

Maximum Organic Carbon Limits at Different Melter Feed Rates (U)

by

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**MAXIMUM TOTAL ORGANIC CARBON LIMITS AT
DIFFERENT DWPF MELTER FEED RATES (U)**

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MAXIMUM TOTAL ORGANIC CARBON LIMITS AT
DIFFERENT DWPF MELTER FEED RATES (U)

The attached report by A. S. Choi documents the results of a study to assess the impact of varying melter feed rates on the maximum total organic carbon (TOC) limits allowable in the DWPF melter feed, as stated in the Technical Task Request HLW/DWPF/TTR-950047. In order to minimize a potential for forming a flammable vapor in the melter off-gas system, the following correlation is recommended to determine the maximum TOC limit, including both formate and aromatic carbons, from a given feed rate and the specific gravity of the feed:

$$\text{max TOC (ppm)} = 45,180 * \text{FR} * \text{SpG} - 108,200 \ln(\text{FR} * \text{SpG}) - 4,860$$

where FR is the feed rate in GPM ranging from 0.7 to 1.5 GPM, and SpG is the specific gravity. If it is desired to determine the highest feed rate that the DWPF melter can tolerate at a given TOC level measured in ppm, the following correlation is recommended:

$$\text{max feed rate (GPM)} = 0.756 + 1,185.5 \ln(\text{TOC} * \text{SpG}) / (\text{TOC} * \text{SpG}) - 5.4E-6 * \text{TOC} * \text{SpG}$$


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

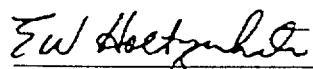
At TOC levels below the maximum limit predicted from the above correlation for a given feed rate, the peak concentration of combustible gases in the quenched off-gas will not exceed 60% of the lower flammable limit (LFL) during a 3X off-gas surge, provided that a steady melter operation is established at the onset of surge, and the following operating conditions are met at all feed rates considered:

- The indicated melter vapor space temperature (TI-4085D) is maintained above 650 °C.
- The air purge to the backup film cooler (FIC-3221B) is maintained above 250 lb/hr including 30 lb/hr line purge.
- The total air purge to the melter (FIC-3221A) is maintained above 850 lb/hr.

The peak magnitude of a 3X 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. At the reference DWPF melter feed rate of 0.9 GPM and a specific gravity of 1.48, the maximum allowable TOC limit thus determined is about 24,000 ppm, and the maximum TOC feed rate is 15.8 lb/hr at 0.9 GPM.

All the necessary calculations for this study were made using the 4-stage cold cap model and the melter off-gas dynamics model. The 4-stage cold cap model was validated earlier against the melter 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, it is recommended that this conservatism still be verified, and the model be calibrated by running a controlled experiment on the IDMS.

In addition, in view of recent DWPF melter cold run data, the 3X surge criteria used in this study, i.e., the 8 minute total surge duration with an average magnitude of 2.25 times nominal for the first 1 minute appear to be conservative. This conservatism will be verified during the upcoming dynamic simulation study which, along with this TOC study, will then satisfy all the requirements for the Technical Task Request HLW/DWPF/TTR-950047. Customer comments by R. E. Edwards of DWPF-Engineering have been incorporated into the attached report.



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WSRC-TR-95-0294 (Revision 0)

DOCUMENT APPROVAL



A. S. Choi, Author
Defense Waste Processing Technology Section / SRTC

11/6/95

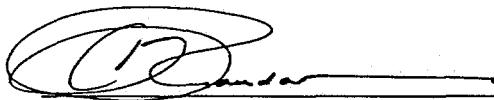
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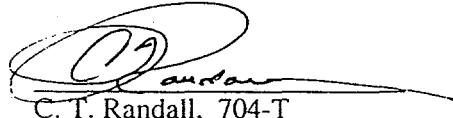
SUMMARY

As partial fulfillment of the Technical Task Request HLW/DWPF/TTR-950047, the maximum total organic carbon (TOC) limits that are allowable in the DWPF melter feed without forming a potentially flammable vapor in the off-gas system were determined at varying feed rates of up to 1.5 GPM. Given a feed rate and the specific gravity of the feed, the following correlation was developed to determine the maximum TOC level in the feed including both formate and aromatic carbons:

$$\text{max TOC (ppm)} = 45,180 * \text{FR} * \text{SpG} - 108,200 \ln(\text{FR} * \text{SpG}) - 4,860$$

where FR is the feed rate in GPM, and SpG is the specific gravity. If one needs to determine the highest feed rate that the DWPF melter can tolerate at a given TOC level measured in ppm, the following correlation can be used:

$$\begin{aligned} \text{max feed rate (GPM)} &= 0.756 + 1,185.5 \ln(\text{TOC} * \text{SpG}) / (\text{TOC} * \text{SpG}) \\ &\quad - 5.4 \times 10^{-6} * \text{TOC} * \text{SpG} \end{aligned}$$



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Authorized Derivative Classifier

DWPT Activity # DWPT-95-0031

At the maximum TOC levels predicted by the above correlation, the peak concentration of combustible gases in the quenched off-gas will not exceed 60% of the lower flammable limit (LFL) during a 3X off-gas surge, provided that the indicated melter vapor space temperature and the total air supply to the melter are maintained above 650 °C and 850 lb/hr, respectively, at the onset of a surge. At the reference DWPF melter feed rate of 0.9 GPM and a specific gravity of 1.48, the maximum TOC level thus predicted is about 24,000 ppm or 15.8 lb/hr.

All the necessary calculations for this study were made using the 4-stage cold cap model and the melter off-gas dynamics model. A high degree of conservatism was included in the calculational bases and assumptions. As a result, the proposed correlations are believed to be conservative enough to be used for the melter off-gas flammability control purposes.

BACKGROUND

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 the LFL at off-gas flow rates 3 times normal.¹ According to the National Fire Protection Association (NFPA) Code 69,² this 60% LFL limit is applicable only when automatic instrumentation with safety interlocks is provided to control the concentration of combustible components. With no LFL analyzers in place, compliance with the Code 69 requires that all the operating variables that can contribute to the potential off-gas flammability be monitored, and necessary safety interlocks and operating procedures to control those variables be devised.¹⁴

It was confirmed during the ninth Scale Glass Melter (SGM-9) run that the melter off-gas flammability during normal operation is largely determined by a set of conditions involving the following operating variables:³

- Carbon content in the 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. 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 a high melt rate consistently. Nevertheless, cold cap instability can still occur during feeding, and it is during these upset periods when abnormally high concentrations of combustible species can be vented into the off-gas system. The strategies currently used in DWPF to prevent potential off-gas flammability under these upset conditions are briefly discussed next.

Carbon Content

According to the reference DWPF Batch 1 sludge melter feed composition shown in Table 1,⁴ the sources for the combustible components in the feed include the formate and aromatic carbons present at 6,370 and 450 ppm, respectively, on an aqueous slurry mass basis. The aromatic carbon level of 450 ppm represents about 1% of that entering the Salt Processing Cell (SPC), i.e., 99% removal efficiency in the SPC and the Chemical Processing Cell (CPC) combined. This flowsheet value is based on the previous pilot-run data which showed that the aromatic carbon removal efficiency in the SPC alone was routinely over 95%, and more than 90% of the remaining phenol was further removed in the CPC.^{5,6} Furthermore, DWPF currently has a technical safety requirement (TSR) on the maximum benzene and phenolboric acid (PBA) levels in the SPC aqueous product. So, the nominal TOC level in the melter feed is about 6,820 ppm, and can be increased mainly by increasing the formate carbon level.

The current DWPF melter feed redox criterion requires that the formate and nitrate concentrations in the feed must satisfy the following:

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

where R is a constant which takes a value of 0.5 at the nominal copper level, and can be greater than 1 at low copper levels. According to Eq. (1), the maximum formate carbon limit is determined by the absolute quantity of nitrate present in the feed as well as the value of R. It is then important to ensure that the maximum formate carbon limit set by the redox criterion does not push the TOC level high enough to lead to a potential for flammability in the melter off-gas system. At a fixed TOC level, this safety issue is determined by the operating characteristics of the melter off-gas system. Of all the operating variables, the feed rate is generally the most influential factor affecting off-gas flammability.

Feed Rate

The reference feed composition in Table 1 shows that the melter feed rate needs to be kept at 0.9 GPM at 44.3 wt% total solids in order to maintain the design glass production rate of 228 lb/hr. With all other operating variables fixed, increasing the feed rate would have more negative impact on 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. This adverse impact is likely to be more pronounced when surges occur more frequently. Currently, DWPF measures the TOC level in the feed, but has no upper limits on the feed rate.

TABLE 1. Reference DWPF Batch 1 Sludge Melter Feed Composition

Formate/Nitrate Species	lb/hr	Organic Species	lb/hr	Other Inorganic Species	Other Inorganic Species	lb/hr
Ca(COOH)2	3.902E-02	(C6H5)2	0.000E+00	Ag	1.245E-02	PbCO3 2.800E-04
Ca(NO3)2	2.607E+00	(C6H5)2C6H4	6.362E-02	Al2O3	1.028E+01	PbSO4 9.870E-02
Co(COOH)2	2.045E-04	(C6H5)2NH	0.000E+00	B2O3	1.296E+01	PuO2 8.545E-03
Co(NO3)2	0.000E+00	C6H5B(OH)2	0.000E+00	Ba(OH)2	0.000E+00	Rh 1.751E-03
CsCOOH	2.135E-01	C6H5C6H4OH	4.791E-02	BaSO4	2.336E-01	Ru 8.130E-03
CsNO3	5.308E-04	C6H5NH2	1.612E-04	Ca(OH)2	0.000E+00	SiO2 1.260E+02
Cu(COOH)2	1.548E+00	C6H5NHCHO	1.786E-01	Ca3(PO4)2	2.407E+00	TcO2 2.888E-03
Cu(NO3)2	0.000E+00	C6H5NO	2.919E-03	CaC2O4	6.364E-02	ThO2 1.343E-01
KCOOH	9.477E+00	C6H5NO2	5.923E-03	CaF2	1.646E-02	TiO2 7.645E-01
KNO3	3.146E-02	C6H5OH	4.956E-02	CaO	3.131E-03	U3O8 2.328E+00
Mg(COOH)2	3.249E+00	C6H6	0.000E+00	CaSO4	5.472E-02	Zeolite 2.187E-03
Mg(NO3)2	0.000E+00	(CH3)2CHOH	0.000E+00	Cr2O3	1.757E-01	ZnO 7.215E-02
Mn(COOH)2	2.349E+00	CH3OH	0.000E+00	Cs2O	2.480E-04	hyd H2O 6.326E+00
Mn(NO3)2	0.000E+00	Total_2 =	3.487E-01	CuO	2.347E-02	H2O 3.337E+02
NH4COOH	0.000E+00	stoichiometric O2 req'd to burn 100% organics =		Fe2O3	2.373E+01	
NH4NO3	2.438E-03		4.544E+00	H2C2O4	7.563E-02	Total_3 = 5.568E+02
NaCOOH	6.296E+00	Total Feed		H3BO3	8.076E+00	
NaNO3	1.584E+01	(lb/hr) =	598.9745	Hg	2.412E-01	
Ni(COOH)2	4.172E-02	(GPM) =	0.9005	K2O	1.125E-01	
Ni(NO3)2	0.000E+00	wt% total solids =	44.2881	Li2O	1.134E+01	
Pb(NO3)2	4.217E-05	wt% insolubles =	35.8538	MgO	3.526E+00	
Pd(NO3)2	0.000E+00	specific gravity =	1.3312	MnO2	2.026E+00	
Sr(COOH)2	1.789E-03	Carbon Feeds	lb/hr	MoO2	1.690E-03	
Sr(NO3)2	2.798E-02	Formate =	3.8194	NH4OH	8.660E-02	
UO2(COOH)2	7.923E-08	Aromatic =	0.2681	Na2O	1.114E+01	
UO2(NO3)2	9.601E-05	Misc =	0.0321	Na2SO4	4.246E-01	
Y(COOH)3	7.190E-04	Total Carbon =	4.1195	Na3PO4	1.020E-02	
Y(NO3)3	1.004E-02	glass prod exc.		NaCl	3.386E-02	
Zn(COOH)2	6.100E-02	entrainm't (lb/hr) =	228	NaF	3.348E-02	
Zn(NO3)2	0.000E+00			NiO	2.937E-01	
Total_1 =	4.180E+01					
COOH - NO3, M	2.196E-01					
tot formate salts*	2.328E+01					
total nitrate salts*	1.852E+01					

* Total formate & nitrate salts includes cations.

Melter Vapor Space Temperature

The Basic Data Report requires that the melter vapor space or plenum temperature be kept at a temperature between 650 and 800 °C in order to evaporate the feed water and to supplement the joule heat in melting the cold cap.¹ DWPF currently has a low vapor space temperature interlock at 650 °C, and this low-temperature interlock is set based on the temperature readings measured in the vapor space thermowells. However, due to thermal radiation effects on the thermowells, the actual gas temperature at the indicated vapor space temperature of 650 °C is estimated to be only about 470 °C using the available correlation.⁷

In the calculations of combustion kinetics, it is the actual gas temperature that counts, and the apparent rate constants for the overall CO and H₂ oxidation in the melter vapor space were shown earlier to vary with the gas temperature according to the well-known Arrhenius form.⁸ During typical off-gas surges lasting only several seconds, the actual cooldown of the vapor space will not be reflected correctly on the indicated temperatures due to thermal inertia of the thermowells. Thus, the temperature correlation mentioned above cannot be used to predict the gas temperature variations during surges for transient combustion calculations.

Combustion / Dilution Air

Much of the air purge required for the combustion of off-gas combustibles is supplied through the backup film cooler (BUFC). In an earlier study,⁹ the minimum air flow rate to the BUFC was determined to be 220 lb/hr, and DWPF currently has a low-flow interlock for the BUFC air FIC-3221B at 250 lb/hr. Additional combustion air is supplied through the seal pot and the TV cameras in the form of air purges, totaling 80 lb/hr. Thus, the total air purge to the melter vapor space is in 50% excess of the stoichiometric requirement at a conservatively low aromatic carbon removal rate of 85% and the nominal formate carbon level.⁹

Under normal operating conditions, the combustion in the melter plenum will be nearly complete,¹⁰ and the combustibles concentration in the off-gas exiting the melter is significantly low, thus requiring little dilution air downstream. However, in the event of a large off-gas surge, the gas temperature in the melter vapor space can drop significantly below its normal operating value, resulting in a marked reduction in combustion efficiency. This reduced combustion efficiency coupled with increased combustibles concentration during off-gas surges could push the combustibles concentration beyond the LFL. So, the dilution air flow rate should be set so as to maintain the combustibles concentration downstream below 60% of the LFL under these abnormal conditions.

In DWPF, this dilution air is supplied through the primary film cooler (PFC). The air flow rate to the PFC is controlled by the FIC-3221A which receives signals from the transmitter which reads the total melter air flow, including the air flows to the BUFC, seal pot and TV cameras. The air purge rates to the seal pot and TV cameras are limited to 20 and 120 lb/hr, respectively. So, at the current low-flow interlock values of 850 and 250 lb/hr for the FIC-3221A and FIC-3221B, respectively, the total dilution air flow to the PFC is 460 lb/hr. Note that 50% of the 120 lb/hr air purge to the TV cameras is vented out to the cell. In addition, the dilution air flow to the PFC also cools the off-gas, and helps transport off-gas entrainments to the quencher. It should be noted that the melter pressure control air flow, which is set at 500 lb/hr during normal operation, and any air inleakages to the melter off-gas system are not considered as dilution sources.

Off-Gas Surges

In both off-gas system dynamics and flammability studies, upset conditions are typically simulated by creating a sudden surge in the vapor flow rate. Off-gas surges are mainly attributed to the inherent instability of the cold cap which is known to be related to many design and operating characteristics, including the size of the melter, vapor space temperature and feed composition. As a result, it is practically impossible to predict both the frequency and characteristics of surges such as peak intensity and duration from a given set of operating conditions. Instead, representative surge patterns have been constructed from the results of pilot melter runs,^{11,15,16} and subsequently used in the design basis calculations.

As stated earlier, the DWPF Basic Data Report (BDR) specifies the design basis abnormal melter off-gas flow rate of 3 times normal (3X) for the flammability control purposes,¹ and it is implicitly assumed that the 3X off-gas flow continues indefinitely. Realistically, however, large surges cannot last for an extended period of time. Based on an earlier study,¹¹ the total duration of the design basis 7X surge for the melter pressure protection was set at 8 minutes, which was subsequently used in all dynamic simulation studies. However, recent DWPF cold run data showed that the peak surge intensity may be greater than 7X, but the surge duration is generally on the order of only several seconds.

Earlier Work on Maximum TOC

SRTC recommended earlier that the TOC level in the DWPF melter feed be less than 24,000 ppm on an aqueous slurry basis.⁸ The composition of the reference melter feed used in the analysis was identical to that shown in Table 1. In order to increase the TOC level above nominal 6,820 ppm, the formate carbon level was first increased from nominal 6,370 ppm to a maximum of 8,900 ppm by imposing the feed redox constraint of $F - N = 0.5$ at the baseline nitrate level of 0.485 molar.

Then, the maximum TOC limit of 24,000 ppm was determined by increasing the aromatic carbon level from nominal 450 ppm to 15,100 ppm at which point the calculated peak concentration of combustible components in the quenched off-gas was at 60% of the LFL during a 3X off-gas surge. In doing so, the overall aromatic carbon removal efficiency across the SPC and CPC was reduced to only 76%, which is considerably lower than the experimentally observed values.^{5,6} As described next, this approach to increasing the TOC level was revised significantly during the present study to better reflect the actual data.

BASES AND ASSUMPTIONS

One of the primary objectives of this study was to extend the scope of the earlier TOC work by varying the feed rate, i.e., to determine the maximum TOC limit as a function of feed rate. Some of the calculational bases assumed in the earlier work were also modified to better reflect the current conditions in DWPF. As a result, the overall approach taken to determine the maximum TOC limit was changed from one of finding the highest aromatic carbon level at a given formate carbon level determined by a fixed redox ratio of 0.5 to finding the highest formate carbon level at a fixed aromatic carbon level set by assuming a conservative aromatic carbon removal efficiency. In doing so, the melter feed redox constraint shown in Eq. (1) was overridden. In summary, the bases and assumptions used in this study include:

- The composition of the reference DWPF melter feed is represented by that given in Table 1, which was calculated using the Tanks 42/51 blend sludge and the average salt feeds, and has the following characteristics:⁴
 - total solids = 44.3 wt%
 - nitrates (N) = 0.485 molar
 - formates (F) = 0.705 molar
 - formate carbon = 6,370 ppm (aqueous slurry basis)
 - aromatic carbon = 450 ppm (aqueous slurry basis)
- The combined efficiency of aromatic carbon removal in the SPC and CPC is set at 95%, i.e., 95% of aromatic carbons entering the SPC remains in the melter feed. This increases the aromatic carbon level from 450 to 3,100 ppm at 44.3 wt% total solids.
- At a given feed rate, the formate carbon level is then increased from nominal 6,370 ppm to a maximum value where the peak concentration of combustible components in the quenched off-gas reaches 60% of the LFL during a 3X off-gas surge.

- The melter vapor space temperature measured in the thermowells is at the low-temperature interlock of 650 °C at the onset of a 3X surge. (At this indicated temperature, the actual plenum gas temperature is about 470 °C.)
- The air purge rate to the BUFC is kept at the low-flow interlock of 220 lb/hr plus 30 lb/hr line purge.
- The total melter air flow rate to the FIC-3221A is kept at the current low-flow interlock of 850 lb/hr.
- The 3X 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 1 minute, and further decreased linearly to 1X normal during the next 7 minutes.¹¹

OVERVIEW OF MODELS

A description of the two models used in this study was given earlier.^{7,8,12,13} The 4-stage cold cap model was first run to calculate the compositions of glass and calcine gases from a given feed composition.^{7,8} The composition of calcine gases was then used in the melter off-gas dynamics model to predict the simultaneous transient responses of the off-gas system parameters during a 3X off-gas surge, including pressures, temperatures and concentrations.^{8,12,13}

Briefly, the 4-stage cold cap model approximates the entire 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. In principle, this model assumes that all the chemical events taking place in the cold cap are at thermodynamic equilibrium, thereby ignoring the effects of chemical kinetics and transport resistances. Once equilibrium compositions are determined for the gas and liquid phases in each stage, the gas phase is fed to next stage above, and the liquid phase is fed to the next stage below, thus establishing countercurrent flows between stages.

The 4-stage cold cap model was validated earlier against the data obtained with the formic acid flowsheet feeds,⁷ but is yet to be validated for the nitric acid flowsheet feeds. Therefore, as described earlier,⁸ the oxidizing effects of nitrate salts were ignored, and the calculated equilibrium off-gas compositions were adjusted to match the conservative formic acid flowsheet compositions.

The melter off-gas dynamics model has been used extensively in DWPF to study the dynamic responses of 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.^{12,13} All the controller hardware and software logic currently used in the DWPF melter off-gas system are simulated by this model. The combustion in the melter plenum is modeled using the apparent first-order rate parameters derived from the SGM-9 data.⁸ When the feed composition is changed, this model requires a new input from the 4-stage cold cap model in order to predict off-gas flammability correctly.

RESULTS AND DISCUSSION

The results of the 3X surge dynamic simulation are shown in Figures A-1 to A-9 in Appendix in the order of increasing feed rates from 0.7 to 1.5 GPM at 0.1 GPM increments. As the feed rate is more than doubled from 0.7 to 1.5 GPM, the peak melter pressure during the 3X surge is shown to increase by only 1 inch H₂O from -4.3 to -3.4 in H₂O. As expected, the decrease in melter plenum gas temperature due to surges is the largest at 1.5 GPM.

Table 2 summarizes the calculated maximum TOC limits at different feed rates. It is clearly shown that as the feed rate is increased, the maximum TOC limit that can be tolerated by the melter without exceeding 60% of the LFL decreases. At 0.7 GPM, feeds containing up to 35,400 ppm TOC can be fed, but the maximum TOC limit drops to only 10,200 ppm at 1.5 GPM. It is also noted in Table 2 that the estimated specific gravity of the feed increases as the TOC level is increased. This is because only the formate level was increased from that of the reference feed in Table 1 to a maximum value at each feed rate, while holding the contents of insoluble solids, other salts and water constant, thereby effectively increasing the total solids content of a batch.

Figure 1 is a plot of wt% total solids vs. specific gravity for three DWPF slurry samples (MFT-5,6,7), and the following correlation for specific gravity was derived and subsequently used in this study:

$$\text{SpG} = 0.3017 + 0.023245 * \text{TS} \quad (2)$$

where TS is the total solids content of the slurry feed in wt% between 43 and 54. At the total solids content of 44.2881 wt%, Eq. (2) predicts the specific gravity of 1.3312, which is identical to that given in Table 1 for the reference feed. Although Eq. (2) shows the specific gravity as a function of total solids content only, it is recommended that the use of Eq. (2) be limited to slurry feeds containing about 30 to 40 wt% insoluble solids. The impact of varying insoluble solids contents is discussed later.

TABLE 2. Results of 3X Surge Dynamic Simulation Runs

Feed Rate (GPM)	Estimated Specific Gravity	Formate Carbon (ppm)	Aromatic Carbon (ppm)	Maximum TOC		Glass Production (lb/hr)
				(ppm)	(lb/hr)	
0.7	1.5525	32,800	2,600	35,400	19.263	219
0.8	1.5032	26,800	2,700	29,500	17.763	239
0.9	1.4614	21,700	2,800	24,500	16.136	259
1.0	1.4322	18,100	2,900	21,000	15.060	281
1.1	1.4071	15,040	2,960	18,000	13.951	301
1.2	1.3846	12,280	3,020	15,300	12.729	322
1.3	1.3678	10,240	3,060	13,300	11.842	344
1.4	1.3545	8,600	3,100	11,700	11.109	365
1.5	1.3419	7,080	3,120	10,200	10.280	387

The calculated maximum TOC limits in Table 2 are plotted next in Figure 2 against the product of feed rate and specific gravity, and the following correlation was derived:

$$\text{max TOC (ppm)} = 45,180 * \text{FR} * \text{SpG} - 108,200 \ln(\text{FR} * \text{SpG}) - 4,860 \quad (3)$$

where FR is the feed rate in GPM, and SpG is the specific gravity of the feed. In order to test the applicability of Eq. (3) to operating conditions other than those shown in Table 2, a case was next considered where one plans to increase the feed rate to 1.2 GPM and, using Eq. (3), has determined a maximum TOC level of 13,200 ppm at the specific gravity of 1.48. Figure 3 is the result of the dynamic simulation run under these conditions, which indeed predicts that the peak concentration of combustibles will not exceed 60% of the LFL during a 3X surge.

The estimated specific gravities and the feed rates in Table 2 are plotted next in Figure 4 against the TOC level. Once the TOC level and the specific gravity are measured, Figure 4 can be used to predict the maximum allowable feed rate. For example, when the measured TOC level is 28,000 ppm, Figure 4 shows that the feed rate can be as high as 0.83 GPM, as long as the measured specific gravity is less than 1.49.

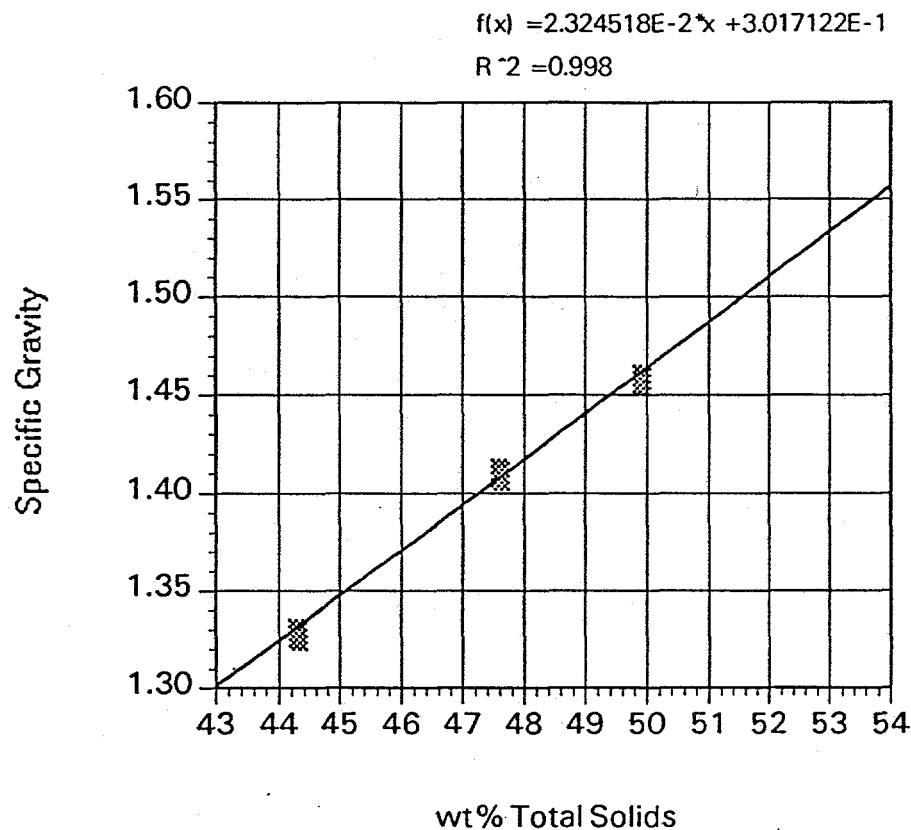


FIGURE 1. wt% Total Solids vs. Specific Gravity for MFT Samples

These maximum feed rates are plotted next in Figure 5 as a function of the product of TOC in ppm and specific gravity, and the following correlation was derived:

$$\begin{aligned} \text{max feed rate(GPM)} = & 0.756 + 1,185.5 \ln(\text{TOC} * \text{SpG}) / (\text{TOC} * \text{SpG}) \\ & - 5.4E-6 * \text{TOC} * \text{SpG} \end{aligned} \quad (4)$$

In order to validate the applicability of Eq. (4) to operating conditions other than those shown in Table 2, another test case was considered where one has experimental measurements on the TOC and specific gravity at 21,000 ppm and 1.48, respectively, and has determined a maximum feed rate of 0.983 GPM using Eq. (3). Figure 6 is the result of the dynamic simulation under these conditions, which indeed predicts that the peak concentration of combustibles will not exceed 60% of the LFL during a 3X surge.

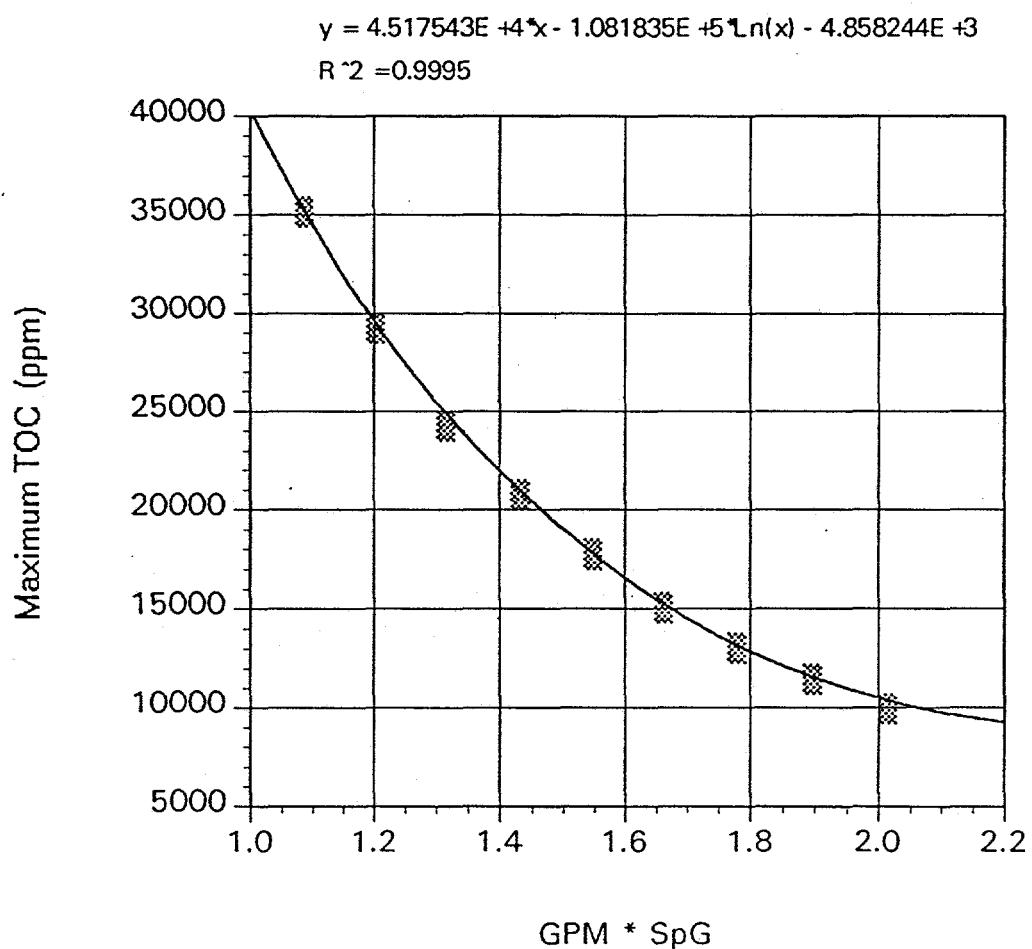


FIGURE 2. Maximum Total Organic Carbon vs. Feed Rate*Specific Gravity.

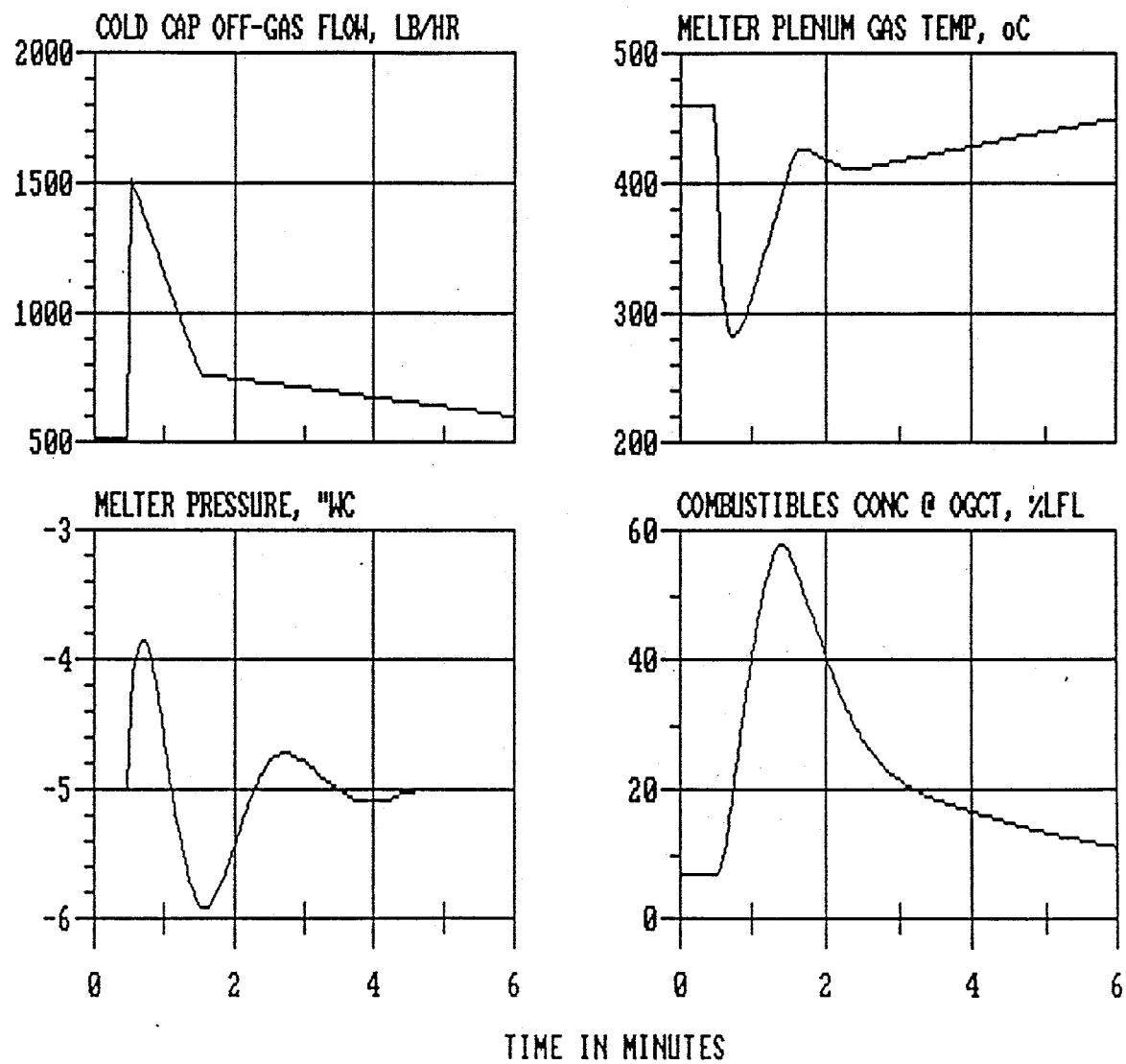


FIGURE 3. 3X Surge Simulation Result (13,200 ppm TOC, 1.2 GPM)

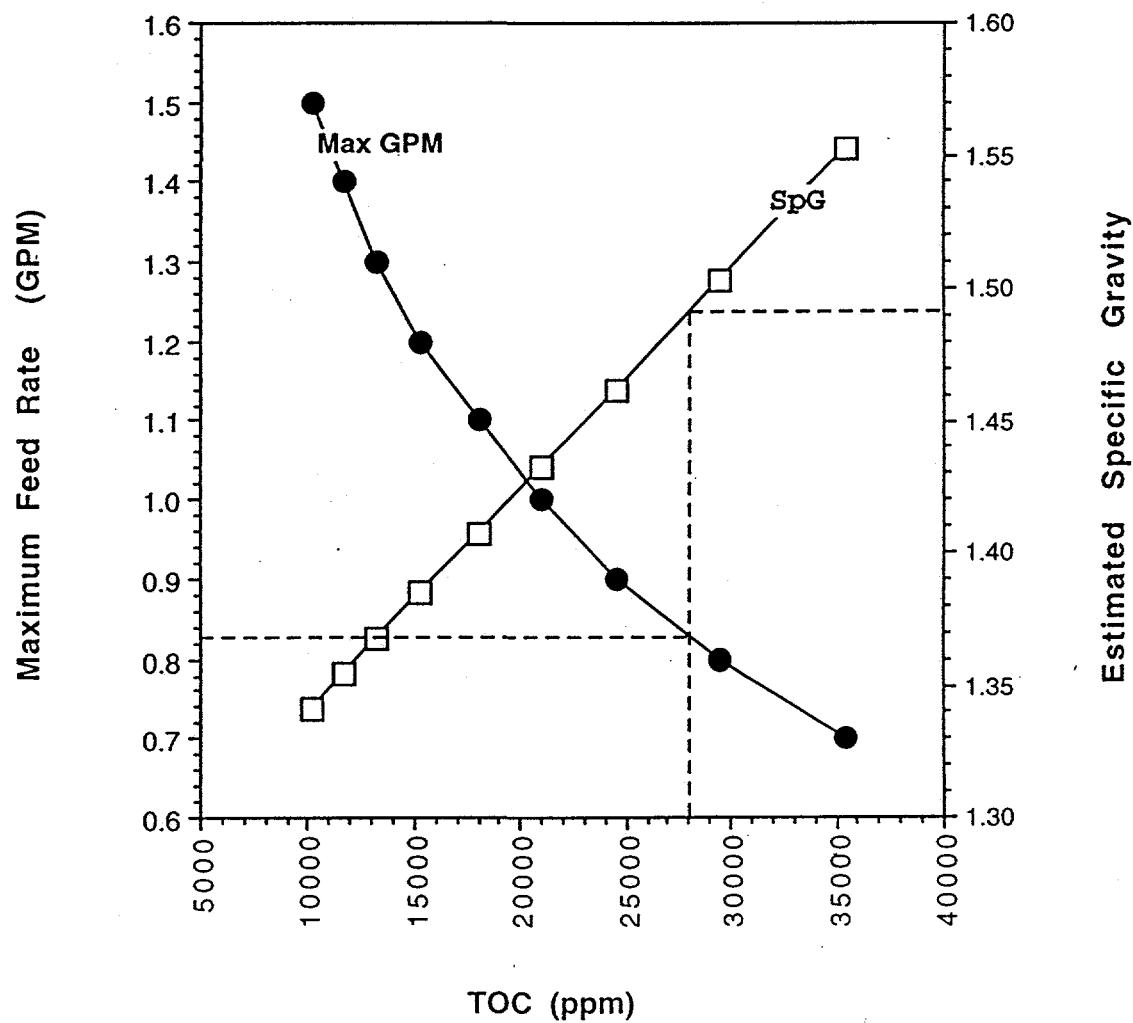


FIGURE 4. Maximum Feed Rate & Estimated Specific Gravity vs. TOC

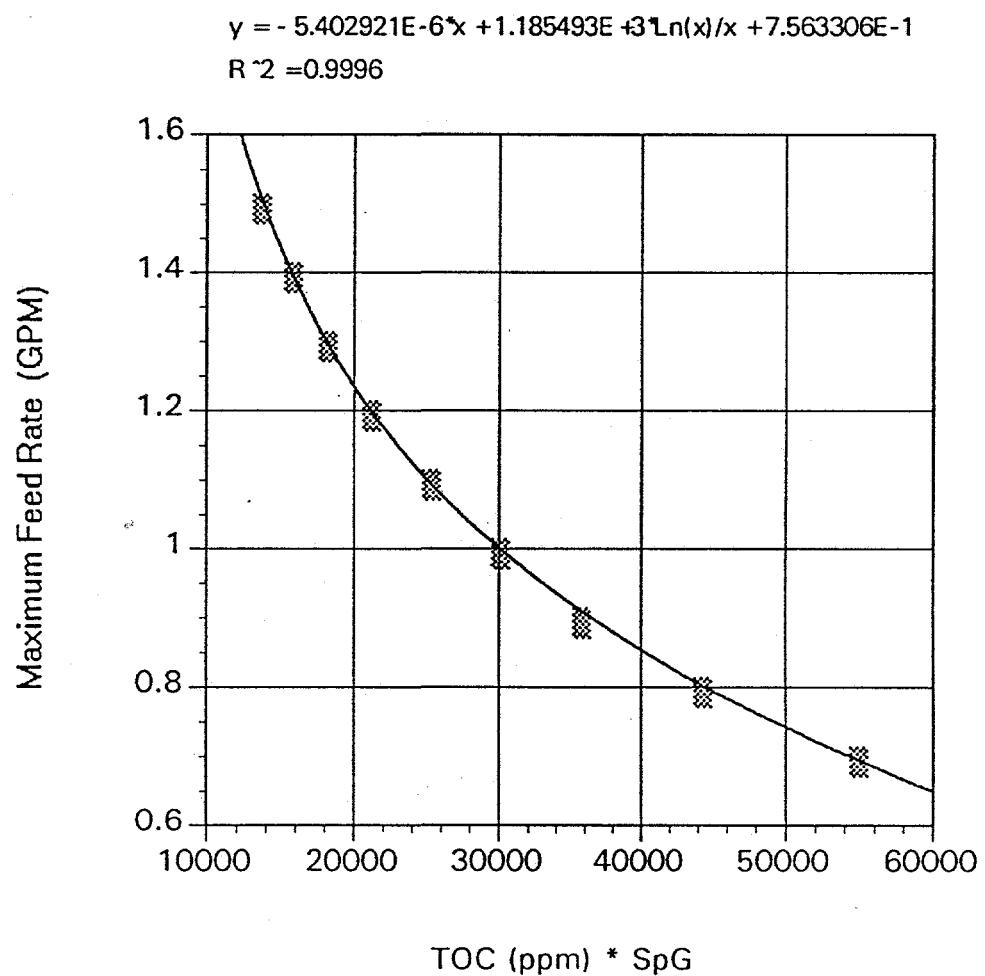


FIGURE 5. Maximum Feed Rate vs. TOC * Specific Gravity

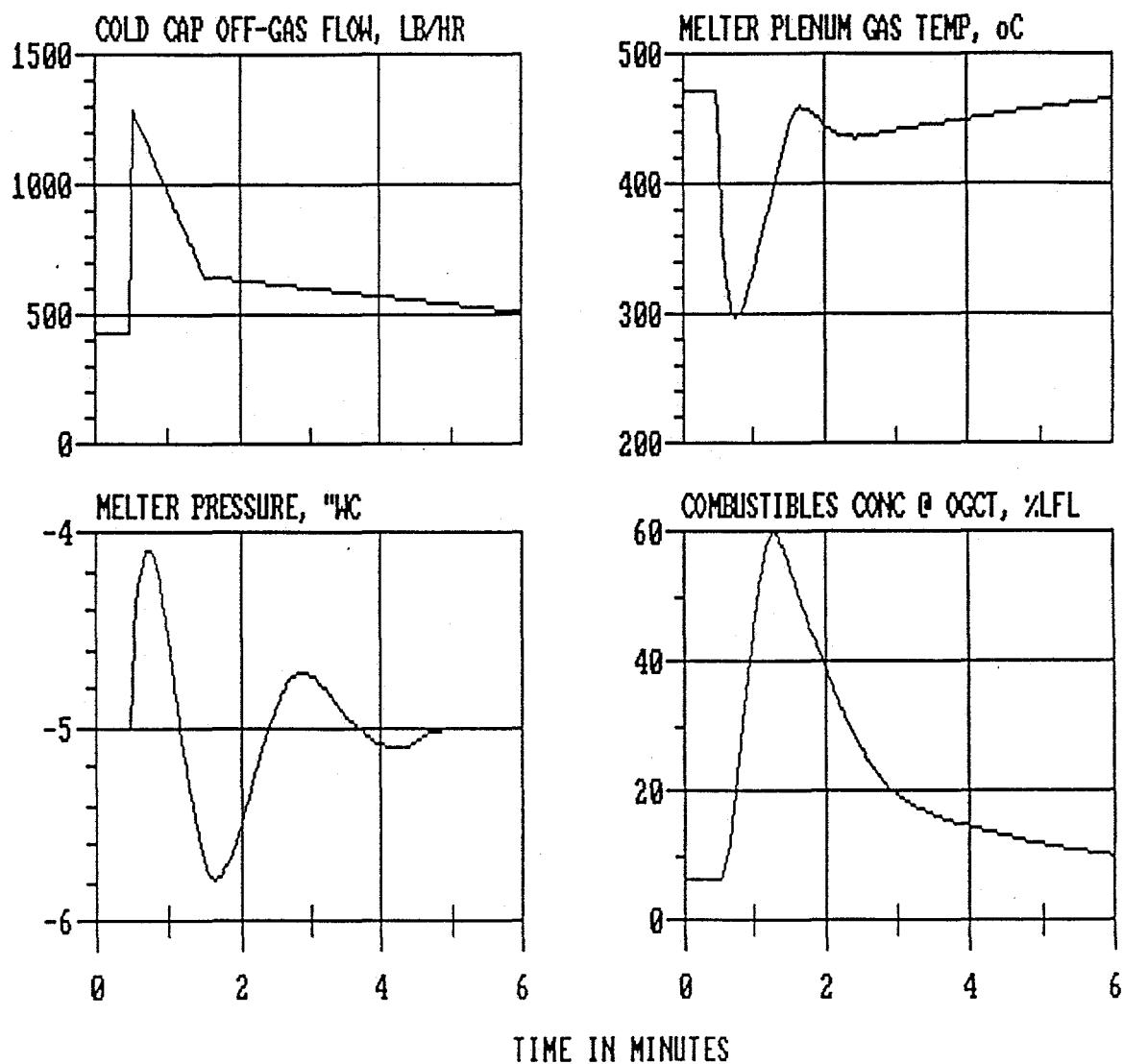


FIGURE 6. 3X Surge Simulation Result (21,000 ppm TOC, 0.983 GPM)

The maximum TOC feed rates in Table 2 are plotted next in Figure 7 against the ratio of TOC in ppm to specific gravity, and the following correlation was derived:

$$\begin{aligned} \text{max TOC feed rate(lb/hr)} = & 9.55 + 4.78 \times 10^{-4} \times (\text{TOC/SpG}) \\ & - 2.5 \times 10^{-3} \ln(\text{TOC/SpG}) / (\text{TOC/SpG}) \end{aligned} \quad (5)$$

It should be noted that it is the feed rate of TOC, not the TOC concentration or the slurry feed rate alone, that directly affects the off-gas flammability calculations. Eq. (5) can be used to convert the measured TOC concentration into the maximum allowable TOC feed rate once the specific gravity of the feed is known. This shows the importance of the specific gravity in this TOC study. Specific gravities are also important in dynamic simulations, since they generally relate the slurry feed rate to the relative ratio of condensable to noncondensable components in the off-gas flow.

As shown in Eq. (2), the specific gravities of the feeds with varying TOC levels were estimated in this study based only on the total solids content of the feed, i.e., Eq. (2) will predict the same specific gravity, as long as the total solids content remains unchanged regardless of the ratio of insoluble to soluble solids contents. In reality, however, the variations in insoluble solids content from one batch of melter feed to the next is small due to tight constraints imposed on many process and operating variables such as the total solids and sodium contents of the sludge feed. For example, the insoluble solids contents of the melter feed samples (MFT-5,6,7) ranged from 37.9 to 39.2 wt%. Although the insoluble solids content of the reference feed in Table 1 is a little lower at 35.9 wt%, the application of Eq. (2) to this feed was shown earlier to be valid. However, when the TOC level was purposely increased in this study from the baseline level of 6,820 ppm, the insoluble solids contents in the resulting batches became even lower, ranging from 30.0 to 35.9 wt%, since the formates added to increase the TOC level are soluble.

Then, one question might arise from all this; what happens to the validity of the proposed correlations when the actual specific gravity becomes a little lower than that predicted by Eq. (2) at the insoluble solids contents below 35 wt%? This can be answered easily from Figures 2, 5 and 7. Figure 2 shows that at a given feed rate the maximum TOC level increases monotonically as the specific gravity is decreased. So, if Eq. (2) indeed overpredicts the specific gravity at lower insoluble solids contents, the resulting maximum TOC level will be lower than that predicted by using the actual specific gravity. This shows that the maximum TOC limits calculated in this study at low insoluble solids contents are conservative. Figure 5 also shows that at a given TOC level the maximum feed rate increases monotonically as the specific gravity is decreased.

Therefore, the maximum slurry feed rates calculated in this study at low insoluble solids contents are also conservative, since they are lower than those predicted by using the actual specific gravities. Figure 7 also shows the same trend that at a given TOC level the maximum allowable TOC feed rate increases monotonically as the specific gravity is decreased, thus making the calculated maximum TOC feed rates conservative at low insoluble solids contents.

All these discussions thus far have been concerned with the impact of insoluble solids on the specific gravity and, more importantly, on the results of this study, and it was implicitly suggested that the proposed correlations, Eqs. (3) to (5), are valid for slurry feeds containing about 30 to 40 wt% insoluble solids. It should also be understood that the application of the proposed correlations are generally limited to those operating ranges shown in Table 2 or Figures 2, 5 and 7.

It should also be noted that the maximum TOC limits or feed rates in Table 2 are the conditions necessary to avoid a potential for forming a flammable vapor in the melter off-gas system, and may not conform to other operating and design criteria. For example, Table 2 shows that up to 35,400 ppm TOC may be tolerated by the melter at 0.7 GPM, but the slurry may be too difficult to transfer at the estimated specific gravity of 1.5525. Table 2 also shows that at 1.5 GPM and a specific gravity of 1.3419, the estimated glass production rate exceeds the design capacity of 228 lb/hr by as much as 70%. This indicates that although the feed containing as much as 10,200 ppm TOC can be fed safely at 1.5 GPM., the melter will not be able to sustain such a high feed rate for any extended period of time.

PATH FORWARD

Both the peak intensity and duration of an off-gas surge have a major impact on the calculations of the maximum TOC limit and off-gas flammability. As stated earlier, surges can occur even during carefully controlled operation, and the frequency and characteristics of surges are difficult to predict. So, all the safety-related calculations should be based on the worst-case surge scenario. In this study, the 3X off-gas surge was assumed to have a total duration of 8 minutes with an average flow of 2.25X normal during the first 1 minute. Although the actual data obtained during recent DWPF melter cold run tests showed that the peak intensity of a surge can be greater than 3X normal, the observed duration was considerably shorter, only on the order of several seconds. In order to confirm the conservatism in the 3X surge scenario used in this study, the melter off-gas dynamics model will be calibrated using recent DWPF surge data as part of requirements for the Technical Task Request HLW/DWPF/TTR-950047. Once the model is calibrated, the impact of those high-intensity surges with relatively short durations on off-gas flammability will be investigated.

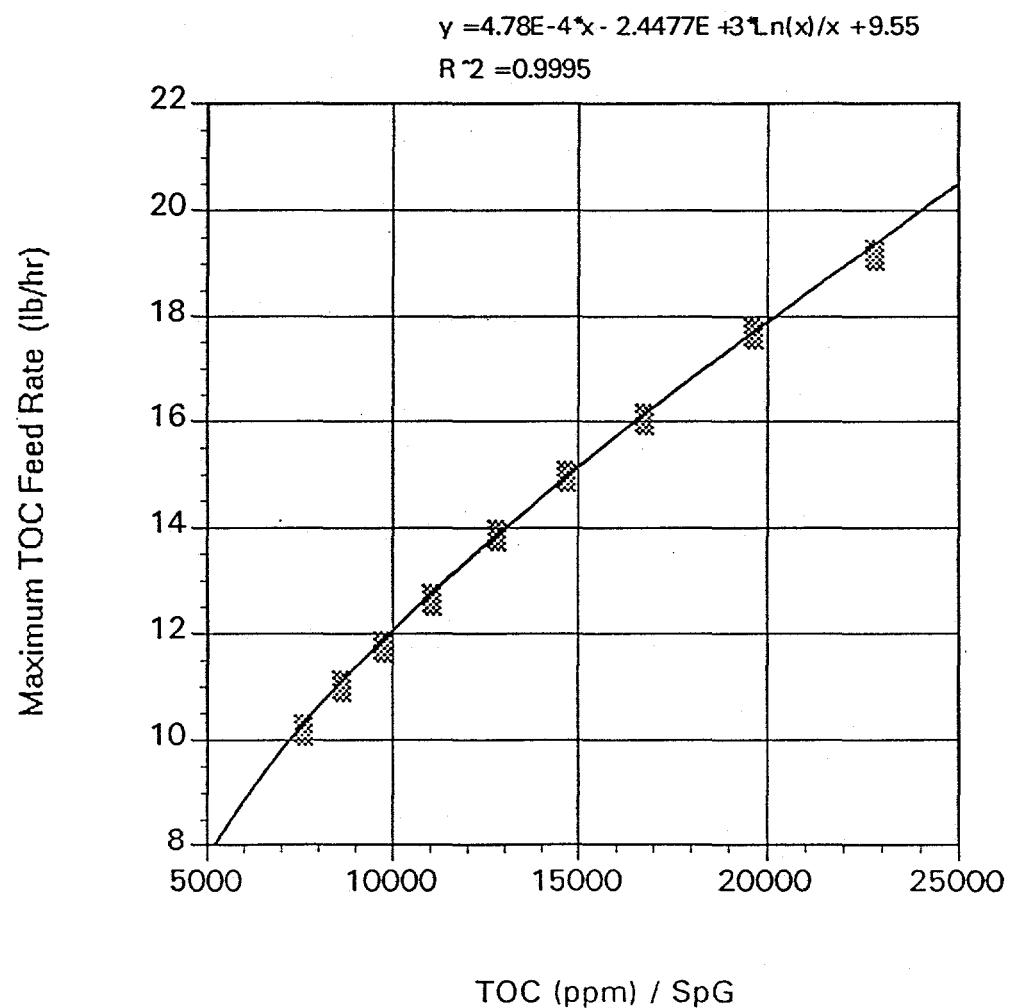


FIGURE 7. Maximum TOC Feed Rate vs. TOC * Specific Gravity

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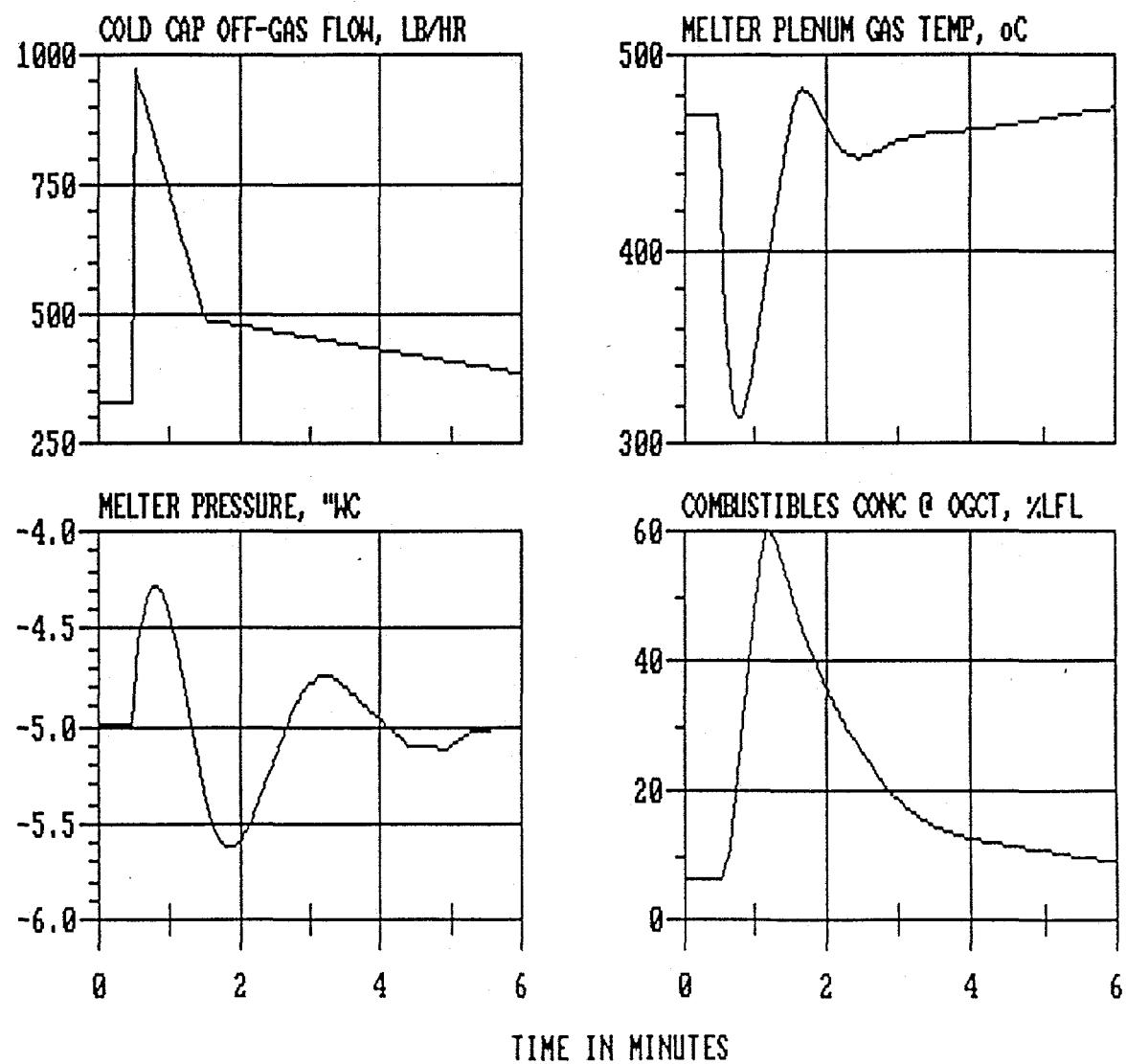


FIGURE A-1. 3X Surge Simulation Result (35,400 ppm TOC, 0.7 GPM)

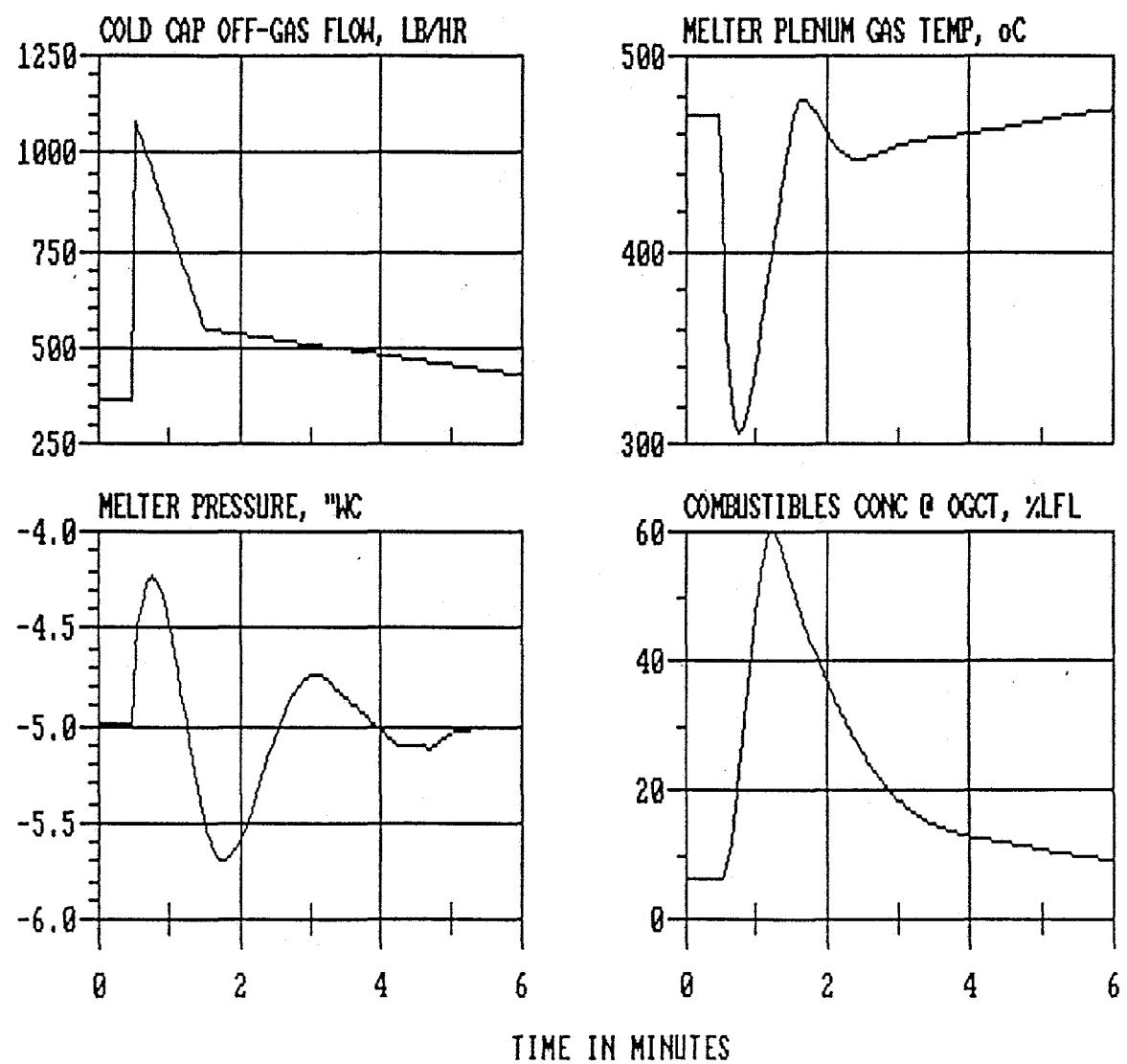


FIGURE A-2. 3X Surge Simulation Result (29,500 ppm TOC, 0.8 GPM)

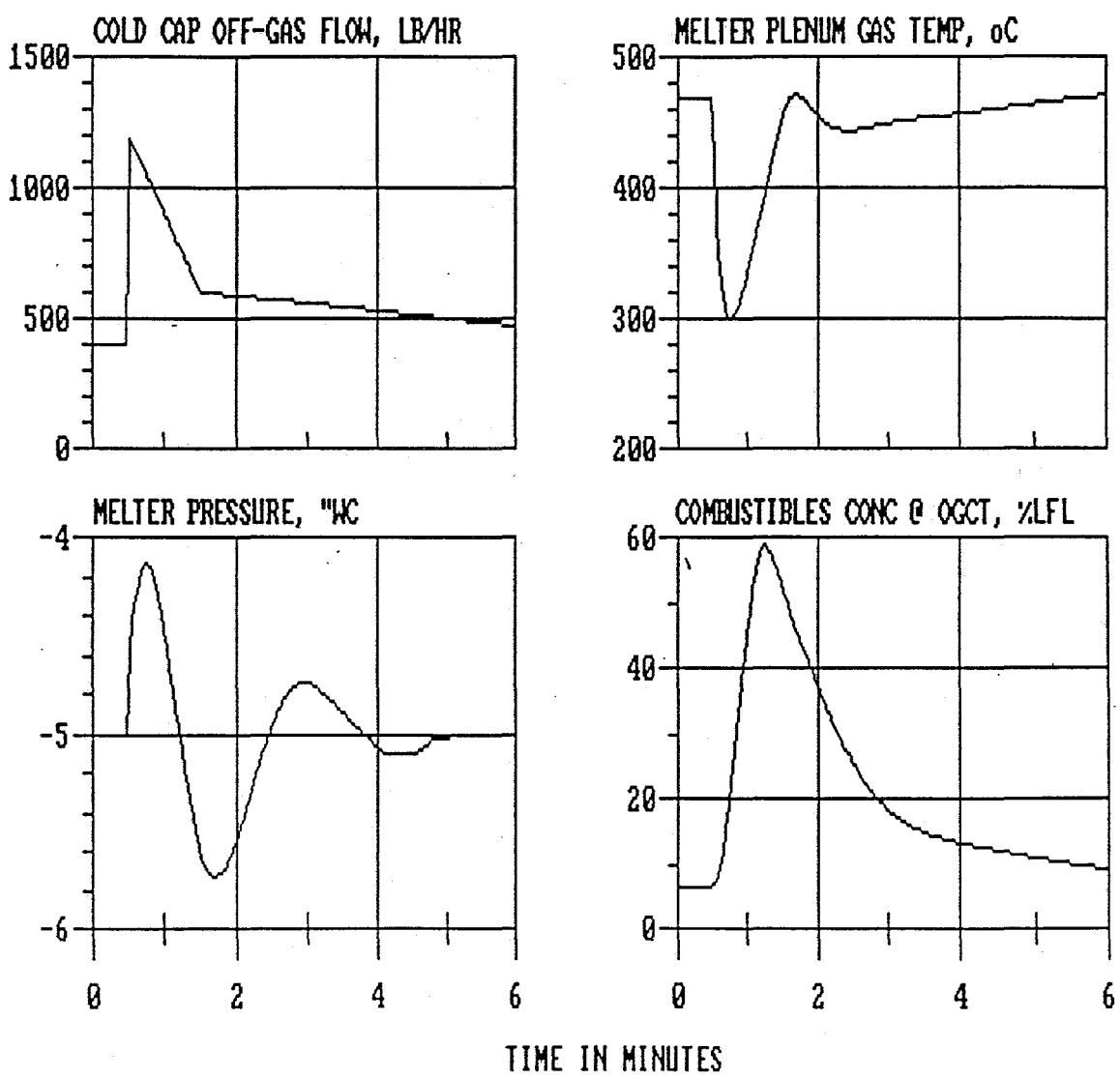


FIGURE A-3. 3X Surge Simulation Result (24,500 ppm TOC, 0.9 GPM)

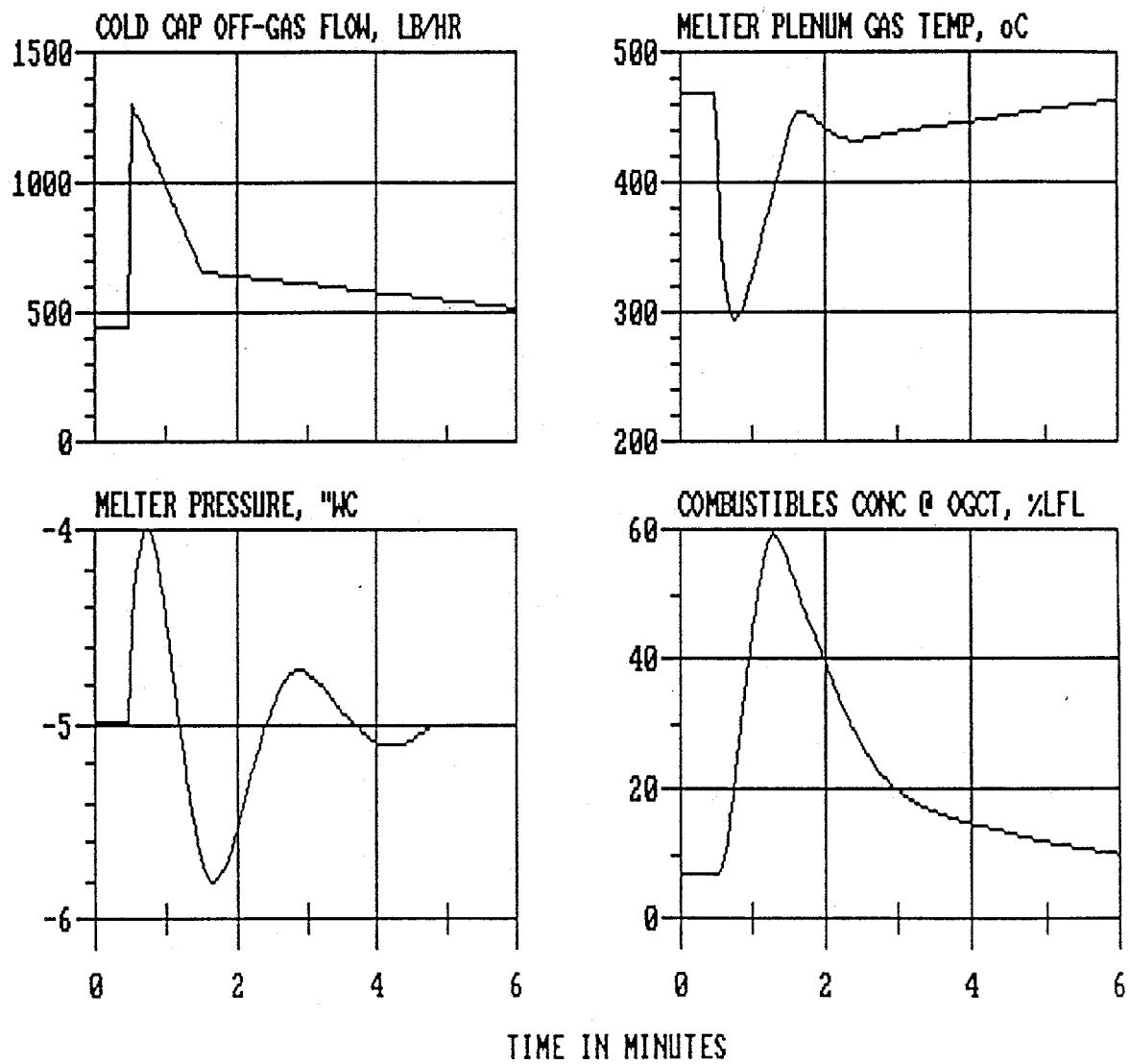


FIGURE A-4. 3X Surge Simulation Result (21,000 ppm TOC, 1.0 GPM)

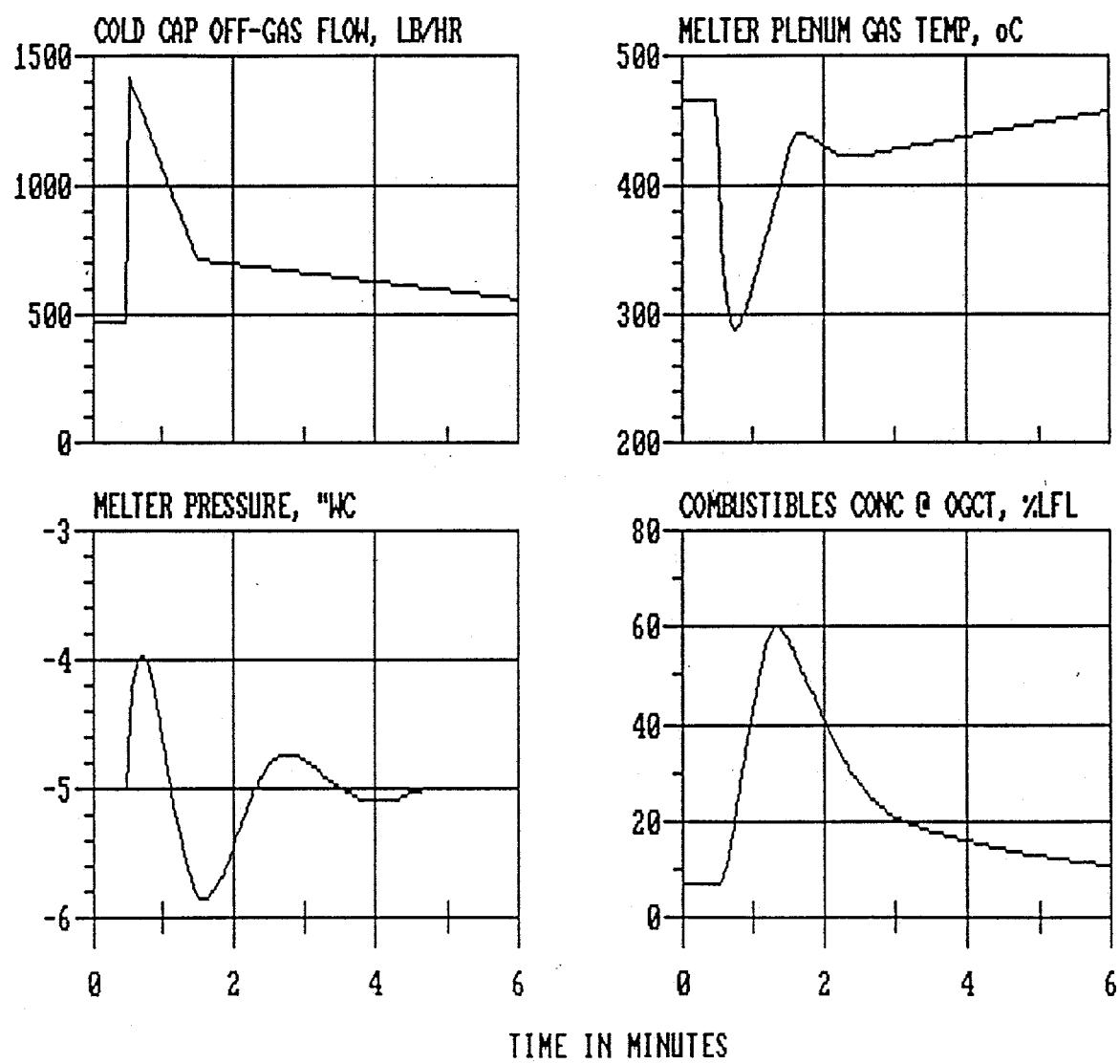


FIGURE A-5. 3X Surge Simulation Result (18,000 ppm TOC, 1.1 GPM)

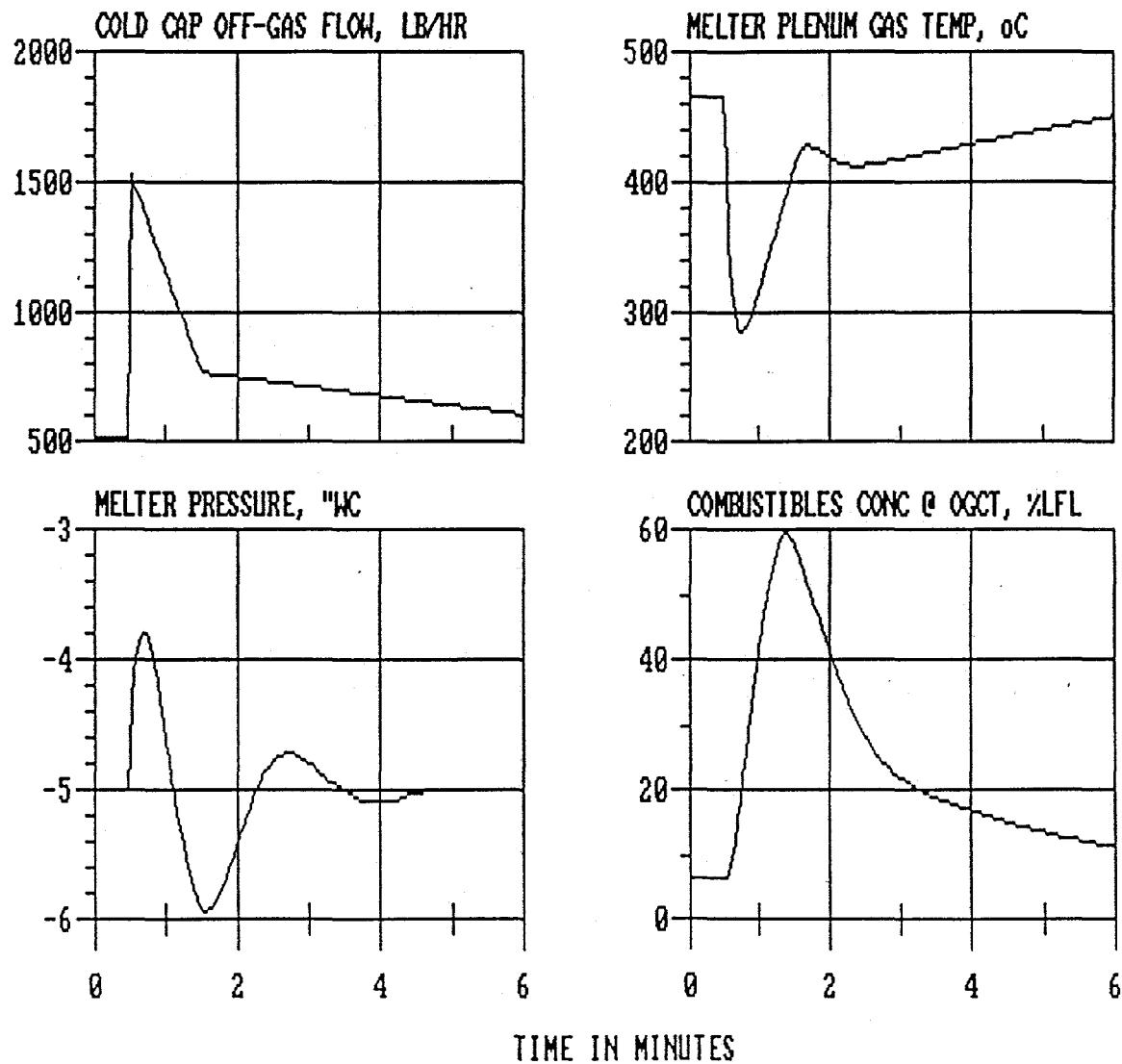


FIGURE A-6. 3X Surge Simulation Result (15,300 ppm TOC, 1.2 GPM)

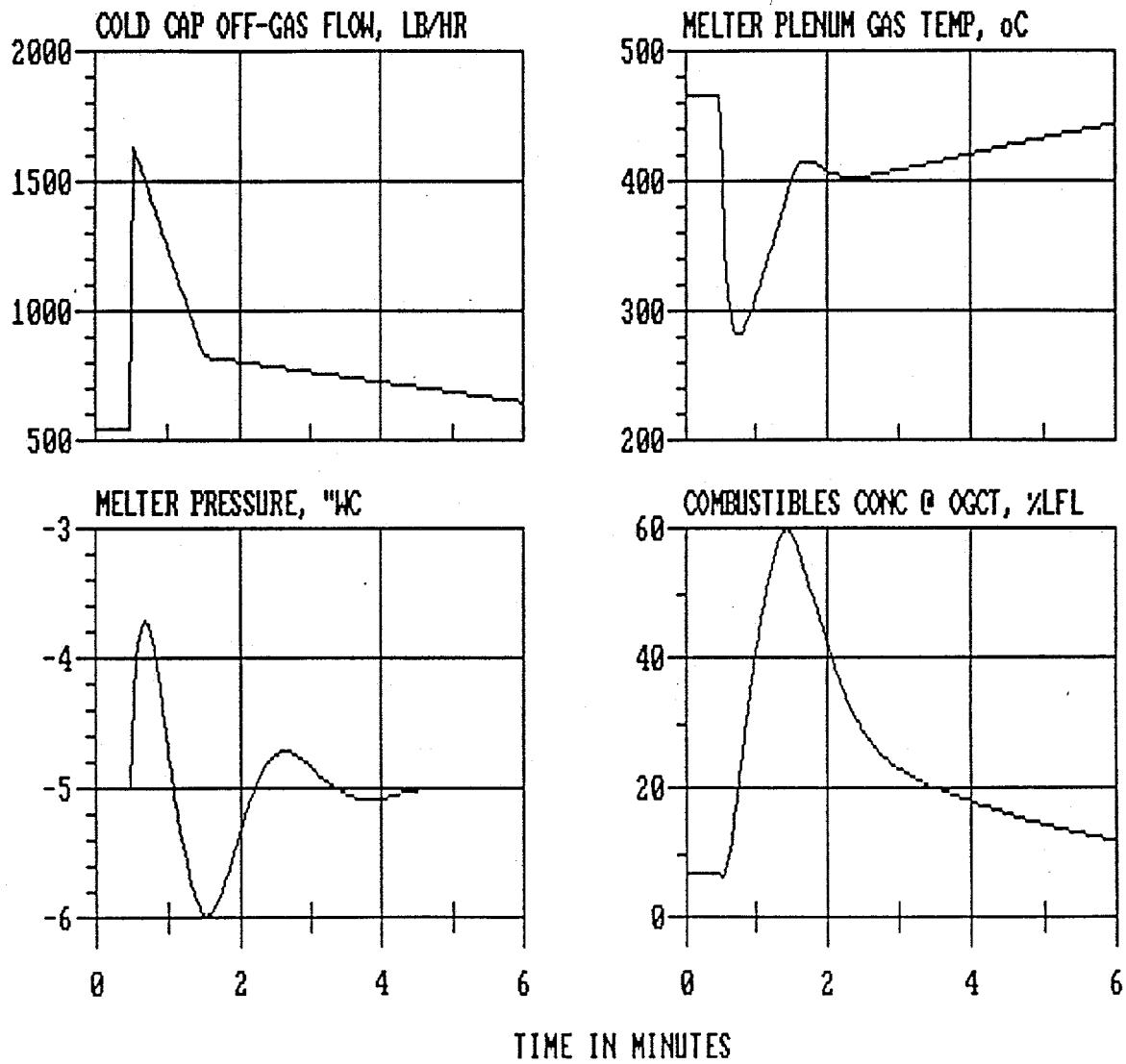


FIGURE A-7. 3X Surge Simulation Result (13,300 ppm TOC, 1.3 GPM)

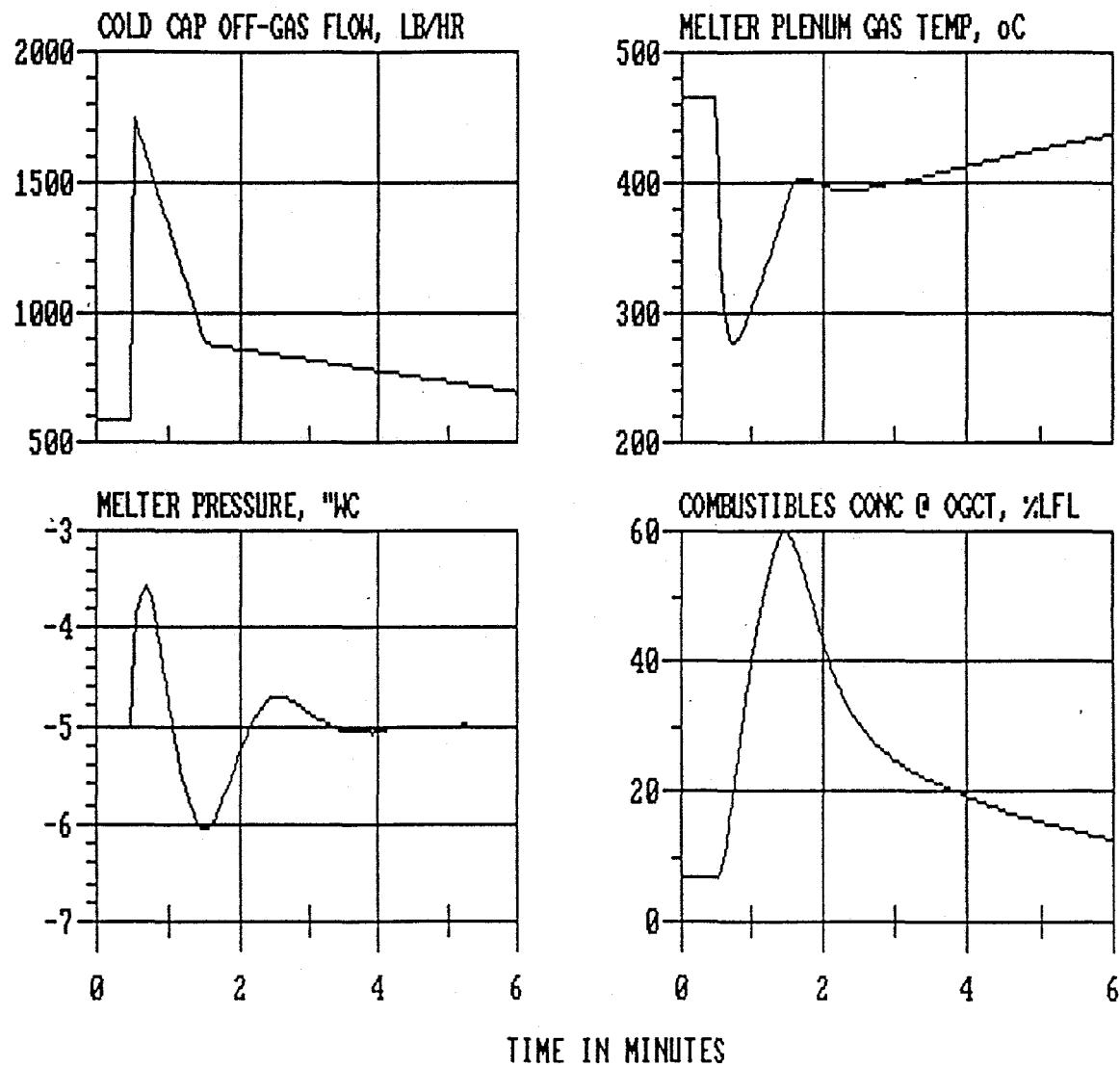


FIGURE A-8. 3X Surge Simulation Result (11,700 ppm TOC, 1.4 GPM)

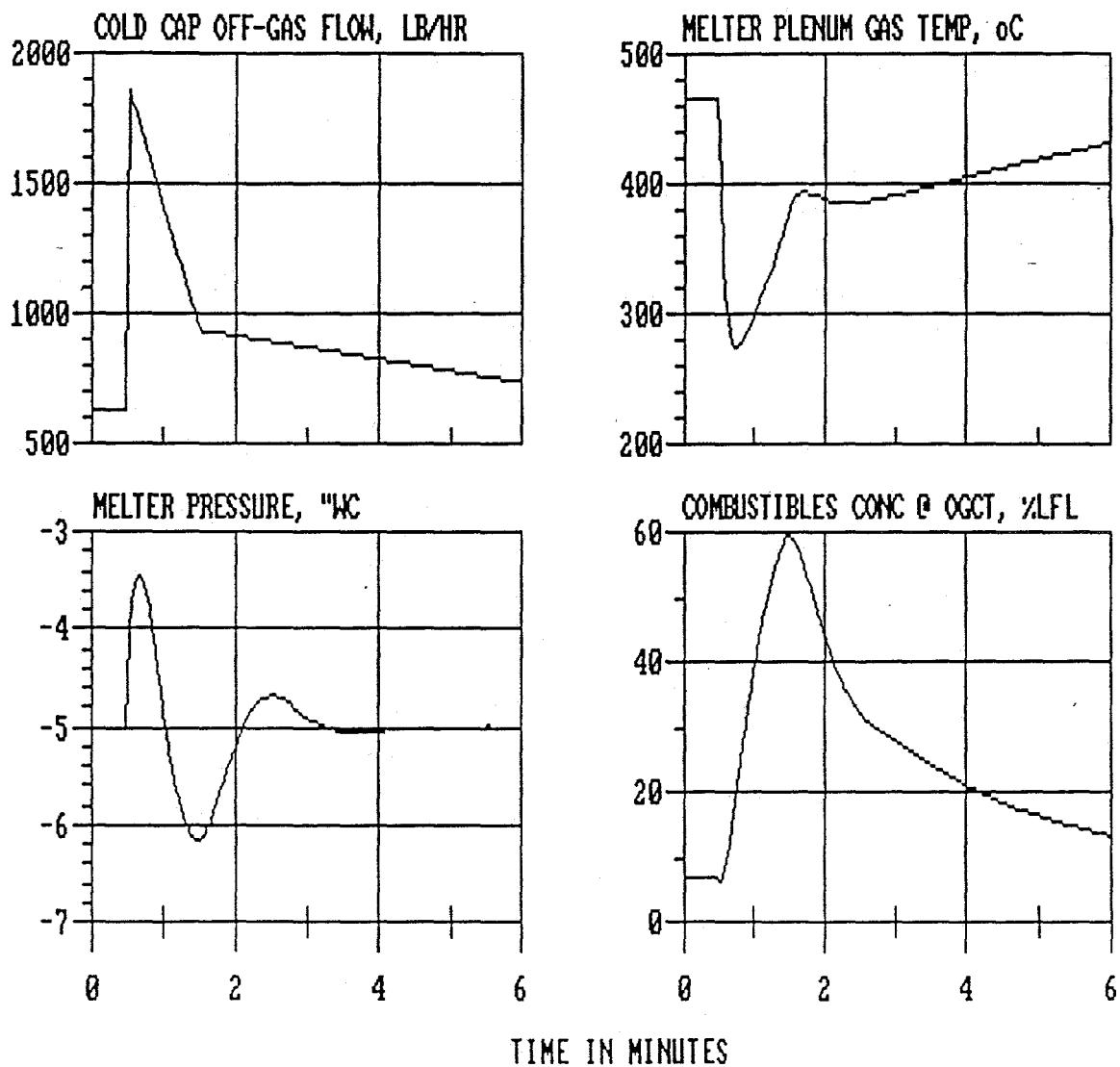


FIGURE A-9. 3X Surge Simulation Result (10,200 ppm TOC, 1.5 GPM)