melting process, the entire cold cap is modeled as a continuous, 4-stage countercurrent reactor, as shown in Figure 3. The gas and solids products are allowed to reach equilibrium in each stage, before the former is passed on to the next stage up, while the latter is passed on to the next stage down, thereby maintaining countercurrent gas-solids flows between stages.

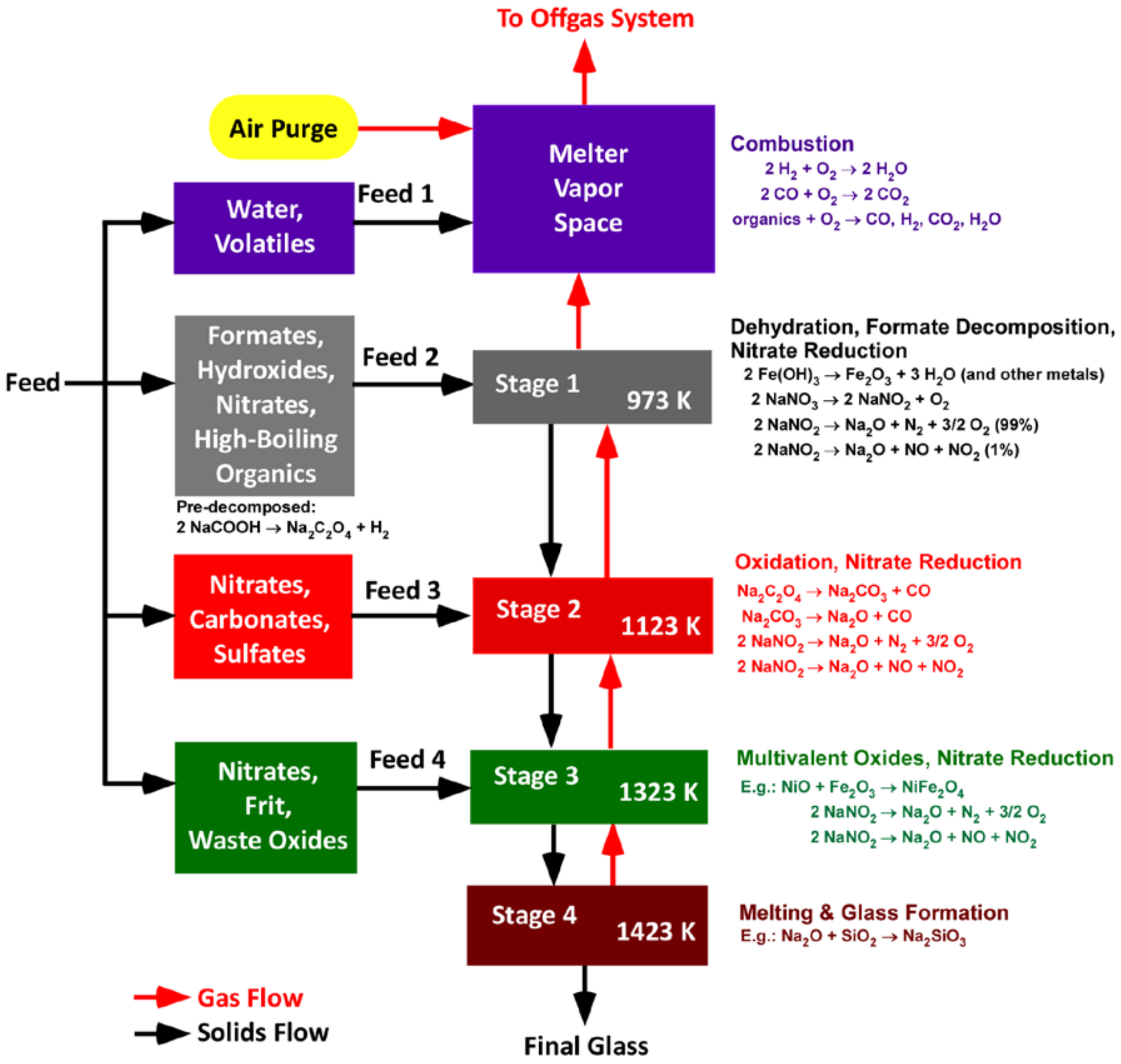


Figure 3 Schematic of 4-Stage Cold Cap Model.

The temperature of each stage is set progressively higher from 700°C at the top (Stage 1) to the final melt temperature of 1150°C at the bottom (Stage 4); therefore, Stage 4 actually represents the bulk melt pool. The temperature of Stage 1 was set based on the finding that the calculated molar ratio of CO to CO_2 in the calcine gases at 700°C closely matched measured data. (Choi ref3) The volatile feed components such as free H_2O and low-boiling organic species are assumed to boil off upon entering the melter and only the remaining non-volatile components enter the cold cap.

Due to its low decomposition temperature, the formate is allowed to decompose into oxalate in Stage 1, thereby releasing H_2 in the process. The oxalate thus formed and that which is already in the feed decomposes into CO and CO_2 with carbonate as the intermediate product in Stage 2. The nitrate first decomposes into nitrite and O_2 and the subsequent decomposition of nitrite is allowed to proceed through Stage 3. At the temperatures of the cold cap and with high cold cap coverage (80-90%), the formation of N_2 and O_2 is thermodynamically favored over NO or NO_2. If the cold cap is in sufficient contact with air due to a low cold cap coverage (~20%), the model is adjusted so that nitrite is forced to decompose exclusively to NO_x, thereby reducing the overall oxidizing potential of nitrate.[5]

In Stage 3, mixed valence metal oxides are allowed to form. For example, the nickel-iron spinels are formed by combining *Ni(II)O* and $Fe(III)_2O_3$. Those species that do not form solid solutions with other species are considered to form separate phases by themselves. Finally, the condensed products from Stage 3 are converted into the glass melt in Stage 4 by forming various silicate compounds.

Validation of the Four-Stage Cold Cap Model

The melter offgas gas composition is typically measured in the offgas exit line. The melter vapor space must be cooled to a temperature low enough to freeze any combustion reactions that might occur so that the resulting offgas would reflect the composition of the calcine gases exiting the cold cap. This has been done by either turning off the vapor space heaters or injection of excess purge air or both. The cold cap model was validated against three sets of data obtained using these methods. Comparisons of model results with experimental data are shown in Table 1. Melter Tests 1 and 2 had 80-90% cold cap coverage. Test 3 had only about 20% cold cap coverage which resulted in a much higher conversion of nitrate to NO_x.

Table 1 4-Stage Cold Cap Model Validation Data

	Melter Test 1		**Melter Test 2**		**Melter Test 3**	
Molar Ratios	**Data**	**Model**	**Data**	**Model**	**Data**	**Model**
CO/CO2	0.13	0.11	0.16	0.16	0.024	0.020
H2/(CO+CO2)	NA	0.48	0.022	0.025	0.016-0.16	0.14
NO_x/NO_3^- fed	NA	~0	NA	~0	0.91	1.00
Glass Redox (Fe^{2+}/Fe^{3+})	<0.22	0.13	0.49-0.59	0.49	0.13	0.12

Vapor Space Combustion Model

The flammable components of the calcine gases along with the volatile feed components that boil off upon entering the melter react further in the vapor space before exiting the melter. The global kinetics approach is used to predict the overall combustion efficiency in the DWPF melter vapor space.

A first-order global kinetics model of CO and H_2 oxidation was developed from experimental data using the formic acid flowsheet feed spiked with high-boiling aromatic compounds:[6]

$$-r = k_o \, e^{(-E_a/RT)} \, C \tag{1}$$

where $-r$ is the reaction rate in lbmole/ft^3/sec, k_o the pre-exponential factor in 1/sec, E_a the activation energy in Btu/lbmole, R the gas constant, T the gas temperature in K, and C the concentration of CO or H_2 in lbmole/ft^3. Assuming that the DWPF melter vapor space is well-mixed, the resulting global kinetic parameters empirically fitted to the data are given in Table 2.

Table 2 First-Order Global Kinetic Parameters for Vapor Space Oxidation

	k_0 (1/sec)	E_a (Btu/lbmole)	R^2
CO	1759	2.219 E4	0.845
H_2	2.795 E7	3.894 E4	0.999

The intrinsic kinetics of oxidation, fluid mixing and heat transfer effects in the vapor space are all lumped into these global kinetic parameters.

Validation of Global Kinetics Model

The global kinetic parameters shown in Table 2 were validated against experimental data.

The calculated concentration profiles of CO and H_2 using the first-order global kinetic parameters given in Table 2 are shown in Figure 4 as a function of gas temperature. At 400ºC the calculated concentration of CO equals the measured data at 391ºC, so the model conservatively over-predicted the concentration by about 7%. The model also predicted that the concentration of H_2 would become zero at gas temperatures above 380ºC, which agrees with the measured H_2 concentration of zero at 391ºC.

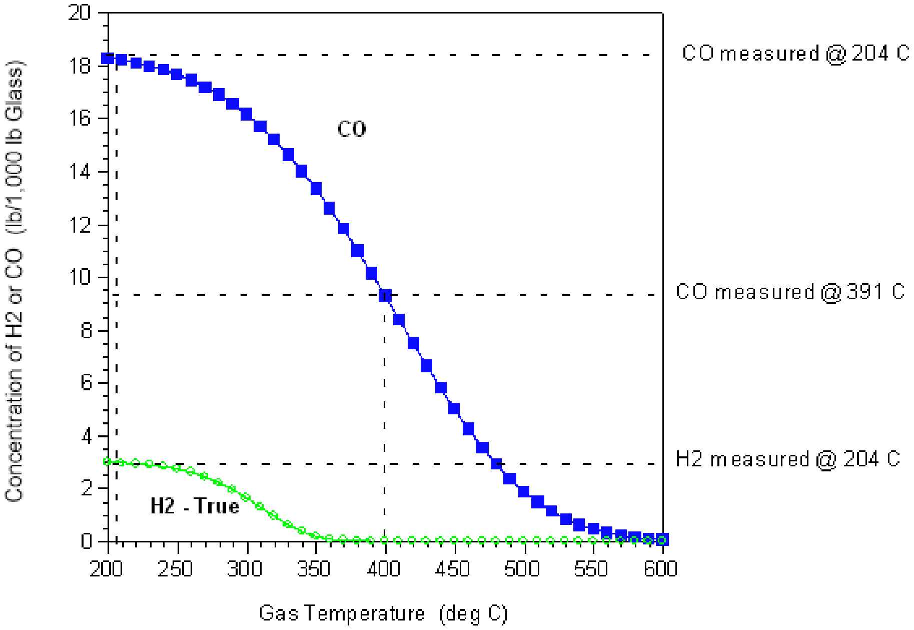


Figure 4 Calculated Concentration Profiles of CO and H_2 vs. SCM-2 Data.

A second set of data was also used to validate the global combustion model. Along with the contribution from the decomposition of free formic acid in the feed, the composition of the calcine gases calculated by the 4-stage cold cap model was used as the input for the global combustion model. In doing so, it was assumed that free formic acid would decompose in the vapor space to form CO and H_2O by the dehydration route shown by Reaction (2):[7,8]

$$\text{Dehydration: } HCOOH \rightarrow CO + H_2O \quad (2)$$

The calculated and measured concentrations of H_2 and CO are compared in Figure 5 as a function of the true gas temperature. The trace amounts of methane produced are ignored.

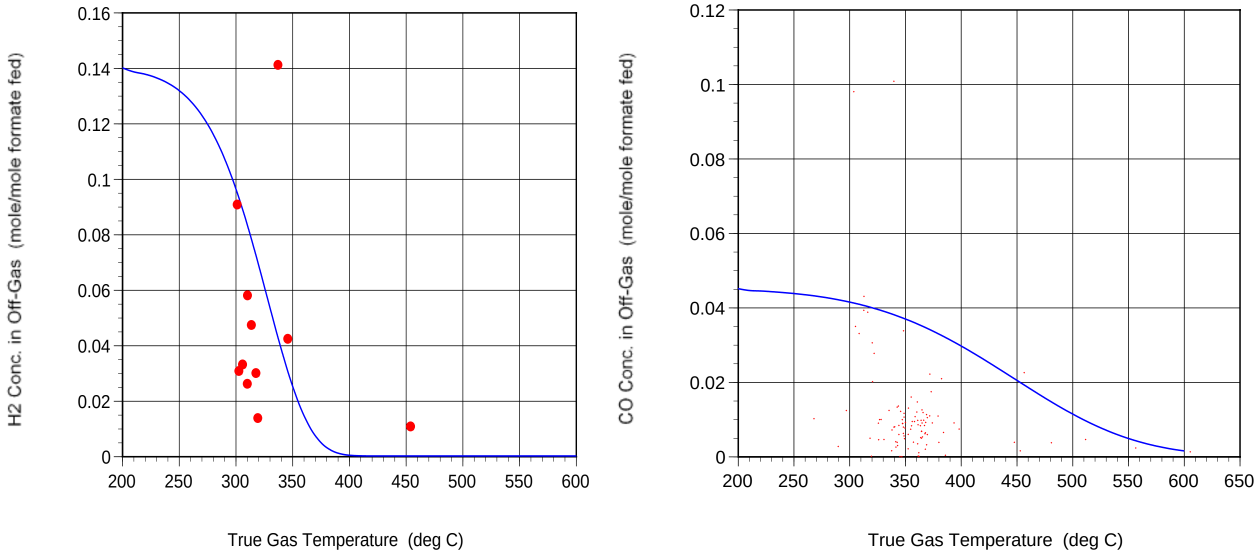


Figure 5 Calculated vs. Measured H_2 and CO Concentrations

Melter Offgas Dynamics Model

A melter offgas system model was developed by Bechtel National Inc. using the proprietary Dynamic Analysis Program (DAP)[9] that predicts the dynamic responses of the DWPF melter offgas system under various upset conditions. It calculates five-component mass and energy balances for H_2, CO, aromatic hydrocarbon, condensable, and non-condensable gases from first principles. It simulates all major DWPF melter offgas system hardware, including 22 controllers, 26 automatic valves, and the distributed control system software logic. A two-step global mechanism for aromatic hydrocarbon combustion and empirical oxidation kinetics of CO and H_2 in the melter vapor space are employed. The dynamic elements of this model were validated against actual DWPF startup data, and the empirical kinetics used for CO and H_2 oxidation in the melter vapor space were validated against pilot-scale melter data.

The dynamics model is run at the minimum vapor space temperature and air purges using the calcine gas composition from the cold cap model as input to determine the peak concentration of flammable gases at the offgas condensate tank exit during a 9X/5X offgas surge. The 9X/5X offgas surge event is defined as 9 times the condensable and 5 times the non-condensable nominal gas flow rates to simulate a melter surge scenario.

In 2010, the small-scale test melter was used to determine if the use of argon bubblers to mix the glass and increase the melting rate had any detrimental effect on the surge behavior of the melter. Baseline data was taken at non-bubbled conditions and several vapor space temperatures, then tests were performed with the bubblers in use. The largest pressure spike during bubbled operation is shown in Figure 6. The responses of the vapor space temperature, pressures, and CO_2 and H_2 concentrations are shown. Carbon monoxide (CO) concentration was not measured during this test. The surge in CO_2 was about 3.7 times the baseline concentration; the surge in H_2 was measured as 0% to about 0.9%, but the accuracy of the mass spectrometer at less than about 0.1% was such that a reading of zero could have actually been about 0.1%.

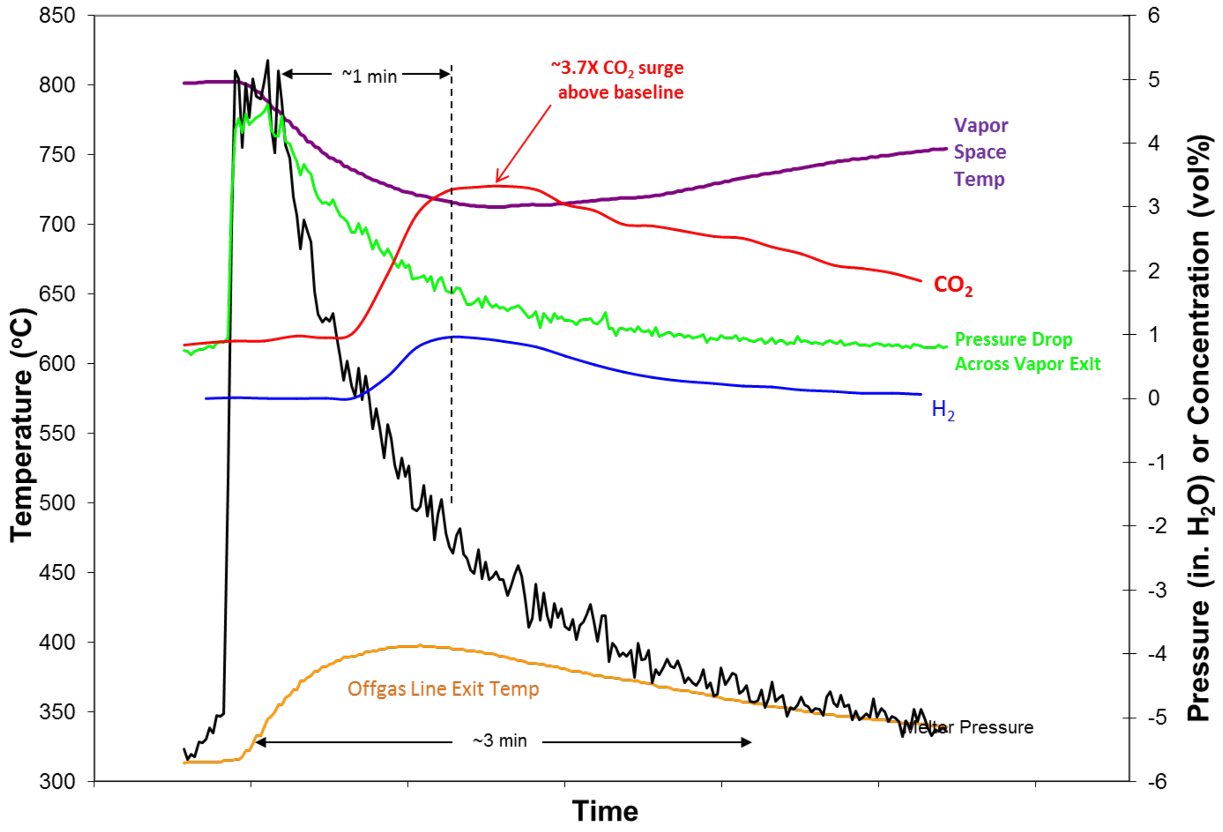


Figure 6 Transient Responses During a Large Surge

The CO_2 concentration also began to increase at the onset of pressurization and reached its maximum at about the same time that the vapor space temperature reached its minimum, which was about 1 minute after the pressure spike. The spike in CO_2 readings was more likely due to surges in both the condensable and non-condensable gas flows considering the fact that CO_2 is produced not only in the cold cap but in the vapor space from thermal decomposition of formic acid. The increase in H_2 concentration could be due to the decrease in vapor space temperature or the decrease in residence time, or both. Table 3 shows the number of CO_2 spikes measured during a ten day run. It is clearly seen that the CO_2 spikes are more frequent and of greater magnitude during bubbled than non-bubbled runs.

Table 3 Number of CO_2 Spikes of Greater than 0.5% During a Ten Day Run

Change in CO_2 (vol% dry)	Non-Bubbled	Bubbled	Total
0.5 – 1.0 %	5	49	54
1.0 – 1.5 %	0	14	14
1.5 – 2.0 %	1	2	3
2.0 – 2.5 %	0	1	1
> 2.5 %	0	0	0
Total	6	66	72

Surge data such as that shown above is used in the dynamic model of the DWPF melter offgas system to determine under what surge conditions 60% of the LFL could be exceeded. An iterative process is used wherein the cold cap model is run at a specific set of input concentrations of oxidants and reductants, then the output of this and the vapor space kinetics model are used as inputs to the dynamic model. The dynamic model then predicts the %LFL given the input concentrations. The iterative process is repeated until the input concentrations that result in 60% LFL are determined. These concentrations then set the processing limits that maintain the offgas system below 60 %LFL during surges.

Typical model results are shown in Figure 7. At about 0.5 minutes, a surge is initiated that results in almost immediately reaching a positive pressure of about 15 in. H_2O and an offgas flow of about 1100 scfm. Simultaneously, the vapor space temperature decreases from 300 °C to about 140 °C. The 60 %LFL point is reached in about 0.5 minutes (at 1 minute on the time scale). The melter pressure quickly decreases to about -22 in. H_2O as the control system attempts to bring the pressures and flows back to stable values. Note that the model predicts about a 0.5 minute lag between the maximum pressure and the flammable gas maximum. This result is similar to what was shown for the test melter in Figure 6.

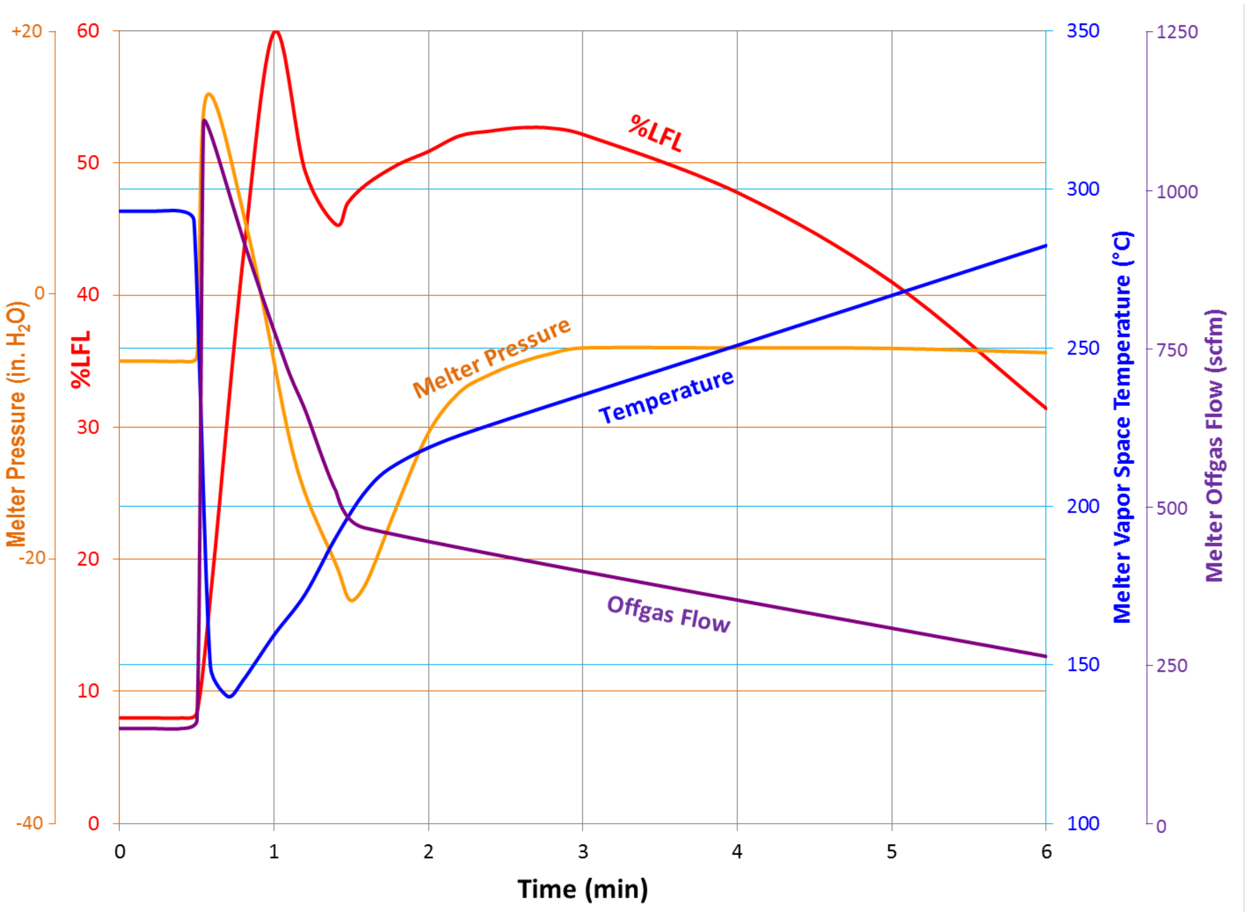


Figure 7 Predictions from the Dynamic Analysis Program

Recent Experimental Work: An Improved Pretreatment Process – The Alternative Reductant Flowsheet, or Glycolic-Nitric Flowsheet

Elimination of the formic acid treatment would greatly simplify the pretreatment system and could result in significant increases in processing rate, which are both desirable. Substitution of glycolic acid in place of formic acid has been shown to achieve all of the required processing results and to virtually eliminate the production of hydrogen in the pretreatment vessel. Some formate is formed during processing with glycolic acid, but negligible hydrogen is formed. The chemical structures of formic and glycolic acids, shown in Figure 8, make it evident why formic acid easily forms H_2 by catalytic decarboxylation whereas glycolic acid does not.

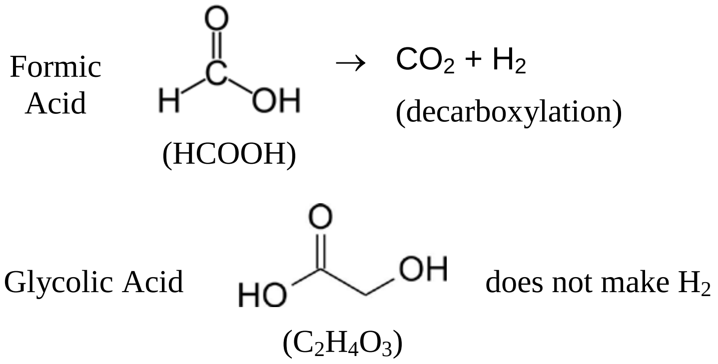


Figure 8 Structures of Formic and Glycolic Acids; Decomposition of Formic Acid

In 2013, additional testing was done with the formic-nitric flowsheet in preparation for tests with melter feed produced by the alternative reductant flowsheet. In these tests, additional process analyzers were used to measure more offgas species that in 2010. This additional capacity was added to address concerns that previously unmeasured organic species from the antifoam agent or the glycolic acid could be formed and contribute to the overall flammability of the offgas. The additional measurement capabilities are shown in Table 4. The mass spectrometer used is an Extrel CMS MAX-300LG process analyzer that has a dual detector including an electron multiplier to measure ppm levels. The FTIR is a MKS MG2030 with a liquid nitrogen cooled detector that can measure infrared active species to ppm levels. The gas chromatograph (Inficon or Agilent Micro Gas Chromatograph) is used primarily to check the MS hydrogen readings. The fast responses of the MS and FTIR are ideal for detecting surges in offgas generation.

Table 4 Instruments to Measure Offgas Composition

	Measured By:		
Offgas Species	**Mass Spectrometer**	**FTIR**	**Gas Chromatograph**
H_2	Y	N	Y
O_2	Y	N	Y
N_2	Y	N	Y
Ar	Y	N	N
CO_2	Y	Y	Y
CO	N	Y	(Y)
CH4	N	Y	N
NO	Y	Y	N
NO_2	Y	Y	N
N_2O	N	Y	(Y)
Organics	N	Y	N
Sampling Frequency	7 s	3.5 s	4 min

(Y): semi-quantitative

The concentrations of flammable gases during a formic-nitric flowsheet run are shown in Figure 9, where the melter vapor space temperature was progressively being lowered from about 700 °C to 300 °C by decreasing the vapor space heat input and increasing the vapor space air purge. As the air purge was increased, the vacuum that could be achieved in the melter decreased. The concentration of CO was generally about 20 times smaller than the CO_2 and the H_2 concentration was generally similar to slightly higher than the CO. During these tests, trace amounts of methane (<16 ppm) were measured. Some unburned or partially combusted organic antifoam agent species were expected to be found, but no organic species other than methane were detected. The FTIR has been used to detect methane, propylene, ethylene, and acetylene from the pyrolysis of the antifoam agent, so it was known that the FTIR would have detected these species had they been present.

The distribution of N_yO_x compounds was predominantly NO, with N_2O about 7 times smaller than NO. The distribution of NO_x between NO and NO_2 would be dependent on the residence time in the analyzer system, and the lower temperature in the sample lines would support conversion of some of the NO to NO_2 by oxidation with the excess O_2. The thermodynamic model of the melter offgas predicts that most of the NO_x should exit the melter vapor space as NO. The total amount of N_yO_x compounds was less than 1% of the total nitrate fed to the melter. This result is typical of a melter with high cold cap coverage, wherein most of the nitrate is converted to N_2.

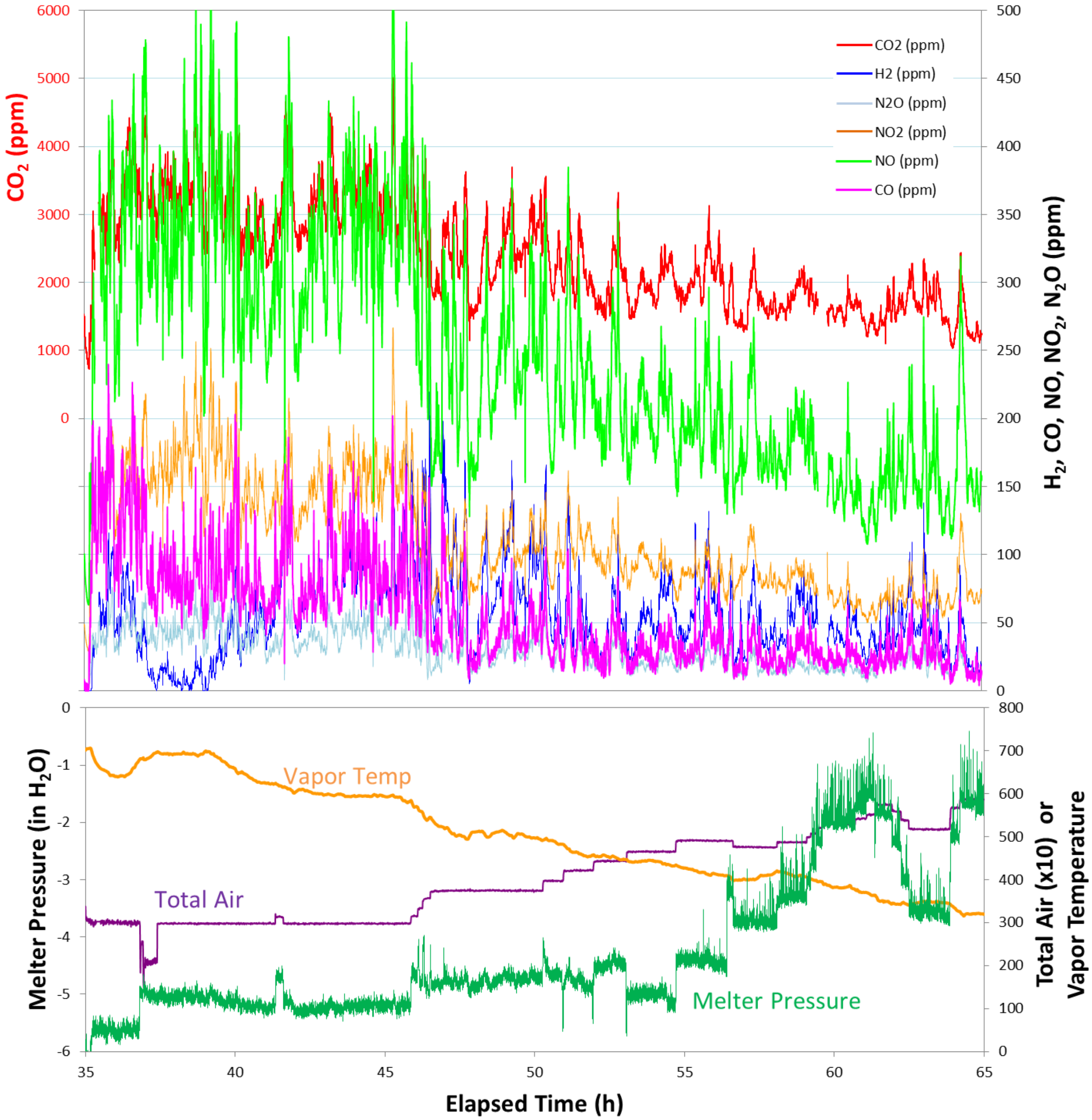


Figure 9 Example Melter Offgas Flammable Species

No large pressure surges were seen during the limited 2013 testing with the formic-nitric flowsheet. Figure 10 shows a relatively small surge in pressure along with the surges in CO_2, CO, and H_2 concentrations. The surge in pressure preceded the surges in the gas concentrations by about 1.8 minutes, which is similar to what was seen in the 2010 tests shown in Figure 6, although the 2010 surge was significantly larger than the one shown in Figure 10. In Figure 10, the surge in CO_2 was about 2X, CO was about 2.5X and H_2 was about 5X, showing that the surge in H_2 can be greater than the surges in CO or CO_2.

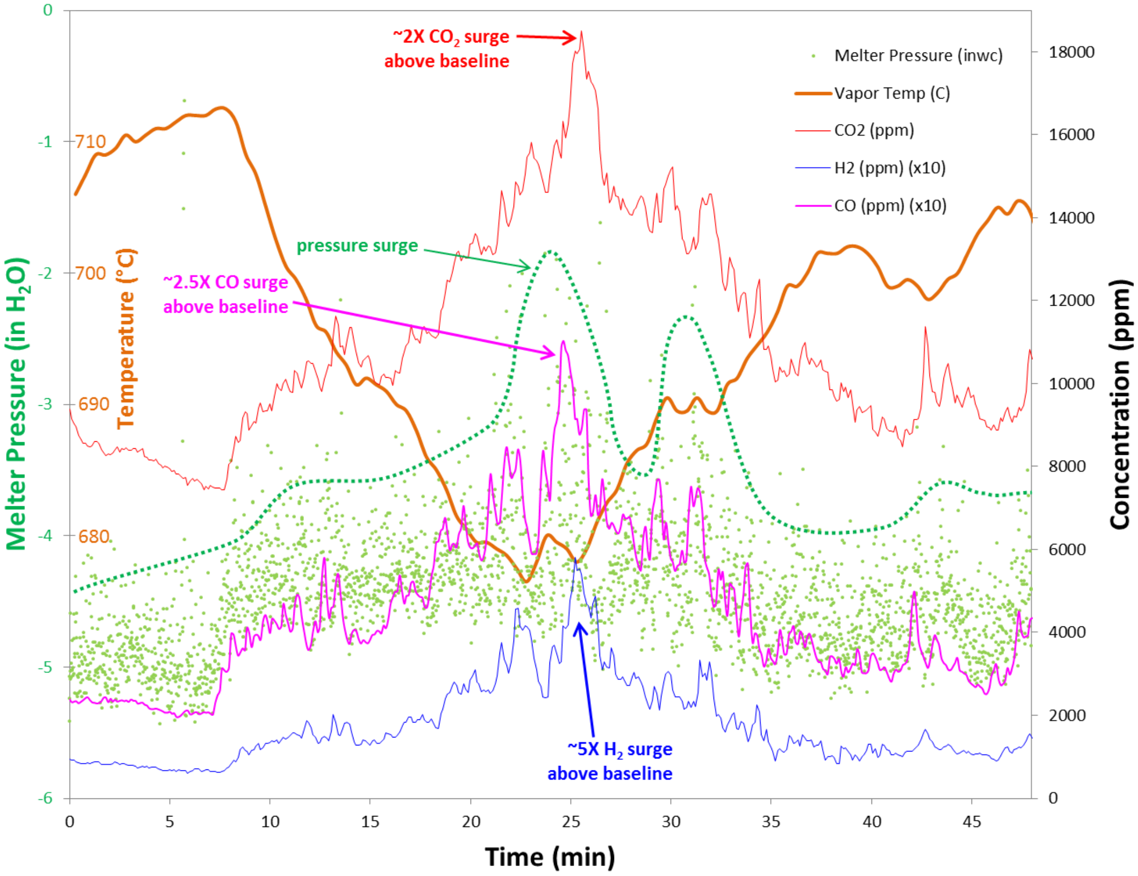


Figure 10 Surges in Condensable and Non-Condensable Flows

Future Work

The pretreatment process with the alternative reductant glycolic-nitric flowsheet has been extensively studied, but a scaled melter demonstration to determine surge behavior and flammable gas generation has not yet been performed. It is not yet known if any significant flammable species other than formic acid are found in the offgas. An experimental testing program has been developed to determine what additional flammable gases, if any, are formed from melter feeds containing glycolate.

The four-stage cold cap model has not yet been applied to the alternative reductant flowsheet. It is expected that the cold cap reactions may be similar to those seen with formate in the feed, but actual experimental results will be required to calibrate the model to the new flowsheet. At the time of this paper, it was expected that this work would be completed, but now it is not expected to be done until 2014.

CONCLUSIONS

The combination of experimental melter offgas data with a melter cold cap thermodynamic model, a vapor space kinetics model, and an offgas system dynamic modeling program have been used to successfully model the behavior of a nuclear waste treatment melter during transient operation when offgas surges have the potential to produce flammable gas mixtures. These modeling techniques have been applied to the formic-nitric flowsheet process for the Defense Waste Processing System. Future work will involve using these same models to evaluate an alternative flowsheet using glycolic and nitric acids. Demonstration of an improved offgas monitoring system capable of faster analyses and analyses of more species has been completed.

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