

Design and installation of a replacement thermal oxidizer for odor abatement

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THE SUBJECT PAPER MILL IS AN integrated swing mill that processes hardwood and softwood pulp. The kraft mill was built in 1972 incorporating a state-of-the-art odor control system. The system collects and burns three sources of odorous gases in a dedicated thermal oxidizer (TO): low volume, high concentration (LVHC) noncondensable gases (NCG) from the evaporator hotwell, condensate steam stripper off gases (SOG), and high volume low concentration (HVLC) blow and relief NCG from the batch digester operation. In 1991, the mill added an alkaline scrubber on the TO exhaust to control SO₂ emissions and recover sulfur. The lime kiln serves as a backup incineration device.

In 1984, the original TO was replaced with a new unit using engineering estimates available then. In 1995, operational problems with this oxidizer that had historically operated near capacity resulted in an unacceptable level of community odor. Nuisance flame-outs also caused problems.

The mill tried to improve odor control performance and assure continued compliance with existing total reduced sulfur (TRS) and SO₂ emission limits. This effort included hiring two engineering firms to give mill staff needed expertise. One company was hired to develop and implement analytical methodology for quantifying TRS and methanol loadings to the TO. Because of this work, the mill decided to replace the existing TO. The mill retained the

other engineering firm to engineer the new oxidizer system. The mill worked closely with the state department of environmental quality throughout the process.

PROCESS GAS CHARACTERIZATION

To assess the TRS and methanol levels in the gas feed streams to the TO and to show variations in composition with process changes, a continuous on-line sampling approach was proposed. Three discrete process streams comprising the gas feed to the TO system were identified:

- Batch digester blow gas system
- Evaporator hotwell system
- Condensate steam stripper system.

Besides the identified process gas testing, condensate samples from the input and output streams of the identified process areas were collected concurrently with the air sampling program. The process liquid samples were analyzed for TRS and methanol. The results from the air sampling program and process liquid analysis evaluated the sulfur loading and fuel values within the identified process areas.

Sampling methodology

Gas stream composition, component mass flow rates, and thermal energy calculations were performed on a continuous and semi-continuous basis. The following paragraphs describe the target component sampling and analytical techniques applied. **Figure 1** shows the overall sampling train.

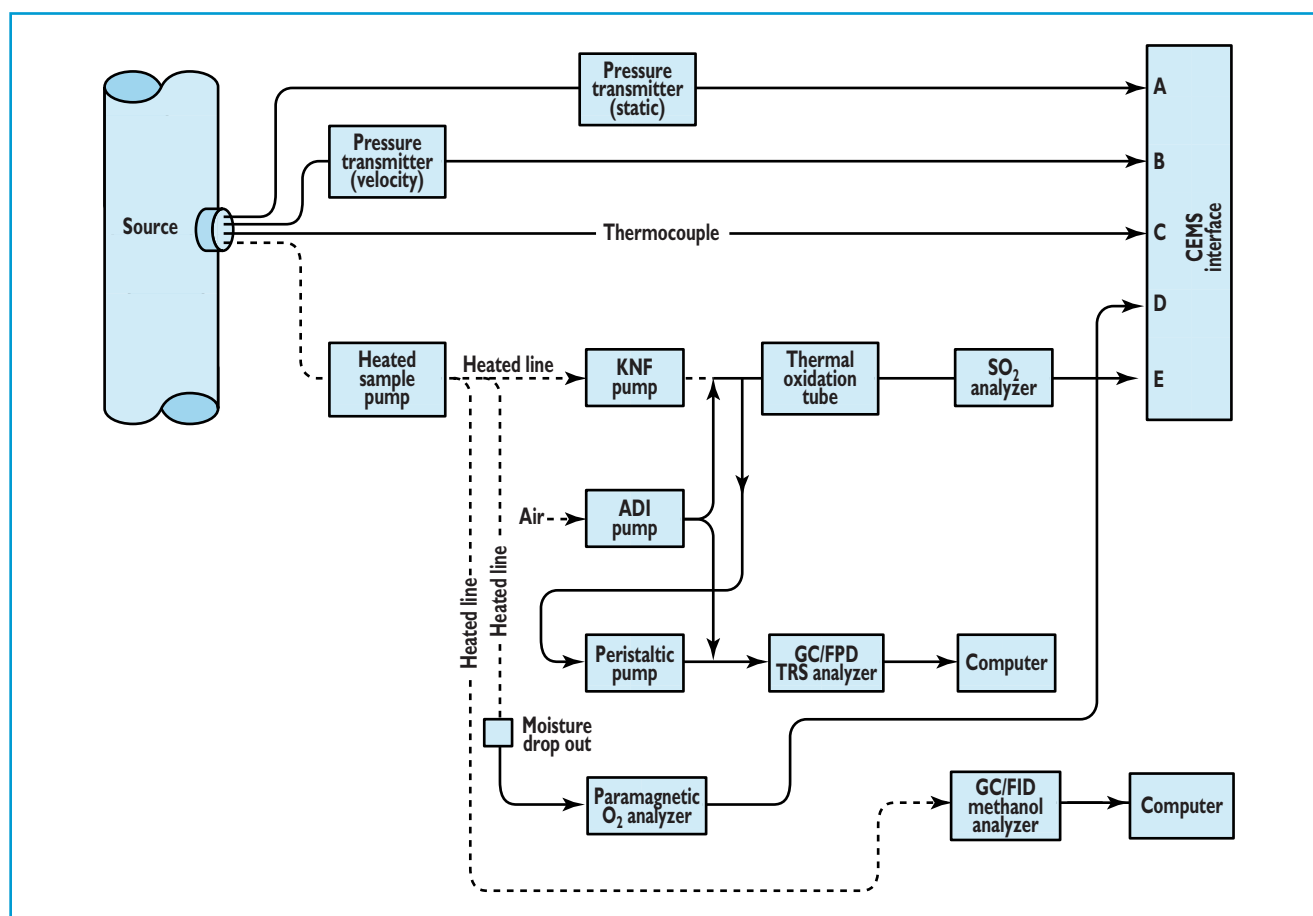
ABSTRACT

In 1995, a paper mill decided to replace its thermal oxidizer (TO) to correct operational problems with the existing unit and provide improved odor control. The mill contracted with an engineering firm to assess and design a system modification or upgrade. The first requirement was a reliable and accurate analysis of the composition and mass flow rates of the gas streams collected and fed to the existing TO. Design considerations included compliance with EPA cluster rules and future production predictions. The resulting TO was operational 12 months after initial design considerations and testing.

Application:

A new thermal oxidizer designed to ensure compliance with EPA cluster rules at predicted future production rates has reduced community odor.

A representative sample of the source gas stream was transported continuously to an on-site mobile laboratory using a heated polytetrafluoroethylene (PTFE) sample line and incorporated a heated PTFE head sample pump. The methanol sampling method and analytical procedures were U.S. Environmental Protection Agency (EPA) Method 18. An aliquot of the "hot and wet" gas sample was periodically injected into a calibrated gas chromatograph incorporating a flame ionization detector (GC/FID). Quantization of methanol in the gas stream occurred approximately every 12 min. The results of the methanol analyses were reported in concentration (ppmdv) terms after correction of the GC/FID analytical result for the measured moisture level of the sample gas stream.



1. On-line TRS and methanol sampling and analytical system

The total TRS level was monitored continuously by performing a dynamic dilution of the sample gas stream with ambient air before thermal oxidation of the sample. After oxidation, the sample gas was monitored using a calibrated, high range SO_2 analyzer. Except the use of a continuous SO_2 analyzer instead of an impinger collection system, the procedures and techniques described in U.S. EPA Method 16A were followed. This modification was appropriate for the analysis of the high concentration gas streams. (This may be acceptable to state and federal observers if the difference between the analytical system results is less than 7%). The continuous—every minute—data collection yielded information concerning variations in

the process operation and generally confirmed the concentration levels of the TRS.

Quantization of the individual TRS species present in the gas streams used U.S. EPA Method 16. The procedure required a second, dynamic dilution of the sample gas stream presented to the total TRS analytical system. The analysis of the sample was performed semi-continuously—every 6 min—using a calibrated GC incorporating a flame photometric detector (FPD). The measured TRS levels were used for mass flow calculations.

To determine the mass flow rates for the target species, volumetric flow rate measurements were necessary continuously. Oxygen levels were monitored continuously using

a paramagnetic oxygen analyzer after conditioning the sample. Moisture levels were calculated from the monitored source gas temperature assuming saturation at the temperature and pressure of the source gas stream. This assumption was confirmed for each source tested by performing moisture determinations using U.S. EPA Method 4. The velocity and static pressure of a representative area of the source duct were continuously monitored using a calibrated pressure transducer and an analog data acquisition system. The measured concentrations of TRS, methanol, and oxygen were used to determine the molecular weight of the source gas stream for the subsequent flow rate calculations.

On-line testing of the condensate steam stripper system proved difficult and could not be performed for more than 1–2 h. After consideration of different sampling approaches, integrated samples for each target species parameter were collected. Methanol samples were collected using evacuated, heated canisters maintained at 250°F for the collection of integrated representative samples. Analysis was performed using the calibrated GC/FID system with correction to a dry basis using the measured moisture level.

The collection of integrated samples for TRS and oxygen levels was performed concurrently with methanol sampling using a chilled sodium citrate buffer solution conditioning system before collection of the gas sample in gas sampling bags. The analysis of the dry gas sample for TRS and oxygen was performed using the GC/FPD and paramagnetic oxygen analyzer, respectively. The TRS and oxygen levels reported were corrected for the measured methanol concentration assuming that the methanol present in the volume of gas samples condensed in the chilled sodium citrate buffer solution.

Discrete volumetric flow rate measurements were performed concurrent with the sampling. The molecular weight of the source gas was determined using the measured concentration levels of the major source gas components.

Quality assurance

Quality assurance and control were significant components of the air testing program. For the sampling procedures used, verification of sample integrity was confirmed by the measurement of sample and diluent gas stream flow rates used for the calculation of sample stream dilution factors. Analytical accuracy was verified from the analysis of audit materials and periodic calibration of the instrumentation within the specifica-

tions outlined in the referenced test methods.

The recovery of a high concentration mixture of 3% hydrogen sulfide in nitrogen through the entire sampling system was used to determine dilution factors for all TRS compounds. Methanol sample recoveries for the hotwell and batch digester systems were performed by presenting a gas sampling bag containing methanol in nitrogen directly to the GC/FID analytical system and then to the sampling system probe. The system recovery was calculated from a comparison of the analytical results. Typically recoveries of 85%–115% were recorded. For the SOG system, methanol recovery from the heated canisters was performed by direct injection of a known mass of American Chemical Society (ACS) grade methanol into a clean canister sampling system. Methanol recoveries of 90%–100% were recorded.

Due to the magnitude of the continuous dilution, blank determinations were performed between process condition changes and source points to verify the integrity of the ambient air-conditioning system. For this purpose, a silica gel tube followed by an activated carbon tube were placed in series at the ambient air intake.

The off-site analysis of the process liquid samples for methanol was performed using established GC/FID analytical and sample preparation techniques. The analysis of foul condensates for TRS concentrations required the development of an appropriate procedure suitable for the determination of high levels of TRS present in nonhomogeneous samples. Discussions with National Council for Air and Stream Improvement (NCASI) yielded a method currently under development for TRS analysis in condensate samples. The procedure developed and initially tested by NCASI involved the heating, acidification, and purging of a

known volume of the liquid sample. The dry purge gas containing the purged target species was collected in a gas sampling bag and subsequently analyzed for TRS using a calibrated GC/FPD. The procedure appeared to work well and yielded the sensitivity required for low compound detection limits necessary for the low concentration, high volume, condensate streams.

An alternative procedure specifically designed for the analysis of high concentration TRS levels was developed that decreased the sample preparation time. The procedure used a heated, silica-coated, steel canister of known volume to prepare and present the sample to the analytical system. A known volume of the foul condensate sample was injected into the clean, heated, and evacuated silica-coated steel canister during pressurization of the canister with zero grade nitrogen. The final temperature of approximately 250°F and canister pressure of approximately 40 in. Hg were recorded, and the volume of the sample gas mixture was calculated. After preparation, the sample gas was immediately presented to a calibrated GC/FPD through a chilled midjet impinger containing sodium citrate buffer solution. The analysis of the dry sample gas, the liquid injection volume of the sample, and the calculated sample volume were used to determine the mass and volume of TRS in the foul condensate.

Without the benefit of an extensive method validation procedure, the heated silica-coated steel canister approach was assessed by comparison to the NCASI method under development. The heated silica-coated steel canister method usually yielded higher TRS levels than the NCASI procedure for foul condensate samples. The lower levels of TRS indicated using the NCASI method for condensate samples with a high TRS concentration may be due to incomplete “stripping” of the sample.

Component	Mass flow, lb/h			
	Hotwell	Digester	Stripper	Total
Hydrogen sulfide	1595	321	170	2086
Methyl mercaptan	392	753	205	1350
Dimethyl sulfide	18	595	111	724
Dimethyl disulfide	14	17	33	64
Methanol	4.7	5.7	468	478
Nitrogen	137	37369	16	37522
Oxygen	48	11410	4.8	11463
Water vapor	870	918	3626	5414
Total	3079	51389	4634	59101

I. Thermal oxidizer design data showing maximum gas flows for hardwood production

Component	Mass flow, lb/h			
	Hotwell	Digester	Stripper	Total
Hydrogen sulfide	420	70	161	651
Methyl mercaptan	176	363	238	777
Dimethyl sulfide	9.3	273	126	408
Dimethyl disulfide	6.4	16	57	79
Methanol	6.8	7.4	461	475
Nitrogen	254	36809	28	37091
Oxygen	77	11185	9.2	11271
Water vapor	847	1033	3669	5549
Total	1797	49756	4749	56302

II. Thermal oxidizer design data showing maximum gas flows for softwood production

For condensate samples with low TRS levels, the NCASI method yielded lower detection limits and increased sensitivity. Additional quality assurance indicators included replicate sample analyses, blank sample analyses, and analysis of audit materials.

SYSTEM DESIGN

Design criteria

A TO system was purchased to meet existing TRS permit limits and comply with regional odor control requirements. The design also allows for flexibility to meet future emission limits of hazardous air pollutants (HAP), particularly methanol, as a result of the cluster rule. **Tables I and II** provide a summary of the design gas flows from the three gas feed streams for hardwood and softwood pulping conditions. The feed stream specifications were developed from data collected from the test program discussed above.

The entire odor control system consists of a combustion chamber, retention chamber and duct, water

quench chamber, SO₂ scrubber, and induced draft fan. Evaporator LVHC NCG and steam stripper SOG are transported to the oxidizer by steam jet ejectors. HVLC NCG from the digester area is transported to the combustion chamber by a fan. **Figure 2** shows a three-dimensional drawing of the TO.

The TO design uses a normal operating temperature of 1600°F and a minimum residence time of 0.75 s. The maximum operating temperature of the unit is 2200°F. The maximum heat release is 45 MMBtu/h. The flue gas scrubber system is designed to limit SO₂ emissions from the stack to a maximum concentration of 40 ppmdv using a 1 h average.

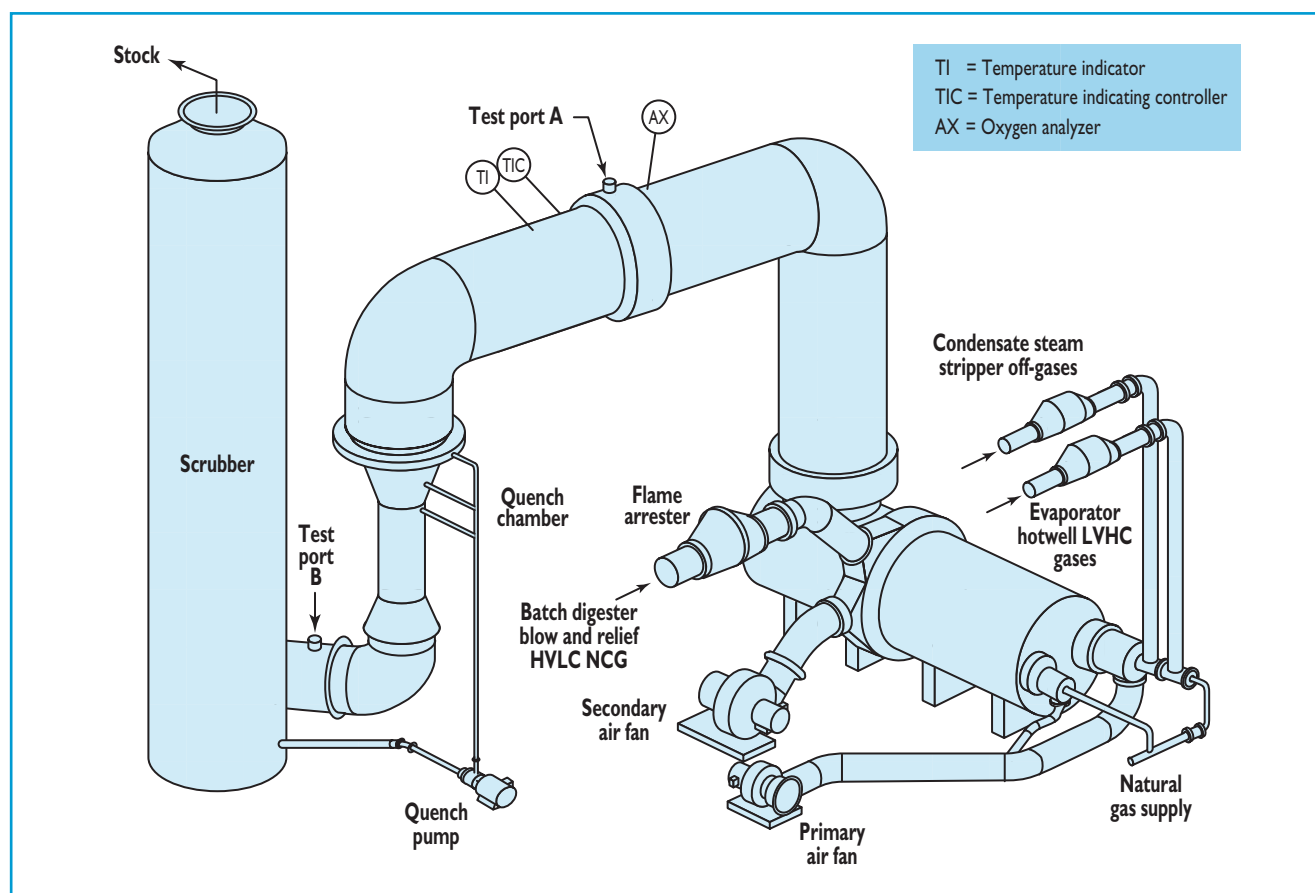
System description

The TO has two low nitrous oxide (NO_x) burners. One burner is designed to burn only natural gas and is rated for 10 MMBtu/h. The second burner is rated for 35 MMBtu/h and is designed with separate nozzles to burn natural gas, NCG from the evaporator hotwell, and SOG from the condensate steam stripper system.

The dilute digester gas is injected into the combustion chamber through a bustle ring that encircles the combustion chamber.

The combustion chamber is approximately 8 ft in diameter by 24 ft in length and has a high alumina refractory brick lining. A 6-ft diameter refractory lined duct connects the combustion chamber to the inlet of the water quench chamber. While most high temperature zones have refractory brick lining, a castable refractory material is used around burners, nozzles, and expansion joints. The refractory lining can operate continuously up to temperatures of 2200°F.

The water quench chamber is a flooded-wall venturi unit designed to cool and saturate the oxidizer exhaust gases. The quench unit has a hastalloy inlet section and 317L stainless steel discharge section. The top of the inlet is lined with a castable refractory section where the hottest flue gases initially contact the quench. The quench chamber reduces the flue gas temperature to an approximate 10°F approach to adiabatic saturation temperature that ranges 170°F–185°F depending on the flue gas composition and the inlet gas temperature. Pressure drop through the venturi quench is between 2–3 in. water column. A packed tower flue gas scrubber removes SO₂ from the flue gas before discharge to the atmosphere. The scrubber is constructed of nickel alloy and 317L stainless steel. The internals consist of an inlet spray and quench section and two 6 ft. high packed beds. Sodium carbonate, caustic soda, or both dissolved in demineralized water are used as the scrubbing solution. Demineralized water is used to minimize salt deposition in the scrubber. A chevron mist eliminator section at the top of the scrubber removes water droplet carryover from the flue gas before discharging.



2. Odor control system

Concept of operation

To meet the stringent emission requirements of the project, careful consideration was given to the three elements of good combustion: time, temperature, and turbulence (1). Besides performance considerations, the system was designed with several key safety features that are important when burning gases from pulp and paper NCG systems. Specifics on the design and control concepts are discussed below.

Control of the oxidizer system is through the mill's distributed control system (DCS) with burner management controlled by a programmable logic controller (PLC) based burner management system. The oxidizer controls are designed to maintain a minimum setpoint temperature and a minimum excess oxygen concentration in the oxidizer discharge duct. A variable speed controller on the ID

fan regulates pressure in the combustion chamber.

Combustion turbulence. Initial mixing of the high concentration gases with combustion air is accomplished with a waste gas burner. The evaporator hotwell gas stream and condensate stream stripper gas stream are both introduced to the combustion chamber through mixing nozzles located in the gas burner. The waste gas burner also has a separate port to add natural gas and a port for adding some combustion air. Combustion air is added at a sub-stoichiometric ratio in the burner. The main natural gas burner is adjacent to the waste gas burner to provide temperature control and flame stability.

NCG stream	Softwood	Hardwood
Batch digester blow gas system	6.5	12.8
Evaporator hotwell system	7.7	16.1
Condensate steam stripper system	5.4	3.8
Total sulfur loading	19.6	32.7

III. Mean sulfur loading to oxidizer in lb sulfur/a.d. ton pulp using data based on measurements performed on the oxidizer feed streams

The dilute, oxygen-rich, digester gases are injected into the combustion chamber through a concentric bustle ring located downstream of the burners away from the main body of flames. The air and gas mixture is injected into the combustion chamber through refractory lined nozzles that encircle the combustion chamber. Injecting the gases in this manner enhances the mixing of oxygen with the burning gases and increases the turbulence within the chamber.

Source/parameter	Instantaneous values		Hourly average values		Permit limitation**
	Actual*	Warranty specification	Actual	Warranty specification	
Thermal oxidizer retention duct (port A Fig. 2***):					
TRS concentration, ppmv	> 16	N/A	> 3.8	N/A	
TRS mass emission rate, lb/h	> 0.93	N/A	> 0.22	N/A	
Methanol concentration, ppmv @ 10% oxygen	N/A	N/A	< 0.4	N/A	
Thermal oxidizer quench chamber (port B, Fig. 2):					
TRS concentration, ppmv	0.5	< 5	0.23	< 3.5	
TRS mass emission rate, lb/h	0.02	< 0.58	0.01	< 0.4	
Sulfur dioxide scrubber outlet:					
TRS concentration, ppmv	0.7	< 5	0.3	< 3.5	< 5
TRS mass emission rate, lb/h	0.04	< 0.58	0.02	< 0.40	< 0.58
Sulfur dioxide concentration, ppmv	33	< 55	24	< 40	< 55
Sulfur dioxide mass emission rate, lb/h	3.2	< 12	2.4	< 9	< 12

* These are the highest concentrations and mass emission rates reported for three 1 h runs.

** The permit concentrations use a 12 h average.

*** The TRS concentrations indicating values as greater than are values that exceeded the calibration range of the analytical system. In general, instantaneous TRS measurements were below 10 ppmv.

IV. Summary of emission test results

A third aspect of the oxidizer system design that provides good turbulence is the configuration of the ducting connecting the combustion chamber to the quench chamber. The ducting that is in effect a continuation of the combustion chamber exits the top of the cylindrical combustion chamber and makes two 90° turns before entering the top of the quench chamber. This design creates good turbulence without the need for internal baffles or flow devices.

Residence time. As mentioned previously, the combustion chamber is designed with a minimum residence time of 0.75 s using the normal operating temperature of 1600°F. These criteria were chosen using the requirements of the EPA cluster regulations for the pulp and paper industry. Due to site layout requirements and configuration of equipment, the actual residence time for the maximum design condition at normal temperature is greater than 1 s. At higher operating temperatures up to 2000°F, the residence time is lower due to the increase in the specific volume of the flue gas, but it remains above 0.75 s.

Combustion controls. The TO controls are designed to maintain a minimum combustion chamber tem-

perature and a minimum excess oxygen concentration in the flue gas. The controls are designed to maintain the minimum setpoint temperature within a range of approximately 15°F. For control purposes, the flue gas temperature is measured near the middle section of the ducting. If the temperature drifts below the setpoint temperature during operation, natural gas and combustion air are added to the burners to maintain the minimum temperature setpoint. If the temperature goes higher, the natural gas flow decreases until reaching the temperature setpoint or the natural gas valves reach the minimal fire position.

If the natural gas valves are at minimal fire position and the setpoint temperature is being maintained by the heating value from the NCG streams, then the controller will allow the temperature to rise until the upper setpoint temperature is reached. Once the upper set point temperature is reached, the controller will open the combustion air valve allowing air to flow to the NCG burner to "quench" the flame with air. If the air valve opens to the fully open position and the flue gas temperature continues to increase, then the temperature is allowed to rise

until the high temperature trip point of 2200°F is reached.

A second controller monitors the excess oxygen content of the flue gas to maintain a minimum setpoint of 3% by wet volume. Because the TO operates with a dilute gas stream, the oxygen concentration is normally maintained at 7%–8% by wet volume. If the oxygen level drops below the setpoint, the oxygen controller will override the temperature controller and allow combustion air to be added until the minimum excess oxygen setpoint is reached. The temperature controller continues to control natural gas as necessary to maintain the temperature setpoint.

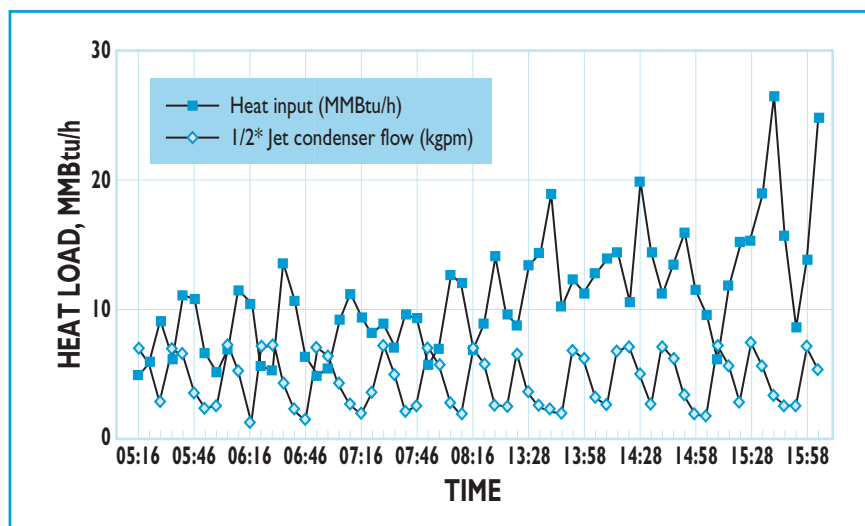
System safety. The process of collecting and incinerating NCG streams in the pulp and paper industry is not a new concept, and common safety practices have been well documented in the literature (2, 3). The two main safety aspects in the system design are protection from explosion hazards and human exposure to hazardous gases. To guard against explosion hazards, the natural gas combustion system is controlled by an approved flame safety system. Besides controlling the startup and shutdown of the

TO, the system will not allow introduction of NCG into the unit until a safe, stable, operating temperature is reached. Detonation arresters were installed on the two high concentration streams and a flame arrester was installed on the digester gas stream to prevent the possibility of flame flashback into the gas lines. The design of the arresters in the piping systems used insurance and industry guidelines (4, 5).

The NCG piping systems include safety interlocks to prevent the gases from being introduced into the combustion chamber if gas pressure and temperature are not operating in the proper range. The systems are designed to vent the gases safely to the atmosphere in case of pressure and temperature excursions or oxidizer trip. The pipelines are properly sloped and adequately drained to prevent the accumulation of condensed turpentine or methanol. Gas monitors are in the TO building to warn personnel of the presence of hydrogen sulfide gas in case of a leak.

RESULTS AND DISCUSSION

Historical industry experience (6, 7) indicates that uncontrolled sulfur emissions from the combustion of pulp and paper odorous gases are typically 5–6 lb sulfur/a.d. ton pulp. The results of the measurements summarized in **Table III** indicate that sulfur loadings from the oxidizer to the alkaline scrubber are higher than expected. These results indicate that sometimes as much as two-thirds of the sulfur added to the batch digesters is stripped from pulping liquors. Crude mass balances using water-side process measurements and historical, independent, stack tests on the TO flue gas also project sulfur loadings that are within 25%–35% of the results in **Table III**. These latter estimates fall within the upper bound of the experimental error (approximately 30%) of the measurement techniques used.



3. Digester NCG heat loading for hardwood pulping

We do not completely understand the reasons for the unusually high sulfur loadings. One factor may be a low black liquor pH in the evaporator system particularly with hardwood liquor. **Figure 3** shows that peak digester loading correlates with digester blows, and that heat input is maximized toward the end of a hardwood run. Most (99.9%+) sulfur present in the oxidizer flue gas is recovered in the SO₂ scrubber medium and returned to the kraft mill liquor cycle, i.e., to weak black liquor storage.

Performance of the odor control system has been excellent since the installation of the new TO. This is demonstrated by stack tests conducted at a sampling port on the horizontal run of the overhead retention duct—port A of Fig. 2—and at a port on the scrubber exhaust stack. **Table IV** summarizes the results of these tests with vendor warranty specifications and permit limitations. At port A, approximately one-quarter of the gas residence time in the combustion zone still remains before the quench chamber. TRS destruction at this location is >99.9% complete, and methanol concentrations are well below the cluster rule limitation of 20 ppmv. The data from port B demonstrates that the vendor warranty for TRS is met. All measurements at this location were below

the method detection limit (MDL). There is minimal potential for scrubbing H₂S, the only TRS specie present in the gas phase at sample port B because of the low pH (approximately 6.5) of the quench water.

Based on stack testing results, we determined that TRS and SO₂ emissions from the scrubber exhaust are well within existing emission limits when the TO is operated at a lower temperature setpoint of 1425°F. This setpoint also assures compliance with a minimum temperature of 1400°F required by state permit. Within the temperature window of 1425°F–1750°F, the natural gas burners remain at minimum fire (0.5–1.0 MMBtu/h/burner) approximately 90% of the time. This mode of operation minimizes natural gas usage and NO_x formation while maintaining regulatory compliance. During hardwood pulping, the oxidizer temperature is driven to the upper setpoint of 1750°F. Conversely, the oxidizer operates at a lower temperature when softwood gases are burned. For softwood pulping runs of sufficient duration, the temperature will reach 1425°F and require the addition of natural gas. Usually, the feed gases have a sufficiently high heating value to sustain combustion.

The mill has experienced no flame-outs or other serious operational anomalies associated with the

TO. The incidence of community complaints has also decreased. The project has reduced community odor and ensured sustained compliance with current and proposed regulatory limits. **TJ**

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The authors thank Barbara J. Bennett (Mead Paper) and Hank W. Lindstedt (D&H Associates) for their many contributions to the project.

Received for review Jan. 6, 1997.

Accepted March 16, 1998

Presented at the TAPPI 1997 Environmental Conference.

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