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P. Adams
DIRECTOR OFFICE STE 23
111 S MAGNOLIA DR
TALLAHASSEE, FL 32301
UNITED STATES Tel:850-921-9505

ORIGIN: TLH

Sender's ref
37550201000 A7 AP255

To: National Park Service
Mr. John Bunyak
12795 W. Alameda Parkway
Air Division
Lakewood, CO 80228
UNITED STATES

POSTCODE:
80228

Tel: 303-966-2818

Description: PSD-FL-367 correspondence

Weight: 1 lbs for 1 pcs
Date: 2006-01-17

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12795 W. Alameda Parkway

Lakewood, CO 80228
UNITED STATES

Attention To: Mr. John Bunyak
Phone#: 303-966-2818

Sent By: P. Adams
Phone#: 850-921-9505

Rate Estimate: 12.51
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Weight (lbs.): 1
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Parcels: 1/1

From: DEP AIR RESOURCE MGMT
P. Adams
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111 S MAGNOLIA DR
TALLAHASSEE, FL 32301
UNITED STATES Tel:850-921-9505

ORIGIN:
TLH

Sender's ref
37550201000 A7 AP255

To: U.S. EPA Region 4
Mr. Gregg M. Worley
61 Forsyth Street
Air Permits Section
Atlanta, GA 30303
UNITED STATES

POSTCODE:
30303

Tel: 404-562-9141

Description: PSD-FL-367 correspondence

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U.S. EPA Region 4
Air Permits Section
61 Forsyth Street

Atlanta, GA 30303
UNITED STATES

Attention To: Mr. Gregg M. Worley
Phone#: 404-562-9141

Sent By: P. Adams
Phone#: 850-921-9505

Rate Estimate: 6
Protection: Not Required
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Weight (lbs.): 1
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RECEIVED
JAN 13 2006
BUREAU OF AIR REGULATION

January 12, 2006

Mr. Jeffrey Koerner, PE – Permitting North Administrator
Bureau of Air Regulation
Florida Department of Environmental Protection
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

RE: Modification to the No. 4 Recovery Boiler
Project No.: 1070005-035-AC/PSD-FL-367

Dear Mr. Koerner:

This letter is in response to your Request for Additional Information (RAI-#1), dated December 16, 2005 regarding modification to the No. 4 Recovery Boiler Project No.: 1070005-035-AC/PSD-FL-367. Attached is a Professional Engineer Certification sheet (DEP Form No. 62-210.900(1) that should be used for Georgia-Pacific Corporation's responses to your RAI. The RAI has been submitted to you under separate cover from the Palatka Mill directly.

If you have any questions regarding this matter, please contact Myra Carpenter at (386) 329-0918.

Very truly yours,

Wayne J Galler

Wayne J. Galler
Senior Environmental Consultant – Air

encl.

Professional Engineer Certification

1. Professional Engineer Name: **Mark J. Aguilar**
Registration Number: **52248**

2. Professional Engineer Mailing Address:
Organization/Firm: **Georgia-Pacific Corporation**
Street Address: **133 Peachtree St**
City: **Atlanta** State: **GA** Zip Code: **30303**

3. Professional Engineer Telephone Numbers...
Telephone: **(404) 652-4293** ext. Fax: **(404) 654-4706**

4. Professional Engineer Email Address: **mjaguila@gapac.com**

5. Professional Engineer Statement:

I, the undersigned, hereby certify, except as particularly noted herein, that:*

(1) To the best of my knowledge, there is reasonable assurance that the air pollutant emissions unit(s) and the air pollution control equipment described in this application for air permit, when properly operated and maintained, will comply with all applicable standards for control of air pollutant emissions found in the Florida Statutes and rules of the Department of Environmental Protection; and

(2) To the best of my knowledge, any emission estimates reported or relied on in this application are true, accurate, and complete and are either based upon reasonable techniques available for calculating emissions or, for emission estimates of hazardous air pollutants not regulated for an emissions unit addressed in this application, based solely upon the materials, information and calculations submitted with this application.

(3) If the purpose of this application is to obtain a Title V air operation permit (check here ☐, if so), I further certify that each emissions unit described in this application for air permit, when properly operated and maintained, will comply with the applicable requirements identified in this application to which the unit is subject, except those emissions units for which a compliance plan and schedule is submitted with this application.

(4) If the purpose of this application is to obtain an air construction permit (check here ☒, if so) or concurrently process and obtain an air construction permit and a Title V air operation permit revision or renewal for one or more proposed new or modified emissions units (check here ☐, if so), I further certify that the engineering features of each such emissions unit described in this application have been designed or examined by me or individuals under my direct supervision and found to be in conformity with sound engineering principles applicable to the control of emissions of the air pollutants characterized in this application.

(5) If the purpose of this application is to obtain an initial air operation permit or operation permit revision or renewal for one or more newly constructed or modified emissions units (check here ☐, if so), I further certify that, with the exception of any changes detailed as part of this application, each such emissions unit has been constructed or modified in substantial accordance with the information given in the corresponding application for air construction permit and with all provisions contained in such permit.

Mark J. Aguilar 1/12/06
Signature Date

(seal)

* Attach any exception to certification statement.

Georgia-Pacific

Palatka Pulp and Paper Operations
Consumer Products Division
P.O. Box 919
Palatka, FL 32178-0919
(386) 325-2001

January 12, 2006

RECEIVED
JAN 13 2006
BUREAU OF AIR REGULATION

Mr. Jeffrey Koerner, PE – Permitting North Administrator
Bureau of Air Regulation
Florida Department of Environmental Protection
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

RE: Modification to the No. 4 Recovery Boiler
Project No.: 1070005-035-AC/PSD-FL-367

Dear Mr. Koerner:

This letter is in response to your Request for Additional Information (RAI-#1) dated December 16, 2005 regarding modification to the No. 4 Recovery Boiler Project No.: 1070005-035-AC/PSD-FL-367. For ease of following our responses, the questions have been repeated prior to the answers.

B. BOILER QUESTIONS:

Q.B.1. The project will overhaul the recovery boiler with extensive replacement of superheater, economizer, generating bank, and floor tubes as well as replace and/or modify components in the combustion air system. The project will also add a crystallizer and make miscellaneous changes to the concentrators (i.e., baffles, heat exchanger, piping, etc.). The application indicates that construction is planned to commence in April of 2006 and be completed over a variety of outages through 2008. Please identify the various stages of construction and the items that are scheduled for completion during each stage.

Answer: As of this date, the schedule should be as follows:

April/May 2006 – 25% of Wall tubes to be replaced
April/May 2006 – Air system upgrades installed

June 2006 to May 2008 – Construct Crystallizer and upgrades to concentrator / evaporator

April / May 2007 – Superheater / Economizer tubes to be replaced
25% of Wall tubes to be replaced

May 2008 -- Start up new crystallizer and upgraded concentrator / evaporator

Q.B.2 The current permitted capacity of the recovery boiler is 1346 MMBtu/hour of heat input and 210,000 lb BLS/hour (24-hour average). What is the corresponding maximum continuous steam production rate for the boiler? What are the design steam conditions (temperature and pressure)? Will the project increase the boiler capacity?

Answer: The RB can achieve a rate of 789,000 lbs/hr steam at 850-900 °F and 1250 psi. As stated on Page 1-2 of the application, the projects will not increase the boiler capacity over the permitted capacity of 5.04 million lbs of black liquor solids per day.

Q.B.3 The pulp mill capacity is specified as 118 ADTUP/hour and 1850 ADTUP/day, maximum monthly average. Will the project increase the pulp mill capacity?

Answer: No, pulp mill capacity will not change.

Q.B.4 On page B-40, the application identifies the maximum flow rate at permitted capacity as 210,000 dscfm @ "2.8%" oxygen (dry). Identify the basis for this rate. Actual test data provided in the application does not indicate typical operation at an oxygen level of 2.8%. Does the unit have an oxygen meter? Is the oxygen level continuously recorded? What is the optimum oxygen operating range for the recovery boiler?

Answer: The flow rate is the "design" flow rate and is documented in PSD applications in 1991 and in 1995. This flow rate at this oxygen level is representative of air flow entering the precipitator. This value is used as the design basis when GP requests quotes from vendors regarding operation of the Recovery Boiler. When the air flow measured in the stack is adjusted to 8% oxygen, the resulting calculated flows are similar at 294,000 dsfcm.

Oxygen meters are located in the economizer outlet going to the precipitator and in the stack. These oxygen levels are continuously recorded. The current / typical range of oxygen in the RB is 1 to 4%.

Q.B.5 Please provide an ultimate and proximate fuel analysis for the BLS fired in this recovery boiler.

Answer: The ultimate and proximate fuel analysis for the BLS fired in this recovery boiler is attached in Attachment A.

Q.B.6 The recovery boiler has been identified as a unit subject to the recently promulgated Best Available Retrofit Technology (BART) provisions. How does the facility propose to comply with the BART requirements for NOx, SO2, and PM/PM10?

Answer: The State of Florida is in the early stages of determining what the BART requirements might be State wide and which sources will be required to install BART. Extensive modeling studies will be required as part of this evaluation. While the Palatka Mill has sources that have been preliminarily identified as being "BART-eligible", we believe it is premature to speculate on any BART alternatives at this time. BART applications will be submitted later this year according to the schedule in the final BART rules promulgated by the Department.

C. CO & VOC EMISSIONS QUESTIONS:

Q.C.1 The current standards for CO emissions in the Title V permit are 800 ppmvd @ 8% oxygen (3-hour average) and 400 ppmvd @ 8% oxygen (24-hour average). These limits were established in Air Permit No. PSD-FL-226 based on "combustion controls". The application indicates that there is an optimum operating level for BLS-to-air ratio, which will minimize CO emissions. Identify the range of operation for this parameter and correlate the range to actual test data.

Answer: Reviewing BLS to air ratio data during stack testing conducted in September 2005 shows that BLS/Air Ratio ranged from 0.213 to 0.224. This data was analyzed along with precipitator oxygen data in order to assess any correlations that might exist with stack Carbon Monoxide concentrations. The correlation analysis results did not indicate that there is a good correlation (i.e. R^2 values were very low) between the BLS/air ratio and CO. The results of the correlation analyses are summarized in the table in Attachment B.

It is important to understand that the existing Recovery Boiler has three levels at which air is added. This project will install a new air system that includes a fourth level of air and this represents an improvement to combustion controls that will help to minimize CO levels.

Attachment D –"BACT Review for #4RB" in the PSD application was updated to reflect the response to this question. The revised section is included in Attachment I.

Q.C.2 Identify the boiler combustion parameters monitored and the operating levels that ensure good operation. Does the current system include any automated combustion controls? Will a new control system be added?

Answer: The RB operators currently set air flows at three air levels (four locations) based on Black Liquor quality and firing rates. These air flows are set and adjusted manually and the system automatically controls air flows to these set points. The operator makes the air flow set point changes manually based upon changes in steam generation needs, fuel oil rates, Black Liquor firing rate (dependent on BL heat values) and changes in emissions levels of oxygen, TRS, SO2 and opacity. These changes are made manually because Black Liquor fuel is variable, depending on the operation of the evaporator and recovery systems.

Since parts of this project are both evaporator improvements and the addition of a Crystallizer, the properties of Black Liquor being burned will change. As the new projects are installed and started up, the control strategy and control systems for burning fuels in the RB will have to be optimized.

N. NOx EMISSIONS QUESTIONS:

Q.N.1 The current NOx standard in the Title V permit is 80 ppmvd @ 8% oxygen based on an annual stack test. This standard was established in Air Permit No. PSD-FL-226. Will the installation of a 4th level of combustion air be able to achieve lower NOx emissions or more steady NOx emissions? The application indicates that NOx emissions from a recovery boiler will range from 75 to 150 ppmvd depending on the levels of combustion air provided. Estimate the fraction of NOx emissions that are fuel NOx compared to thermal NOx. Are the combustion air

requirements manually set for fixed operating levels or is there an automated control system? Describe the parameters that are monitored to ensure effective staged combustion with low NOx levels.

Answer: (Q.N.1) One of the upgrades to the No. 4 Recovery Boiler that was described in the PSD permit application was the installation of a new Crystallizer. The Crystallizer will increase the solids content of the black liquor from approximately 65% (wt.) to 75% (wt.). The combustion of black liquor with higher solids content will result in higher temperatures in the combustion chamber that will lead to slightly higher NO_x levels in the Recovery Boiler. The addition of the 4th level of combustion air will help to maintain NOx levels at their present concentration. The predominant quantity of NO_x emissions generated in a Recovery Boiler is due to the fuel nitrogen content of black liquor with a small fraction of NO_x emissions attributed to thermal effects. This is based on information contained in a NCASI Special Report (No. 03-06), dated October 2003, entitled "Effect of Kraft Recovery Furnace Operations on NO_x Emissions: Literature Review and Summary of Industry Experience". **(Copy attached in Attachment C).**

The combustion air requirements are manually set for fixed operating levels. As stated in the response to Q.C.2 the parameters that are monitored to ensure effective staged combustion are air flows, oxygen, TRS, SO2, opacity, steam generation needs, and Black Liquor flow rate. An annual stack test is conducted to confirm that NOx levels are within the permitted limits.

Q.N.2. Please identify the source of the cost estimate for a cold-side SCR system and provide the supporting information. *{The BACT analysis in...}(sic)* **The application assumes that an SCR system would be installed after the ESP and therefore the exhaust would have to be reheated to provide the proper operating window. Would it be possible to locate an SCR system prior to the ESP to avoid costly reheat? What existing circumstances at the plant would prevent this? Otherwise, please provide a cost estimate for a hot-side SCR system.**

Answer: The source of information regarding the cost estimate for a cold-side SCR system comes from Page 2-3, Section 4.2 of EPA's Cost Control Manual (Sixth Edition, January 2002). It appears that we inadvertently omitted Appendix D-1 from the Permit Application which will provide more details of how the SCR costs were derived. Appendix D-1 is attached with this submittal. (See Attachment D). GP does not believe it is possible to locate an SCR system prior to the ESP because the particulate loading would quickly clog and contaminate the SCR catalyst bed. Ammonia salts, fly ash, and other particulate matter in the flue gas can cause binding, plugging, and/or fouling of the catalyst. The particulate matter deposits in the active pore sites of the catalyst resulting in a decrease in the number of sites available for NO_x reduction and an increase in flue gas pressure loss across the catalyst bed. Additionally, certain fuel constituents released during the combustion process can act as catalyst poisons. Catalyst poisons include calcium and magnesium oxides, potassium, sodium, arsenic, chlorine, fluorine, and lead. These constituents deactivate the catalyst by diffusing into active pore sites and occupying them irreversibly so it is not technically possible to locate the SCR prior to the ESP. Since we do not believe the installation of a "hot-side" SCR system is technically feasible, a cost analysis for this activity has not been provided.

Q.N.3 The application rejects SNCR as a technically infeasible control option. To be effective, SNCR requires the a proper operating temperature window in which to inject ammonia or urea, sufficient residence time for the reaction to take place, and turbulence for mixing. Please provide supporting information based on the actual boiler design and operating condition to support GP's belief that SNCR is not technically feasible. Please provide a cost estimate on installing an SNCR system for the recovery boiler.

Answer: GP has discussed the issue of applying an SNCR system to a recovery boiler with two of the leading suppliers of SNCR systems in the United States, Fuel-Tech, Inc. and Aker Kvaerner Power, Inc. According to both of these companies, SNCR systems for recovery boilers are not commercially available from any vendor. While the use of SNCR technology may be theoretically applied to a recovery boiler, there is not currently a sufficient amount of information available to assure that it is a viable technology. Both of these companies are working together on studies in Sweden to determine if SNCR can be applied for use on recovery boilers. GP has been told that the studies will not be completed for a number of years, and for this reason, SNCR systems are not being made commercially available to the Pulp & Paper Industry at this time. Some of the issues that are causes for concern with the use of an SNCR system in a recovery boiler are boiler tube corrosion and increased boiler pluggage rates caused by ammonia gases (from ammonia injection).

For the reasons explained above, a cost estimate for an SNCR system for a recovery boiler cannot be provided at this time. In the future, if the studies Fuel-Tech, Inc. and Aker Kvaerner Power, Inc.in Sweden are successful, SNCR systems may become a viable technology for recovery boilers.

P. PM/PM10 Emissions

Q.P.1 The application indicates that the PM10 emissions are approximately 75% of the total PM emissions. Please provide emissions data for this recovery boiler to support this statement. Other information suggests that approximately 90% of total PM emissions are PM10 emissions and of the PM10 emissions, approximately 50% is actually about 1 micron in diameter or less (Davis, 2000). Describe the difficulties in controlling particles in this size range with a 2-field ESP. Please identify any improvements to the existing ESP that would result in better performance. Can the existing unit be modified to add a 3rd field?

Answer: GP has no actual PM10 data for this Recovery Boiler. GP used data contained in Table 10.2-3 of AP-42, "Cumulative Particle Size Distribution and Size-Specific Emission Factors for a Recovery Boiler without a Direct-Contact Evaporator but with an ESP" to estimate the quantity of PM_{10} emissions emitted from the No. 4 Recovery Boiler. Based on the data in Table 10.2-3, 74.8% of the cumulative mass percent of particulate matter emissions emitted from recovery boilers without direct-contact evaporators are 10 μm in size or smaller. GP rounded off this value to 75% for purposes of determining the baseline and potential emission rates. This information is in close agreement with particle size data contained in Table 4.12 of NCASI Technical Bulletin No. 884, August 2004, which estimates that 67.2% (average of stack test results from 14 recovery boilers) of the particulate matter emitted from recovery boilers with non-direct contact evaporators is 10 μm in size or smaller. Table 4.12 also indicates that 51% of the particulate matter emitted from recovery boilers with non-direct contact evaporators is 2.5 μm in size or smaller.

It is important to point out that the Recovery Boiler has two precipitator chambers each of which houses 6-fields. The chambers are operated in parallel with each side treating approximately 50% of the air flow from the unit.

Q.P.2 As suggested by the application, 25% of the total PM emissions are greater than PM10 in size. Identify control devices (i.e., settling chambers, cyclones, wet cyclones, etc.) that could be installed prior to the ESP to reduce loading so that the ESP could be tuned to remove additional PM emissions. Provide a cost analysis for feasible add-on controls.

Answer: As gases exit the RB economizer, there is a hopper there to "drop out" the heaviest particles prior to the gases entering the 2-chamber, 12-field precipitator.

GP contacted GE Energy, a vendor that provides ESP support and consulting services, regarding retrofits to an existing ESP to reduce PM load going to an ESP. Their experience is that ESP's are generally added after existing control devices when additional PM removal is needed. Adding a treatment system in between a process and an existing ESP is technically very difficult and not very cost effective.

Other comments received include the fact that settling chambers are not technically feasible because PM exiting a recovery boiler do not settle well. Wet systems prior to an ESP are not recommended because any added moisture in the ESP can inhibit its effectiveness. Furthermore, systems prior to the ESP are inconsistent with the way that GP handles salt cake and this would add additional costs to any pre-ESP system.

Q.P.3 The application states that an ESP can achieve greater than 99.9% control and identifies the ESP as the top control. What is the control efficiency of the existing ESP? Have there been any major improvements or overhauls to the ESP within the last 5 years? If so, when did this occur, what work was performed and how much did it cost? Are any future major improvements or overhauls planned?

Answer: In general an ESP can achieve greater than 99.9% PM control depending upon a myriad of factors. GP has no recent data on the inlet PM to the ESP and therefore does not have an actual efficiency value for the ESP. However, based on information generated for the projects to upgrade the Recovery Boiler, it is believed that after the air system upgrades, the inlet to the ESP will contain 8 grains/dscf (at 10% O_2). Using this value and assuming a 20% reduction in PM due to the projects, it is estimated that the current ESP inlet contains about 10 grains/dscf (at 10% O_2). This equates to a 99.7% efficiency for the ESP at the current ESP outlet limit of 0.03 grains/dscf (at 10% O_2). If the PM reduction from the economizer hopper was included in this estimate, the total PM reduction would exceed 99.9%.

From a physical facility perspective only routine maintenance projects (*i.e.* drag chain and tubes replacements) have been done on the unit during regular spring outages. In 2004 an Automatic Voltage Control system was installed on the precipitator to monitor the performance of each TR to minimize opacity while maximizing energy efficiency.

Other than routine maintenance items, there are currently no plans for major improvements or overhauls to the Recovery Boiler ESP.

Q.P.4 The application indicates that GP operates two recovery boilers in another state (St. James River Corp.), each with a combination of an ESP and wet scrubber. The application states that the wet scrubbers were installed to recover heat and supply hot water to the plant and not reduce PM emissions. Nevertheless, identify the control efficiency of the wet scrubbers for reducing PM emissions. What are the PM emissions standards for these units? What are the actual tested PM emissions from these units? Provide test data for the units operating only with the ESP and with the ESP/wet scrubber combination. What is the calculated PM removal efficiency of these wet scrubbers? Does the wet scrubber also remove SO2, TRS and HCl emissions? Provide a cost analysis for a similar wet scrubber.

Answer: GP does not have any data to document the particulate matter control efficiency of the wet scrubbers for the recovery boilers at the Camas, WA Mill because PM emissions have never been tested from only the wet scrubbers. Since the scrubbers are located downstream of the ESPs, the particulate loading exiting the ESPs and entering the scrubbers is very low. The reason for this is because the ESPs were designed to meet the state PM/PM_{10} emission limit of 0.033 grain/dscf @ 8% oxygen, from each of the recovery boilers. The scrubbers were not part of the design to control particulate matter emissions; rather, they were specifically installed to recover heat. The ESPs are always in service when the recovery boilers are in operation. Test results from the combination of the ESP followed by the wet scrubbers' exhausts indicate compliance with the State permit limits. Based on stack testing conducted over the past two years, the average PM emission rate emitted from the combination of ESPs and wet scrubbers is well below 0.02 grain/dscf.

The wet scrubbers, which are designed as "Packed Bed" units, do remove SO_2 emissions. GP does not have any stack testing data on the scrubber's ability to remove TRS or HCl emissions from the recovery boilers. GP does not believe TRS emissions are affected by the wet scrubbers since the scrubbing solution is maintained at a pH level of approximately 7.0. To reduce TRS emissions from the recovery boilers, the pH level of the scrubbing solution would need to be raised to 11.0 or higher. There is no practical reason to use the wet scrubbers to further reduce TRS emissions from the recovery boilers since the TRS emission rates from recovery boilers are routinely less than 5.0 ppmvd @ 8% oxygen. As stated above, GP has never tested the recovery boilers' exhaust gases downstream of the scrubbers to determine what the HCl emission rates are, however, based on our knowledge of how the scrubbers operate, any HCl in the recovery boiler exhaust gases should be readily adsorbed in the caustic scrubbing solution and HCl emissions to the atmosphere should be very low.

GP does not believe it is necessary to provide a cost effective analysis for wet scrubbers regarding the PSD Permit Application for the No. 4 Recovery Boiler, as SO_2 and TRS emissions were not triggered under the PSD applicability analysis. Therefore, a BACT analysis, which would include cost effective analyses for control equipment, is not required for these pollutants.

Q.P.5 The RACT/BACT/LAER Clearinghouse shows several recovery boilers with PM BACT limits of 0.021 grains/dscf. Much of the recent test data shows that the existing ESP could also achieve this level of control. However, test data collected during 2000/2001 shows much higher emission levels. Identify the cause of the elevated PM emissions. Was the unit undergoing maintenance or about to undergo maintenance? Were both fields of the ESP operating during the tests? Were repairs or corrective actions taken after the tests were conducted? When the existing ESP is properly tuned and operating both fields of the ESP, can the unit achieve a PM emission rate of 0.021 grains/dscf or less?

Answer: Stack test reports for April 11, 2000, July 11, 2001, and March 2, 2004 were reviewed. These are the same reports that were submitted to the DEP Air office in Jacksonville. During these stack tests, the RB experienced individual runs where the PM results ranged from 0.023 gr/dscf to 0.034 gr/dscf. Operating personnel also checked available records to determine if the ESP was under going maintenance or was about to undergo maintenance around the time of the stack tests. This check did not result in any findings.

It was determined that during the April 2000 tests, the 5th effect on the South precipitator chamber (note that there are 6 effects per chamber) was off-line during all three test runs. During the July 2001 test runs, the 6th effect on the north chamber was on-line but it was showing no secondary current. However, during the March 2004 tests, all effects in both chambers were operating. Method 9 opacity tests were conducted on the three stack test dates and the test results showed mostly zero opacity on all three dates.

It is not surprising that the precipitator could meet the permit limit despite a field being down. It is good engineering practice to over design ESP's so that they can operate so as to comply with emission limits even if all fields are not operating.

Based on a review of July 2001 to September 2005 stack testing results, it appears that the ESP can achieve individual tests runs with an average PM emission rate of 0.021 gr/dscf. However, several test runs have been above this level and to account for this anticipated variation, GP concludes that the 0.03 gr/dscf standard ought to remain.

Q.P.6 Has any PM10 emissions testing ever been conducted on this RB? If so, please provide the date(s) and a synopsis of the test(s) results.

Answer: GP could locate no records or knowledge of PM10 testing on the Recovery Boiler.

S. SAM EMISSIONS:

Q.S.1 The application indicates that SAM emissions are completely in a gaseous form when exiting the stack at 425° F. Stack test data provided indicates that the actual stack exhaust temperature is about 400° F. At what temperature will SAM condense out of the exhaust?

Answer: SAM will condense from a boiler exhaust gas stream at a temperature in the range of 140-170 degrees Celcius (284-338 degrees Fahrenheit), depending on the SAM concentration and pressure of the gas stream (Reference: Page 12 of "Guidance for Reporting Sulfuric Acid (acid aerosols including mists, vapors, gas, fog, and other airborne forms of any particle size)", EPA-745-R-97-007, November 1997). A copy of the reference for this information is included as part of this submittal. (See Attachment E)

Q.S.2 Is it possible to reduce the exhaust temperature with a heat exchanger to form SAM droplets that can be removed with mist eliminators? Is this technique used on other recovery boilers? Are mist eliminators installed on other recovery boilers within the pulp and paper industry?

Answer: The best way to remove SAM emissions from a boiler exhaust gas stream would be to use a wet scrubber or wet ESP. While a heat exchanger can reduce the temperature of an exhaust gas, this alone does not guarantee that SAM emissions will be removed from the gas stream. Due to the very small, sub-micron particle size of SAM emissions (as an aerosol), only some of the SAM emissions would be captured and condensed from the use of a heat exchanger.

The use of mist eliminators is not used to reduce SAM emissions from recovery boilers. The reason for this is because recovery boilers that employ the use of non-direct contact evaporator (NDCE) systems generate very small quantities of SAM emissions. Typical SAM emission rates from NDCE recovery boilers are usually less than 3.0 ppmv, corrected to 8% oxygen (NCASI Technical Bulletin # 701, Table 12C, Volume No. 1, October 1995). SAM emission rates from recovery boilers are low because the SAM emissions are adsorbed as part of the smelt that is formed in the bottom of the furnace during the combustion process. SAM emissions from the No. 4 Recovery Boiler at the Palatka Mill have been tested and found to be in agreement with the NCASI data reported in Technical Bulletin # 701.

Based on the low SAM emissions found during stack testing in 2004/2005 (less than 0.5 lbs/hr – 2.2.tons/yr) and the high cost for a mist eliminator to treat over 400,000 acfm of gas; it is estimated that the "cost effectiveness" for SAM removal would be in the low $100,000's per ton. Therefore, it would not be economically feasible to install mist eliminators, or any other SAM control device, such as a wet scrubber or wet ESP given the small quantity of SAM emissions generated in NDCE recovery boilers.

M. MISCELLANEOUS:

Q.M. 1. On page A-39 (Section F1) of the application, potential benzene emissions were listed as "296.1 TPY". Please correct and submit the revised pages.

Answer: The revised page is included in Attachment F. Please replace the page in the permit application booklet in your possession with this new page.

Q.M.2 We are still reviewing the modeling and will ask any questions that arise by December 21 of next week.

Answer: On December 28, 2005 GP received Cleve Holladay's December 20, 2005 letter regarding the Federal Land Manager's (FLM) comments on the modeling for haze in Class 1 areas. Based on those comments and other input from DEP and the FLM office, GP's consultant, Golder Associates, conducted revised modeling studies. A response to the December 20th letter and the results of the revised modeling are included in Attachment G.

Please replace Table C-38 in the permit application booklet in your possession with the revised table that is also included in Attachment G.

Q.M .3 If any response to the above issues affect the application submittal, please correct and/or change the application to reflect the additional analyses and submit.

Answer: Changes to the Permit Application are included as follows:

ATTACHMENTS	DESCRIPTION
F	Revised page A-39 - Benzene
G	Haze modeling results and table.
H	Revised TRS related pages to reflect 5ppm as an annual average limit and 11.2 ppm as 12-hr average limit.
I	PSD Application revised "Attachment D" – updated to reflect GP's response to Question C.1.
J	Professional Engineer signature page for this response (Copy).

If you have any questions regarding this matter, please contact Ms. Myra Carpenter at (386)329-0918.

Sincerely,

For TDK

Theodore D. Kennedy, Vice-President.
Georgia-Pacific – Palatka Operations

cc: Myra J. Carpenter, G-P

ATTACHMENT A

Response to Question B.5.

Ultimate and proximate fuel analysis BLS fired in Recovery Boiler.

Liquor Analysis (as fired)	
Sodium	18.70
Hydrogen	4.00
Carbon	34.60
Oxygen	36.78
Sulphur	3.99
Potassium	1.09
Chlorine	0.56
Nitrogen	0.10
Inerts	0.18
TOTAL	100.00%

% Solids	66.57 (1)
HHV virgin (BTU/lb)	6,390
HHV as fired (BTU/lb)	5,890

(1) – This a current value. The work under this PSD application will increase this value.

ATTACHMENT B

Response to Question C.1

SUMMARY TABLE – FOR STACK TESTS 9/6-7/2005

CORRELATIONS BETWEEN STACK CARBON MONOXIDE LEVELS

VERSUS PRECIPITATOR INLET AVERAGE OXYGEN AND

VERSUS BLS TO AIR RATIO

			Column A	Column B	Column C	Corr. Coff. – R^2	Corr. Coff. – R^2
DATE	**RUN #**	**TIME**	**PPT INLET Average O2 -%**	**BLS TO AIR Average Ratio**	**STACK CO Average PPM**	**"A" vs "C"**	**"B" vs "C"**
9/6/05	**1**	**1254-1355**	**2.20**	**0.214**	**338**	**0.0068**	**0.238**
9/6/05	**2**	**1706-1807**	**2.25**	**0.222**	**100**	**0.0126**	**0.018**
9/7/05	**3**	**0850-0951**	**2.61**	**0.220**	**208**	**0.180**	**0.0002**

NOTE – Correlation coefficients are based on comparing 60 minutes of data for the entire run.

ATTACHMENT C

Response to Question N.1

NCASI Special Report (No. 03-06), dated October 2003, entitled

"Effect of Kraft Recovery Furnace Operations on NO_x Emissions: Literature Review and Summary of Industry Experience".

ATTACHED TO HARD COPY ONLY

Att. C

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NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT

EFFECT OF KRAFT RECOVERY FURNACE OPERATIONS ON NO_X EMISSIONS: LITERATURE REVIEW AND SUMMARY OF INDUSTRY EXPERIENCE

SPECIAL REPORT NO. 03-06

OCTOBER 2003

by
Arun V. Someshwar, Ph.D.
NCASI Southern Regional Center
Gainesville, Florida

Acknowledgments

This report was prepared by Arun V. Someshwar, Ph.D., Principal Research Engineer at the Southern Regional Center. Susan Kirkland was responsible for report preparation.

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National Council for Air and Stream Improvement, Inc. (NCASI). 2003. *Effect of kraft recovery furnace operations on* NO_x *emissions: Literature review and summary of industry experience.* Special Report No. 03-06. Research Triangle Park, N.C.: National Council for Air and Stream Improvement, Inc.

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PRESIDENT'S NOTE

Regulatory pressure for NO_x emission reductions has increased because of the role NO_x emissions play in ground-level ozone formation and the more stringent 8-hour average ambient air quality standard of 0.08 ppm for ozone. NO_x emissions also contribute to acidic deposition, formation of fine particulates, and reduced visibility. Additional attention on NO_x emissions has resulted from new EPA efforts related to achieving the $PM_{2.5}$ ambient air quality standards and reducing regional haze events in national parks and other Class I areas. While utility and larger industrial boilers using fossil fuels have been the primary stationary source targets for NO_x emission reductions, sources with lower NO_x emissions are coming under scrutiny as candidates for controls. As a result, NCASI has investigated NO_x emissions from several sources unique to the forest products industry in order to quantify emission levels and identify factors that affect the emissions. This report deals with kraft recovery furnaces.

Relating furnace design parameters and operating conditions to NO_x emissions has been attempted by many investigators. It is a complicated subject with many apparently conflicting results. The last NCASI review on this subject was published in 1992. Since then, a significant amount of research in this area has been carried out and reported in the literature. Thus, there was a need to summarize the more recent literature on NO_x formation in kraft recovery furnaces. It was found that liquor nitrogen content continues to be the main determinant of a furnace's NO_x emissions. New studies suggest the temperature profile within a furnace may have a marked effect on the amount of NO_x formation by the fuel NO_x pathway.

In addition, with the growing regulatory interest in NO_x emission reductions, a need existed for a compilation of current information and industry experience with techniques for minimizing recovery furnace NO_x emissions. One of the most promising means for in-furnace NO_x reductions appears to be modification of the combustion air distribution, including the installation and use of quaternary air ports. This review also examines the technical feasibility of employing add-on NO_x controls such as selective non-catalytic reduction.

This report is meant to serve as a resource document to assist member companies in responding to NO_x emission limitations or control technology requirements that might be proposed by regulatory agencies as a result of mill-specific permitting reviews or more general State Implementation Plan (SIP) requirements.

Ronald A. Yeske

October 2003

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MOT DU PRESIDENT

Aux États-Unis, les exigences réglementaires visant la réduction des émissions de NO_x se font de plus en plus pressantes car ces émissions jouent un rôle important dans la formation de l'ozone troposphérique. On a vu également apparaître une norme plus sévère pour l'ozone dans l'air ambiant (moyenne de 0,08 ppm calculée sur huit heures). Les émissions de NO_x contribuent également aux dépôts acides, à la formation de particules fines et à la réduction de la visibilité. Cette attention accrue envers les émissions de NO_x a encouragé l'EPA à déployer de nouveaux efforts pour faire en sorte que les normes de qualité de l'air ambiant pour les $PM_{2,5}$ soient atteintes de même que pour réduire les épisodes de brume sèche en régions (*regional haze*) dans les parcs nationaux et autres zones appartenant à la classe I. Les chaudières de centrales thermiques de même que les chaudières industrielles de grande capacité qui utilisent des combustibles fossiles ont été ciblées comme étant la principale source fixe d'émissions de NO_x pour laquelle une réduction s'imposait. Toutefois, les sources comportant des émissions de NO_x moindres sont actuellement examinées afin d'évaluer si un meilleur contrôle s'avère nécessaire. Par conséquent, NCASI a effectué des recherches sur les émissions de NO_x de plusieurs sources que l'on retrouve uniquement dans l'industrie forestière afin de quantifier les niveaux d'émissions et d'identifier les facteurs qui affectent ces émissions. Ce rapport traite des fournaises de récupération kraft.

Plusieurs chercheurs ont tenté de relier les paramètres de conception ainsi que les conditions d'opération des fournaises de récupération aux émissions de NO_x. Il s'agit là d'un sujet compliqué qui présente des résultats plutôt conflictuels, du moins en apparence. La dernière revue de NCASI à ce sujet a été publiée en 1992. Depuis, de nombreux travaux de recherches ont été réalisés à ce sujet et publiés dans la littérature. Conséquemment, il était nécessaire d'effectuer une synthèse de la littérature récente traitant de la formation des NO_x dans les fournaises de récupération kraft. On a trouvé que la quantité d'azote présente dans les liqueurs demeure le principal facteur déterminant les émissions de NO_x d'une fournaise de récupération. De récentes études indiquent que le profil de température dans la fournaise peut avoir un effet marqué sur la quantité de NO_x générée par le mécanisme de formation des NOx-du-combustible (*Fuel-NOx*).

De plus, étant donné l'intérêt grandissant des autorités réglementaires face à la réduction des émissions de NO_x, il était nécessaire de compiler l'information actuelle et l'expérience de l'industrie en ce qui à trait aux techniques de minimisation des émissions de NO_x des fournaises de récupération. Il semble qu'un des moyens prometteurs pour réduire les NO_x à la source soit la modification de la distribution de l'air de combustion, incluant l'installation et l'utilisation de ports d'air quaternaire. Cette revue examine également la faisabilité technique associée à l'utilisation d'options de contrôle de NO_x telles que la réduction sélective non-catalytique.

Ce rapport se veut un document ressource afin d'aider les compagnies membres à répondre aux limitations des émissions de NO_x ou aux demandes d'installation d'équipements de contrôle qui peuvent être exigées par les autorités réglementaires dans le cadre des revues de permis et des exigences plus générales contenues dans le Plan de mise en oeuvre de l'état (*State Implementation Plan, SIP*).

Ronald A. Yeske

Octobre 2003

EFFECT OF KRAFT RECOVERY FURNACE OPERATIONS ON NO_X EMISSIONS: LITERATURE REVIEW AND SUMMARY OF INDUSTRY EXPERIENCE

SPECIAL REPORT NO. 03-06
OCTOBER 2003

ABSTRACT

Literature published over the last decade on kraft black liquor combustion NO_x emissions and their control is reviewed. The review encompasses results from both laboratory-scale liquor burning experiments and full-scale kraft recovery furnaces. The impact on NO_x emissions from varying furnace operational parameters, such as liquor load, liquor solids content, and combustion air distribution, is examined. The potential applicability of add-on control systems, such as selective non-catalytic reduction (SNCR), is discussed. The limited experience of kraft mills that burn stripper off-gases in recovery furnaces is summarized with respect to the potential impact on NO_x emissions. The experience of selected U.S. mills operating continuous NO_x monitoring systems with reducing NO_x emissions is also described.

Kraft recovery furnaces typically have low NO_x emissions due to a) the low N concentrations in most "as-fired" black liquor solids (around 0.1%), b) low overall conversions of liquor N to NO_x (around 10 to 25%) via the fuel NO_x formation pathway, c) insufficient temperatures for thermal NO_x formation, and perhaps, d) the existence of sodium fumes that might participate in "in-furnace" NO_x reduction or removal. Studies suggest nearly three-fourths of the liquor N is released during pyrolysis or devolatilization, partly as NH_3 and partly as N_2. The remainder stays with the smelt product, most likely as a reduced N species. NH_3 released during black liquor pyrolysis partly oxidizes to NO and partly reduces to N_2. A review of the NH_3–NO–O_2 chemistry at various temperatures and residence times suggests that temperatures within a furnace can have a significant effect on the extent of oxidation of this NH_3 to NO. Laboratory and limited field measurement data also suggest that, where feasible, "staged combustion" using quaternary air ports can minimize conversion of this released NH_3 to NO. Most of the NO is formed by oxidation of the NH_3 volatilized during pyrolysis of the liquor droplets. Very little NO_x originates from char burning or from the char or smelt bed.

With respect to post-combustion controls, no operating kraft recovery furnace utilizes SNCR at the present time. Short-term test trials with SNCR have been conducted on furnaces in Japan and Sweden. There are a number of critical unresolved issues around the use of urea or ammonia injection for NO_x control in a recovery furnace, especially over the long term. The use of selective catalytic reduction on a kraft recovery furnace has never been demonstrated. Optimization of the staged combustion principle within a large, existing kraft recovery furnace to obtain from 20% to 30% reduction in prevailing NO_x emissions is perhaps the only technologically feasible option at the present time. However, the effects of such air staging on emissions of other pollutants, mainly total reduced sulfur (TRS), SO_2, and CO, and on other furnace operational characteristics, including fouling, plugging, and chloride buildup, need to be examined with longer term data. The impact of burning ammonia-rich stripper off-gases (SOGs) in furnaces on NO_x emissions is unclear, but introducing the SOGs below the liquor guns is expected to result in no additional NO_x.

KEYWORDS

ammonia, black liquor, fuel NO_x, mechanism, NO_x CEMS, pyrolysis, quarternary air, SNCR, SOG burning, staged combustion, thermal NO_x

RELATED NCASI PUBLICATIONS

Special Report No. 03-04 (August 2003). *NO_x control in forest products industry boilers- a review of technologies, costs and industry experience.*

Technical Bulletin No. 802 (March 2000). *Effect of stripper off-gas burning on NO_x emissions.*

Special Report No. 99-01 (April 1999). *A review of NO_x emission control strategies for industrial boilers, kraft recovery furnaces, and lime kilns.*

Technical Bulletin No. 636 (July 1992). *An analysis of kraft recovery furnace NO_x emissions and related parameters.*

Atmospheric Quality Improvement Technical Bulletin No. 105 (December 1979). *A study of nitrogen oxides emissions from kraft recovery furnaces.*

EFFET DE L'OPERATION DES FOURNAISES DE RECUPERATION KRAFT SUR LES EMISSIONS DE NO_X : REVUE DE LITTERATURE ET SOMMAIRE DE L'EXPERIENCE DE L'INDUSTRIE

RAPPORT SPECIAL NO. 03-06
OCTOBRE 2003

RESUME

Dans ce rapport, on a fait la revue de la littérature publiée depuis la dernière décennie traitant des émissions de NO_x générées lors de la combustion de la liqueur noire kraft et du contrôle de ces émissions. Cette revue comprend des résultats d'expérience de combustion de liqueur à l'échelle du laboratoire de même qu'à l'échelle des fournaises de récupération en usine. On examine l'impact des émissions de NO_x associé à différents paramètres d'opération de fournaise, tels que la charge de liqueur, le contenu en solides de la liqueur et la distribution de l'air de combustion. Le rapport contient une discussion sur l'application potentielle d'options de contrôle telles que la réduction sélective non-catalytique (*SNCR*). L'expérience limitée en matière de combustion des gaz de systèmes de rectification à la vapeur dans les fournaises de récupération est résumée ici, en tenant compte de l'impact potentiel sur les émissions de NO_x. On décrit également l'expérience de certaines fabriques américaines (opérant des systèmes de surveillance en continu des NO_x) en matière de réduction de leurs émissions de NO_x.

Les fournaises de récupération kraft produisent habituellement de faibles émissions de NO_x étant donné a) les faibles concentrations d'azote (N) dans la majorité des solides de liqueur noire (environ 0,1%), b) les faibles taux de conversions de l'azote dans la liqueur en NO_x (environ 10 à 25%) selon le mécanisme de formation de NO_x du combustible, c) les températures trop faibles pour permettre la formation thermique de NO_x et peut-être, d) la présence de vapeurs de sodium qui sont susceptibles de participer à la réduction ou l'enlèvement des NO_x à l'intérieur même de la fournaise. Les études suggèrent qu'environ les trois quarts de N contenu dans la liqueur soient rejetés lors de la pyrolyse ou lors du dégagement des matières volatiles, en partie sous forme de NH_3 et en partie sous forme de N_2. Le reste demeure avec le produit salin, probablement sous forme d'espèces de N réduits. Le NH_3 généré lors de la pyrolyse de la liqueur noire est oxydé en partie sous forme de NO et est réduit en partie sous forme de N_2. Une revue de la réaction entre NH_3–NO–O_2 pour différentes températures et temps de résidence laisse supposer que les températures dans la fournaise peuvent avoir un effet significatif sur la capacité d'oxydation de ce NH_3 en NO. Des données de laboratoire et des données limitées obtenues sur le terrain laissent également supposer que, lorsque c'est faisable, une « combustion étagée » utilisant des apports d'air quaternaire peut minimiser la conversion du NH_3 en NO. La majeure partie du NO est formée lors de l'oxydation du NH_3 volatilisé à l'étape de la pyrolyse des gouttes de liqueur. La combustion du produit de carbonisation ou le produit de carbonisation en tant que tel de même que le lit de salin produisent très peu de NO_x.

En ce qui concerne les contrôles post-combustion, aucune fournaise de récupération kraft utilise la SNCR actuellement. Des essais à court terme impliquant la SNCR ont été réalisés sur des fournaises au Japon et en Suède. Il existe des enjeux critiques qui demeurent sans solution pour ce qui est de l'utilisation d'urée ou l'injection d'ammoniac pour le contrôle des NO_x dans une fournaise de récupération, principalement à long terme. La démonstration qu'il est possible d'utiliser la réduction catalytique sélective dans une fournaise de récupération kraft n'a jamais été faite. L'optimisation du principe de combustion étagée dans une fournaise de récupération kraft de grande capacité afin d'obtenir 20% à 30% de réduction des émissions de NO_x constitue probablement la seule option technologique faisable actuellement. Toutefois, les effets de cette combustion étagée sur les émissions des autres polluants, principalement les soufres réduits totaux (SRT), le CO et les autres caractéristiques opérationnelles de la fournaise (colmatage, obstruction, accumulation de dépôts chlorés) doivent faire l'objet d'un examen à partir de données à long terme. L'impact de la combustion des gaz riches en ammoniac du système de rectification à la vapeur (*SOG*) dans les fournaises sur les émissions de NO_x n'est pas certain. Cependant, on anticipe que l'introduction des *SOG* sous les buses d'injection de liqueur ne devrait pas créer d'émissions de NO_x additionnelles.

MOTS CLÉS

ammoniac, liqueur noire, NO_x du combustible, mécanisme, système SCE pour NO_x (*NO_x CEMS*), pyrolyse, air quaternaire, *SNCR*, combustion des *SOG*, combustion étagée, NO_x d'origine thermique

AUTRES PUBLICATIONS DE NCASI DANS CE DOMAINE

Rapport spécial no. 03-04 (août 2003). *NO_x control in forest products industry boilers- a review of technologies, costs and industry experience.*

Bulletin technique no. 802 (mars 2000). *Effect of stripper off-gas burning on NO_x emissions.*

Rapport spécial no. 99-01 (avril 1999). *A review of NO_x emission control strategies for industrial boilers, kraft recovery furnaces, and lime kilns.*

Bulletin technique no. 636 (juillet 1992). *An analysis of kraft recovery furnace NO_x emissions and related parameters.*

Bulletin technique sur l'amélioration de la qualité de l'air no. 105 (décembre 1979). *A study of nitrogen oxides emissions from kraft recovery furnaces.*

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EFFECT OF KRAFT RECOVERY FURNACE OPERATIONS ON NO_X EMISSIONS: LITERATURE REVIEW AND SUMMARY OF INDUSTRY EXPERIENCE

1.0 INTRODUCTION

Compared to both biomass and fossil fuel-fired boilers, black liquor combustion in kraft recovery furnaces results in fairly low emissions of the oxides of nitrogen (NO_x), typically in the range of 60 to 120 ppm. Nevertheless, it is often the largest source for NO_x emissions at kraft pulp mills. Thus, the causes of NO_x formation and emission from a furnace, the factors responsible for the range in NO_x emissions observed among similar furnaces, and the potential ways NO_x formation can be minimized and/or NO_x emissions controlled, are of continuing interest to the forest products industry. Past literature provided conflicting information on whether NO_x emissions from kraft recovery furnaces could indeed be controlled, considering that NO_x generated from black liquor combustion is predominantly of the "fuel NO_x" type and most furnaces already function, by virtue of their design, with a high degree of "air staging." It is not clear, for example, to what extent additional staging of combustion air could help in reducing existing NO_x emissions from kraft recovery furnaces. Neither is it clear whether or not the application of post-combustion NO_x control technologies such as selective non-catalytic reduction (SNCR) with ammonia or urea injection would be economically or technologically effective in reducing NO_x. Other emerging issues with recovery furnace operations that need to be reviewed and resolved, relative to their impact on furnace NO_x emissions, include the firing of increasingly high solids liquor, burning low volume high concentration (LVHC) gases and stripper off-gases (SOGs) in the furnace, and co-firing of fossil fuels.

Over a decade ago, NCASI carried out a detailed investigation of kraft recovery furnace NOx emissions and the role of several furnace operating and design parameters on NOx emissions (NCASI 1992). This earlier technical bulletin reviewed long- and short-term NOx emission data for several furnaces and contained a comprehensive review of literature through 1991. In 1999, NCASI published Special Report No. 99-01, which while mainly focusing on NOx emissions from boilers, also briefly reviewed more recent literature on mechanisms and causes for kraft recovery furnace NOx emissions (NCASI 1999).

This report provides a review of the literature on black liquor combustion NO_x emissions published during the past decade, including both laboratory-scale liquor burning experiments and tests in full-scale kraft recovery furnaces. It examines the impact of making changes in certain furnace operational parameters, such as load, liquor solids content and combustion air distribution, on furnace NO_x emissions. A theoretical review of the kinetics between ammonia, NO and O_2 is also provided in order to better understand the impact of temperature and residence time on NO_x formation in kraft recovery furnaces. The report summarizes the limited information available on the experiences of mills that have attempted to install SNCR systems in their furnaces in an attempt to control post-combustion NO_x emissions. Experience of mills that burn LVHC or high volume low concentration (HVLC) non-condensible gases (NCGs) and/or SOGs in their recovery furnaces is also summarized with respect to the potential impact on furnace NO_x emissions. Finally, the report summarizes the experience of U.S. mills that have installed continuous monitors for NO_x measurement on their furnaces and have had to deal with tight NO_x limits or permitting issues related to NO_x control.

2.0 BACKGROUND

Prior to reviewing the effect of various operating factors on NO_x emissions from black liquor combustion and how such factors may be varied in an attempt to minimize NO_x emissions, it is perhaps instructive to benchmark the levels of NO_x emitted by such furnaces. Table 2.1 provides estimates of range and mean for NO_x emissions from 11 NDCE (non-direct contact evaporator) and 16 DCE (direct contact evaporator) kraft recovery furnaces summarized from test reports during the first NCASI study (NCASI 1993). A 1995 NCASI survey of the industry's kraft recovery furnaces yielded average NO_x emission factors of 1.81 lb/ADTP (air-dried tons of pulp) for 16 direct contact furnaces and 2.40 lb/ADTP for 49 non-direct contact kraft recovery furnaces (NCASI 1997). Using a nominal conversion factor of about 1.6 t BLS/ADTP, these averages translate to about 1.13 lb/t BLS for DCE furnaces and 1.50 lb/t BLS for NDCE furnaces, similar to the averages of 1.20 and 1.45 lb/t BLS (black liquor solids), respectively, obtained during the earlier study.

Table 2.1 NO_x Emissions from Kraft Recovery Furnaces (NCASI 1993)

11 NDCE Kraft Recovery Furnaces		16 DCE Kraft Recovery Furnaces	
Range, lb/ton BLS	Mean, lb/ton BLS	Range, lb/ton BLS	Mean, lb/ton BLS
0.73 to 2.44	1.45	0.63 to 2.30	1.20
lb/10^6 Btu	lb/10^6 Btu	lb/10^6 Btu	lb/10^6 Btu
0.08 to 0.20	0.13	0.05 to 0.19	0.10
ppm @ 8% O_2	ppm @ 8% O_2	ppm @ 8% O_2	ppm @ 8% O_2
53 to 92	73.3	30 to 110	57.4

In NCASI Technical Bulletin No. 636 (NCASI 1992), the theoretical principles underlying NO_x formation during black liquor combustion in kraft recovery furnaces were briefly reviewed, especially with respect to the role of "fuel NO_x" and "thermal NO_x" formation mechanisms. This report also reviewed the literature for the impact of furnace operating variables (e.g., liquor nitrogen content, liquor solids content, liquor heating value, furnace excess air or oxygen, furnace load, and combustion air distribution) on NO_x formation. Full-scale NO_x emissions data for four furnaces were also examined to see whether furnace NO_x emissions correlated in any fashion with other routinely recorded furnace operating variables such as percent black liquor solids (BLS), furnace load, furnace (or stack) O_2, and concentrations of SO_2 and CO in the stack. This study concluded that "temperatures in the lower furnace under normal operating conditions are likely not high enough to result in NO_x formation by the thermal NO_x mechanism pathway. NO_x formation by the fuel NO_x mechanism pathway is thus perhaps the most dominant mechanism for black liquor combustion, just as for biomass or wood combustion." Among factors that could potentially influence furnace NO_x emissions, liquor N content was deemed the most important, with hardwood liquors exhibiting on average somewhat higher N contents than softwood liquors. Excess O_2 in the combustion zone was deemed the second most important factor in determining kraft recovery furnace NO_x emissions. The role played by black liquor solids content in determining furnace NO_x emissions was determined to be unclear, with the firing of higher solids liquors resulting in both unchanged and increased furnace NO_x emissions in different furnaces. Long-term continuous emission monitoring (CEM) NO_x emissions data showed the level of excess air used had the greatest impact on furnace NO_x emissions, with higher NO_x emissions occurring at higher levels of excess air. All other parameters such as stack

CO and SO_2 emissions, liquor solids content (limited range) and furnace load exhibited poor correlations with observed NO_x emissions.

NCASI Special Report No. 99-04 (NCASI 1999) provided a review of the literature on the fundamentals of NO_x formation and their control in wood-fired boilers and combination wood-fired boilers. It also provided a brief review of the literature on the fundamentals of NO_x formation during black liquor combustion and on potential control techniques for NO_x emissions from kraft recovery furnaces. A more detailed review of the literature on the causes for NO_x emissions from black liquor burning in kraft recovery furnaces and the potential for kraft recovery furnace in-furnace and post-combustion NO_x emissions control is provided in this report.

3.0 MECHANISMS FOR NO_X FORMATION IN KRAFT RECOVERY FURNACES: A LITERATURE REVIEW

Since it was first concluded in NCASI Technical Bulletin No. 636 (NCASI 1992) that fuel NO_x and not thermal NO_x was likely the dominant NO_x formation pathway in kraft recovery furnaces, several other researchers (Nichols, Thompson, and Empie 1993; Nichols and Lien 1993; Veverka et al. 1993; Adams, Stewart, and Jones 1993) have confirmed this finding. Current research focuses primarily on understanding how black liquor fuel nitrogen is converted to NO_x emissions. Nichols, Thompson, and Empie (1993) reviewed the chemistry and formation of NO_x and the applicability of the two principal mechanisms (i.e., thermal NO_x and fuel NO_x) for NO formation in kraft recovery furnaces. They concluded that based on theory it appears unlikely that recovery furnace temperatures are high enough to produce significant thermal NO_x. Fuel NO_x is much less temperature-dependent, and thus fuel NO_x in recovery furnaces will not be affected by increasing solids concentrations to the same degree as will thermal NO. Black liquor solids nitrogen contents measured in 13 liquors ranged from 0.05 to 0.24% (average 0.11%), and a conversion of just 20% of the liquor N to NO would have resulted in NO_x emission levels ranging from 60 to 120 ppm, which is similar to the range of reported recovery furnace NO_x emissions.

The observation that NO_x formation by the fuel NO_x pathway is much less temperature-dependent is generally true for fossil fuel burning where the bulk of the nitrogen volatilized from the fuel during the initial stages of combustion may be expected to oxidize to NO because of the extremely high combustion zone temperatures. However, as shall be seen later in Section 4.0, fuel NO_x in the context of black liquor combustion could indeed be significantly affected by temperature. The temperatures in the lower furnace could markedly affect the degree of oxidation of the nitrogen initially volatilized as ammonia to NO.

Nichols and Lien (1993) further went on to confirm that fuel NO_x was the dominant pathway in recovery furnaces by conducting a laboratory study to measure the fuel NO_x and thermal NO_x contributions in gases resulting from combusting black liquors in two laboratory furnaces. Combustion at 950°C in air (8% O_2) produced NO_x concentrations between 40 and 80 ppm. Combustion at 950°C in synthetic air containing no nitrogen (21% O_2 in Ar) produced the same result. This clearly demonstrated that all of the NO_x produced at 950°C was fuel NO_x. From the data gathered, they made the following conclusions: a) nitrogen in the black liquor is partially converted to fuel NO_x during combustion and is a major source of NO_x emissions from recovery furnaces; b) the formation of fuel NO_x is moderately sensitive to temperature in the range of 800 to 1000°C; c) higher levels of N in the black liquor are expected to yield higher levels of fuel NO_x for the same combustion conditions; d) nitrogen evolves from the liquor solids during both devolatilization and char burning; and e) fuel NO_x is formed during both in-flight and char burning.

Jones and Anderson (1993) described high-solids firing test results on a CE kraft recovery furnace in which liquor with solids content ranging from 65 to 79% was fired. NO_x emissions rose in an almost linear fashion from about 50 to 90 ppm as the percent liquor solids increased from 65 to 80%. In a follow-up paper, Jones and Stewart (1993) examined the relationship between NO_x emissions and percent liquor solids for this CE furnace. They explained that as the solids level increases, the lower furnace temperature also increases, roughly 10°F per percent solids increase, which promotes the formation of thermal NO_x. By assuming a) a 35% conversion of fuel nitrogen to NO_x, b) thermal NO_x formed equals the NO_x generated at equilibrium according to a simplified Zeldovich reaction scheme (Hanson and Salimian 1984), and c) a best fit of the observed NO_x emissions data from the CE furnace, they predicted that as the percent solids in fired liquor rose from 65 to 80%, fuel NO_x rose modestly from about 41 ppm to 43 ppm, while thermal NO_x rose more dramatically from about 15 ppm to 46 ppm. They concluded that "NO_x formation increases above 75% solids liquor firing due primarily to additional thermal NO_x formation." However, in a subsequent paper published the same year, Adams, Stewart, and Jones (1993) retracted this observation by presenting the results of a detailed computational fluid dynamic (CFD) study of thermal NO formation in recovery furnaces for two cases of black liquor solids concentration, 67% and 80%. The CFD study results showed the contribution to thermal NO_x rose from a negligible 0.09 ppm at 67% solids firing to about 8.3 ppm at 80% solids firing. They concluded that thermal NO_x was probably not a major contributor to NO_x emissions from kraft recovery furnaces.

Clement and Barna (1993) studied the effect of black liquor fuel-bound nitrogen on NO_x emissions from full-scale kraft recovery furnaces. A linear regression analysis of 17 sets of data from short duration NO_x emission tests, during which the nitrogen content in the black liquor fired had been simultaneously determined, yielded the following preliminary correlation of NO_x emissions as a function of liquor nitrogen content ($r^2 = 0.611$)

$$NO_x = 138.6\ N + 55.2 \tag{1}$$

where NO_x = ppm at 8% O_2, and N = percent nitrogen in as-fired liquor (dry solids basis).

Several tests for NO_x emissions were also conducted at one furnace where the nitrogen content of the black liquor fired was fortified with urea. The following linear fit relating the percentage of fuel-bound nitrogen in the black liquor that is emitted from the furnace after conversion to NO_x to the nitrogen in the liquor was determined ($r^2 = 0.748$)

$$NC = -40.0\,N + 21.7 \tag{2}$$

where NC = percent of nitrogen in the liquor converted to NO_x, and N = percent nitrogen in as-fired liquor (dry solids basis).

Data analysis determined that 10 to 20% of the nitrogen in the black liquor was emitted as NO_x, and that the fraction of the N converted to NO_x decreased with increasing nitrogen content.

The capture of SO_2 by alkali fume particles within a kraft recovery furnace is a well known phenomenon. Thus, similar capture mechanisms could be instrumental in partial NO removal within a furnace. Thompson and Empie (1993) examined NO_x destruction mechanisms and their impact on NO_x emissions from a kraft recovery furnace. They looked at several reactions of NO_x with fume

[Na(g), Na_2O (s), Na_2CO_3 (s,l)], similar to reactions postulated in the literature for SO_x with fume, and found these reactions to be thermodynamically feasible at temperatures in the upper furnace. They also reported the measurement of between 1,590 to 10,780 ppm nitrate (NO_3^-) in three industrial smelt samples, purportedly providing evidence of the reaction between NO_x and sodium in the recovery furnace.

Veverka et al. (1993) looked at N-containing additives such as brownstock defoamers and evaporator anti-scale agents and found these additives to have a neglible contribution to the black liquor N content. They also conducted experiments to test the efficiency of transfer of wood-nitrogen to black liquor during pulping. Three samples of chips, one of loblolly pine and two of Western hemlock were pulped using a synthetic white liquor under conditions of 30% sulfidity and 25% active alkali. One of the Western hemlock samples was doped with egg albumin to increase its nitrogen content. Egg albumin was used because of the similarity of the nitrogen compounds in albumin to those found in wood, which are primarily proteins and amino acids. Kjeldahl nitrogen was measured for the chips, the pulp, and the black liquor. Results showed that between 70 and 90% of the wood-nitrogen passes directly to the black liquor.

Aho, Hupa, and Vakkilainen (1994) studied the behavior of fuel nitrogen during black liquor pyrolysis in laboratory-scale tests on two laboratory cooked liquors: a pine liquor with about 0.12% N, and a birch liquor with about 0.17% N. They determined that most of the fuel N release occurred during pyrolysis or devolatilization of the liquor droplets and very little during drying. Further, ammonia was the main fixed N species (N_{fix}) formed (besides N_2), along with small amounts of NO. No formation of HCN was detected, HCN being the common nitrogen intermediate in fossil fuel pyrolysis. From 15 to 20% of the fuel N was released as N_{fix} compounds NH_3 and NO, with the rate of N_{fix} release increasing with temperature. The level of N_{fix} released by birch liquor was about twice that for pine liquor, both releases being large enough to account for typical recovery furnace emission levels of NO_x. The maximum amount of N_{fix} release occurred between the temperatures of 600 and 800°C.

In a second part of the study, Aho, Hupa, and Nikkanen (1994) looked at the variation between different liquors in their fuel N release behavior during laboratory tests and in their tendency to form NO_x in full-scale recovery furnaces. From the lab-scale tests, they concluded that a large portion (20 to 60%) of the fuel N is released during pyrolysis, roughly half as NH_3, the rest as N_2. The total amount of N_{fix} released was almost linearly proportional to the liquor N content. They also concluded from full-scale test data for five mills that the one main variable in determining NO_x levels in a furnace is the liquor type. Combustion of birch liquors, which had the highest N content of four different liquors burned (the other three being pine, eucalyptus, and redwood), gave the highest levels of NO_x. Heat-treated liquors appeared to result in slightly lower NO_x emissions than the burning of the same liquors without heat treatment.

Iisa et al. (1995) conducted black liquor pyrolysis experiments in a laminar entrained flow reactor. Their results confirmed that a significant amount of N was released during pyrolysis of the black liquor in a very short residence time (<0.1 sec), and up to 20% of the fuel N converted to NO. They also observed a maximum in the NO formation which indicated the importance of reactions that reduce NO in the furnace. They developed a simple model to describe both formation and destruction of NO observed in the pyrolysis experiments. The results indicated that black liquor char was important in the reduction of NO whereas fume particles were not. They suggested that improving the contact between black liquor char and NO at suitable temperatures may abate NO emissions from a kraft recovery furnace.

Forssén et al. (1997) studied the fate of char nitrogen during char oxidation by burning or gasifying single liquor droplets in the laboratory furnace at well defined conditions (700-1000°C, 1-10% O_2, 0-

30% CO_2) and by analyzing the NO formed. They concluded their findings by presenting a novel overall schematic of the key reaction routes for NO formation in black liquor combustion. This overall schematic is reproduced below in Figure 3.1. The upper part of the figure ($N_{pyrolysis}$) was based upon the work of Aho, Hupa, and Vakkilainen (1994) and Aho, Hupa, and Nikkanen (1994). The authors conclude that a) 70 to 80% of the black liquor N is released during pyrolysis or devolatilization as gaseous nitrogen species, mainly ammonia and N_2, and the oxidation of NH_3 is perhaps the main contributor to the overall NO in normal black liquor combustion, and b) the remaining liquor nitrogen (20 to 30%) will be bound in the char residue, much of which will remain as a reduced nitrogen species in the salt residue or smelt. Some of the char N may be converted to NO if the liquor droplets are burned out completely in the combustion air before reaching the char bed. They also speculated that the majority of the char N which leaves the furnace along with the smelt is probably the source of the ammonia reported to be present in the green liquor and in the exhaust gases from the smelt dissolving tank (Tarpey, Tran, and Mao 1996).

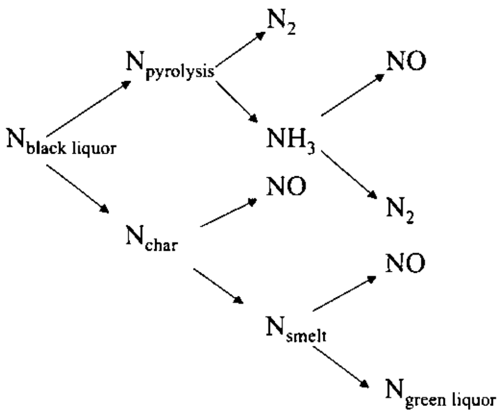


Figure 3.1 Suggested Fuel Nitrogen Pathways in Black Liquor Combustion

Tao, Blasiak, and Fakhrai (1998) used a three-dimensional computer model to simulate the flow, heat transfer, combustion, and NO_x emissions from a kraft recovery furnace. They stated that the key controlling parameter for NO_x emissions from a recovery furnace is the quaternary to tertiary air flow ratio. Using a computational fluid dynamics (CFD) package STAR-CD they presented the results for two cases: Case 1 in which the ratio of quaternary to tertiary air flow was set at 0.25, and Case 2 in which all the overfire air was injected through the tertiary air ports. The predicted average NO_x concentration at the bull-nose level rose from 48 ppm in Case 1 to 57 ppm in Case 2 as the overfire air to the quaternary air ports was shut off.

For Case 1, the authors also estimated that of the 48 ppm NO_x predicted, 29 ppm was from the fuel NO_x and 19 ppm was from the thermal NO_x mechanism pathway. Such a large fraction of thermal NO_x in kraft recovery furnaces contradicts the now well known conclusion that thermal NO_x is of little significance (NCASI 1992 Nichols, Thompson, and Empie 1993), since recovery furnace temperatures are typically well below 2800°F. These authors used the following equation to predict the maximum thermal-NO formation rate (Bowman 1992)

$$R_{t\text{-}NO}\ (\mathrm{gmol/cm^3sec}) = d[NO]/dt = 1.45 \times 10^{17} T^{-1/2} \exp[-69{,}460/T].[O_2]^{1/2}[N_2] \qquad (3)$$

where gas concentrations are in gmol/cm^3; reaction time t is in seconds; and gas temperature T is in °K.

This equation was first provided as equation 22 in a review chapter by Bowman in *Fossil Fuel Combustion – A Source Book* (Bowman 1991). In 1992, while preparing the report *Analysis of Kraft Recovery Furnace NO_x Emissions and Related Parameters* (NCASI 1992), NCASI alerted Dr. Bowman to two mathematical errors leading up to this final equation for maximum thermal NO generation rate, and Dr. Bowman agreed the errors had occurred in transmission. The corrected equation was presented as equation (vi) in the NCASI report (NCASI 1992) as follows:

$$d[NO]/dt = (1.198 \times 10^{22}/T) \times \exp(-68{,}750/T] \times [O_2]^{1/2} \times [N_2] \qquad (4)$$

where [NO] is in ppm; $[O_2]$ and $[N_2]$ are mole fractions; t is in seconds; and temperature T is in °K.

The review paper by Nichols, Thompson, and Empie (1993) on kraft recovery furnace NO_x mechanisms also used this corrected equation, but in units similar to those employed by Tao, Blasiak, and Fakhrai (1998). Their equation was as follows:

$$d[NO]/dt = 3.79 \times 10^{15} T^{-1/2} \exp[-68{,}700/T].[O_2]^{1/2}[N_2] \qquad (5)$$

where gas concentrations are in kgmol/m^3; reaction time t is in seconds; and gas temperature T is in °K.

The erroneous equation used by Tao, Blasiak, and Fakhrai (1998) likely resulted in an overprediction of NO concentrations formed by the thermal NO_x mechanism by several orders of magnitude. A similar error in the equations used for thermal NO_x generation was most likely responsible for the conclusion arrived at earlier by Jones and Stewart (1993) that thermal NO_x played a major role in black liquor combustion in a CE recovery furnace in which liquor with solids content ranging from 65 to 79% was fired (Jones and Anderson 1993). However, as previously mentioned, calculations carried out later by the same authors using a CFD model showed thermal NO_x contributions to be fairly negligible (Adams, Stewart, and Jones 1993).

Jones and Nagel (1998) compared the results of a performance test on a SAPPI-Warren kraft recovery furnace at three black liquor solids levels (71%, 76%, and 81%) on four consecutive days with previously published test results. They derived conclusions on the impact of solids concentration on several boiler operating parameters such as thermal efficiency, superheater absorption, temperatures entering the generating bank, smelt reduction efficiency, and deposit chemistry, as well as on emissions of SO_2, TRS, carryover, NO_x, and dust emissions out of the economizer. Relative to impact on NO_x emissions, as in the earlier tests with a CE recovery furnace (Arkansas Kraft) (Jones and Anderson 1993), they found once again that NO_x emissions increased with increasing percent solids content in the fired liquor, almost in identical fashion (near linear relationship). NO_x emissions increased about 2 ppm for each 1% increase in dry solids. However, in light of the now widely accepted view that thermal NO_x played a minor role in black liquor combustion NO_x formation in recovery furnaces, they make an important observation that both the Arkansas Kraft and SAPPI-Warren furnaces (both CE) were short and required relatively high excess air (~25%) in order to reach low CO levels. In contrast, the furnaces that are reported to have NO_x emissions insensitive to percent dry solids content in the liquor are generally newer, larger furnaces with significantly greater furnace volumes per pound of dry solids fired, requiring lower excess air levels (10-15%). They cite the work of Iisa et al. (1995) described earlier which stated that NO_x reduction within a furnace could occur when fume reacts with NO_x to reduce the NO_x to N_2. Hence, the high excess air used in the SAPPI-Warren and Arkansas Kraft furnaces could have suppressed bed temperatures and thus fume formation; also, the short height would reduce residence time. Both of these factors, reduced fume formation and reduced residence time, would thus seem to work against NO_x destruction mechanisms by reaction with fume. It should be noted, however, that the work of Iisa et al. (1995) showed that black liquor char was important in the reduction of NO while fume particles were not.

Malte and Nichols (1998) examined the emissions of NO_x from black liquor gasifiers integrated with combustion turbines by estimating the release of NH_3 from the gasifier based upon black liquor pyrolysis and based upon chemical equilibrium calculations. Ammonia concentrations in the gasifier product were estimated to range from 30 to 300 ppmv, depending on gasifier type. Assuming the combustor technology prevalent at that time, the emission of NO_x from the black liquor gasifier/combustion turbine engine system was indicated to range from 20 to 40 ppmv at 15% O_2 dry, which is essentially the same as for ppmv NO_x emissions from recovery furnaces when corrected to 8% O_2. However, if significant removal of NH_3 in the gas cleanup train between the gasifier and the gas turbine engine is practiced, or if combustors are engineered to efficiently convert small concentrations of NH_3 to N_2, significant NO_x emissions reductions can be realized over conventional recovery furnaces.

Forssén, Hupa, and Hellström (1999) studied the behavior of single liquor droplets or small liquor samples corresponding to 17 spent chemical liquors (14 kraft, two soda, and one sulfite) with regard to the split between volatile N and char N. They also studied the tendency of the liquors to form NO during char combustion and the total NO formation tendency of the liquors. The results showed differences among the liquors in their tendency to form NO in char combustion and black liquor droplet combustion. Total NO formation tendency test results also showed good agreement with measured recovery furnace NO emission field data.

Iisa et al. (2000) presented a detailed model for NO formation and destruction in recovery furnaces. According to this model, nitrogen is released from black liquor droplets during pyrolysis as NH_3 and N_2. The intermediate NH_3 may be oxidized to NO or reduced to N_2. The reactions may be gas phase or they may be affected by Na_2CO_3 fume particles. During char burning, nitrogen may also be released as NO or N_2, depending on whether or not O_2 can reach the char surface. In addition, the NO released in the furnace may be reduced to N_2 by several different reactions: gas-phase reactions, char-catalyzed reactions, or fume-NO reactions.

Using a laminar entrained-flow reactor to study NO formation during black liquor pyrolysis and combustion, Iisa et al. (2000) also observed a small increase in NO when the combustion was carried out in pure nitrogen vs. an argon/helium inert gas mixture. Further experiments to assess NO formation from combustion air during the char burning stage alone in both nitrogen and in an argon/helium inert mixture showed no change in NO formation, indicating that the increase in NO formation observed during black liquor combustion stemmed from pyrolysis and volatiles burning, consistent with the "prompt" NO_x mechanism (in which N_2 is attacked by hydrocarbon radicals). For perhaps the first time, these authors showed that while N in the liquor remains the main source of NO during black liquor combustion (fuel NO_x), a small amount of NO may also be formed from the nitrogen in the combustion air by the so-called "prompt" NO_x mechanism. They concluded this may have importance in particular for liquors with low nitrogen contents.

Forssén, Kilpinen, and Hupa (2000) provided a summary of recent research findings concerning the behavior of black liquor nitrogen and NO formation pathways in recovery furnaces. They demonstrated how key operating parameters can influence furnace NO emissions using four different furnace operating modes: a) base case with coarse liquor spray and no explicit air staging, b) fine liquor droplet spray and no explicit air staging, c) coarse liquor spray with efficient air staging, and d) strong air staging with very fine liquor spray. Compared to the base case, furnace NO_x emissions increase in Mode B due to increased NO from droplet char burning in flight, decrease from base case in Mode C due to benefits of air staging on oxidation of volatilized NH_3 to NO, and both decrease and increase in Mode D due to benefits of air staging and drawbacks of fine droplet char burning in flight, respectively.

The authors concluded that a major portion of recovery furnace NO is formed from oxidation of the ammonia formed during devolatilization of the liquor droplets. Kinetic modeling showed the efficiency of this oxidation is strongly dependent on the temperature and on the number of stages by which air is mixed with the devolatilized gases. Formation of NO can be minimized by allowing the oxidation to take place in several stages and at a relatively low temperature, preferably 850-900°C. In practice, this can be achieved by suitable adjustment of the air distribution and by introducing additional air feed levels in the upper furnace. A second significant source for the final NO emission is the oxidation of nitrogen remaining in the char residue after the devolatilization stage. The authors mentioned that laboratory tests with single black liquor droplets have shown that this char N is readily oxidized to NO if the droplets are allowed to burn out completely in flight. In a recovery furnace, this usually happens only with the smallest of droplets. Consequently, NO formation and release from char nitrogen can be minimized if the droplet size is large enough and/or the spraying of the liquor is carried out such that most of the droplets reach the smelt surface before being fully burned out. In such a case, the nitrogen in the char will be converted into an inorganic nitrogen compound that leaves the furnace with the smelt.

Tamminen et al. (2002a and 2002b) and Tamminen, Forssén, and Hupa (2002) conducted full-scale studies on two Finnish kraft recovery furnaces in order to shed new light on the formation mechanism of fume and gaseous emissions (NO_x) measured during dynamic changes in furnace load. They presented their results in three parts. In part 1 (Tamminen et al. 2002a), the test procedures and results of dust formation were described. An on-line dust analyzer, located in the flue gas duct just before the ESP, was used to measure the amount and composition of flue gas dust from the furnaces. Furnace load was reduced by removing liquor guns while keeping liquor spraying pressure and droplet size constant. In a special test, the liquor spraying was totally interrupted for a short time (15 to 30 minutes) in both furnaces so that the relative contribution to fume and NO_x formation from sprayed liquor droplets vs. from the char bed could be estimated. The amount of dust measured showed clear dependency on the furnace load. The amount of fume formed was 6 to 8 wt% of the BLS load during full load operation in both furnaces. The tests conducted when liquor firing was completely interrupted showed that the major fraction of dust (90 to 95%) in flue gases originated from black liquor droplets, and only 5 to 10% of the dust originated from the surface of the char bed in these two furnaces.

In part 2 (Tamminen et al. 2002b), the authors studied the results of changes in liquor firing on fume composition, especially the behavior of potassium and chloride. Both the furnaces tested burned softwood liquors, although the dry solids contents of the two liquors were different (boiler A 71 to 74%, boiler B 78 to 80%). The results showed the dust composition (Na, K, Cl) behaved similarly in both furnaces. About 6 to 9% of input sodium was released in fume, while some 11 to 15% of input potassium and 25 to 35% of input chloride were found in fume. Just as for dust, the tests with turning off liquor firing showed that the majority of Na and K in the fume originated in the liquor droplets. The SO_4 and CO_3 contents of the dust also indicated that in-flight release may be the main source of sulfur release.

In part 3 (Tamminen, Forssén, and Hupa 2002), the authors presented results of formation of gaseous emissions, especially NO_x, during rapid changes in furnace dynamics. When the liquor guns were taken off, oil burners were operating. The contribution to furnace NO_x at such times from oil burning alone was subtracted in order to arrive at the NO_x generated from the char bed. The black liquor interruption tests in both furnaces indicated that all or an absolute majority of the NO_x emissions from a recovery furnace originate in black liquor droplets during in-flight burning, and the surface reactions of the char bed play little or no role in NO formation. Also, NO_x emissions increase linearly as the amount of nitrogen in black liquor dry solids increases. The nitrogen conversion to NO_x in flue gases was about 25 to 30% of the total nitrogen in the BLS, consistent with earlier laboratory studies with single droplet combustion systems used by these same authors. Their results were also in agreement with earlier findings that the liquor nitrogen content mostly determines NO_x emission levels from recovery furnaces.

4.0 NO_X FORMATION AND KINETICS OF THE GAS PHASE NH_3-NO-O_2 SYSTEM

The previous section reviewed mechanisms presented in the literature for NO_x formation in kraft recovery furnaces. In general, this review suggested that 70 to 80% of the nitrogen present in black liquor solids is released within the furnace during pyrolysis, roughly half as NH_3 and the rest as N_2, and that the formation of NO resulted from oxidation of this volatilized NH_3. The efficiency of oxidation of this NH_3 to NO is governed by the localized temperatures and other factors such as the availability of oxygen in the zone where the NH_3 could be oxidized. The latter is, of course, related to the level of air staging practiced within the furnace. For a furnace firing black liquor with about 0.1% N on a solids basis and a heat content of about 6,200 Btu/lb BLS, a 100% conversion of the liquor N to NO would result in about 304 ppm NO at 8% O_2 (assuming an F factor of 9,000 scf/10^6 Btu for black liquor). Thus, if one-half of 70 to 80% of the liquor N is expected to volatilize as NH_3 within a furnace, the initial NH_3 concentration in such a furnace would be on the order of 106 to 122 ppm (½ x (0.3 or 0.4) x 304). Average NO_x emissions for DCE and NDCE furnaces were given in Table 2.1 to be about 57 and 73 ppm at 8% O_2, respectively. Thus, only about one-half to two-thirds of the NH_3 volatilized within a furnace is expected to oxidize to NO, the rest presumed to go to N_2.

This section reviews the generalized kinetics between NH_3, NO, and O_2 in gas mixtures to better understand why only a fraction of the NH_3 volatilized from liquor droplets in a furnace oxidizes to NO, and also to understand what happens to the remaining unoxidized ammonia. The theoretical kinetics governing the reactions of ammonia, nitric oxide, and oxygen in homogeneous mixtures have already been described in NCASI Technical Bulletin No. 802 (NCASI 2000). This report investigated the relationship between NH_3, NO, and O_2 at various temperatures and residence times to shed light on the fate of NH_3 present in stripper off-gases (SOGs) when these gases are burned in various pulp mill combustion devices. The kinetics were originally developed by Duo, Dam-Johansen, and Ostergaard (1992) using laboratory experiments. The ammonia in gas mixtures may either be oxidized to NO via reaction with O_2, or it may be reduced to N_2 via reaction with NO and O_2, or it may remain unreacted. Several investigators have described the overall reactions by two competitive (for NH_3) or successive (for NO), essentially irreversible reactions (Lyon and Benn 1978), as shown below:

$$NH_3 + NO + \tfrac{1}{4} O_2 \Rightarrow N_2 + 3/2\, H_2O \qquad (6)$$

$$NH_3 + 5/4\, O_2 \Rightarrow NO + 3/2\, H_2O \qquad (7)$$

The factors that affect the overall outcome of these reactions are: the initial concentrations of ammonia and nitric oxide, the concentration of oxygen, temperature, residence time, and the presence of other compounds such as hydrocarbons. The simplified kinetic scheme developed by Duo, Dam-Johansen, and Ostergaard (1992) assumed oxygen to always be in excess and the gas-phase reactions between NH_3, NO, and O_2 to occur in a plug flow, isothermal reactor.

The NCASI report also provided results of numerical simulations of the fate of NH_3 in gas mixtures containing an excess of O_2 at temperatures ranging from 1340 to 2960°F and for cases with initial NH_3 concentrations of 500, 100, and 20 ppm and an initial NO concentration of 100 ppm. In the current context, since typical initial NH_3 concentrations within a kraft recovery furnace are expected to be on the order of 100 ppm (as shown above), and initial NO concentrations are expected to be non-existent (0 ppm), these simulations are repeated for the case with $NH_{3i} = 100$ ppm and $NO_i = 0$ ppm.

Figures 4.1 to 4.3 present the results of these simulations on the fate of NH_3 at various temperatures and residence times. Figure 4.1 shows the formation of NO from oxidation of NH_3 at temperatures ranging from 1340 to 2960°F. It shows that for typical temperatures found in kraft recovery furnaces that range from about 1600 to 2300°F, an initial NH_3 concentration of 100 ppm results in NO concentrations ranging from about 30 to 75 ppm, or an average conversion of NH_3 to NO closer to about one-half as predicted by several researchers. The figure also provides an important observation, namely, that although NO_x formed in kraft recovery furnaces has been shown to be predominantly via the "fuel NO_x" pathway (and not the thermal NO_x pathway where temperature plays a very critical role), the fuel NO_x pathway involves oxidation of the volatilized NH_3 to NO which, however, appears to be strongly dependent on the furnace temperature profile.

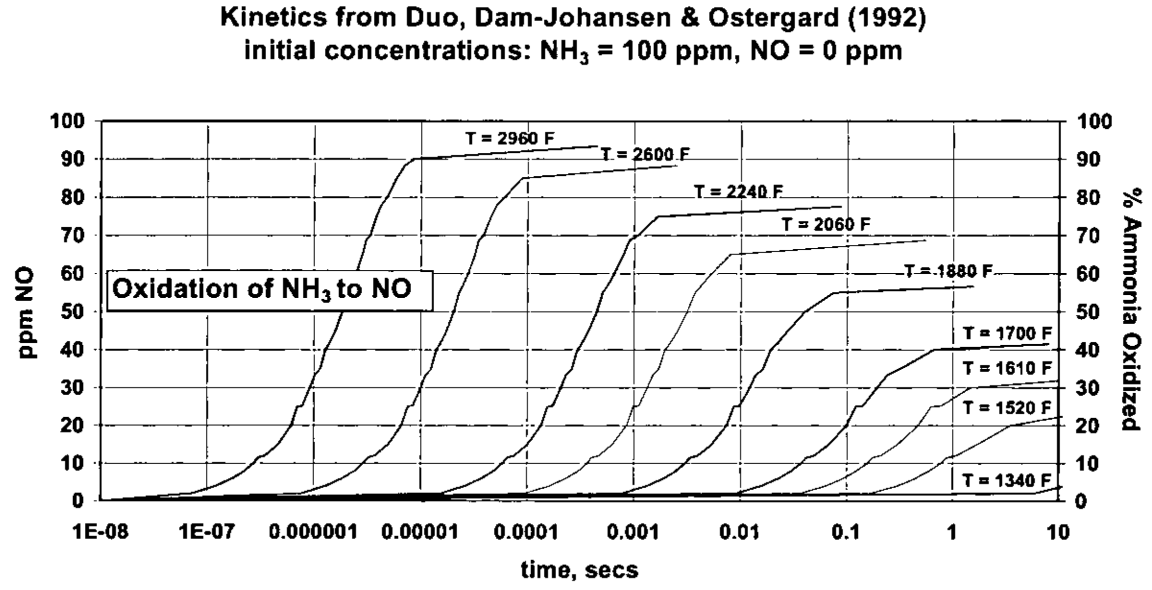

Kinetics from Duo, Dam-Johansen & Ostergard (1992)
initial concentrations: NH_3 = 100 ppm, NO = 0 ppm

Figure 4.1 Oxidation of Ammonia to NO in Ammonia-NO-O_2 Gas Mixtures

Figure 4.2 shows the fate of NH_3 in this gas mixture, again at temperatures ranging from 1340 to 2960°F. The ammonia is almost completely destroyed, either oxidized to NO or reduced to N_2, at temperatures greater than about 1700°F and in relatively short time periods (residence times less than about 1 sec). These conditions of temperature and gas residence times are consistent with those in the lower section of a kraft recovery furnace.

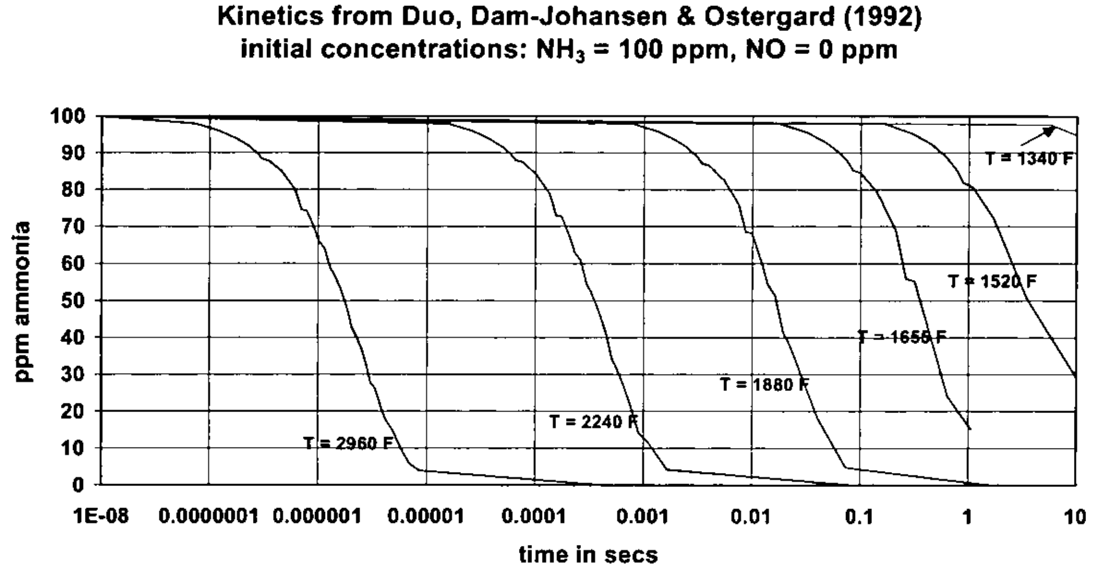
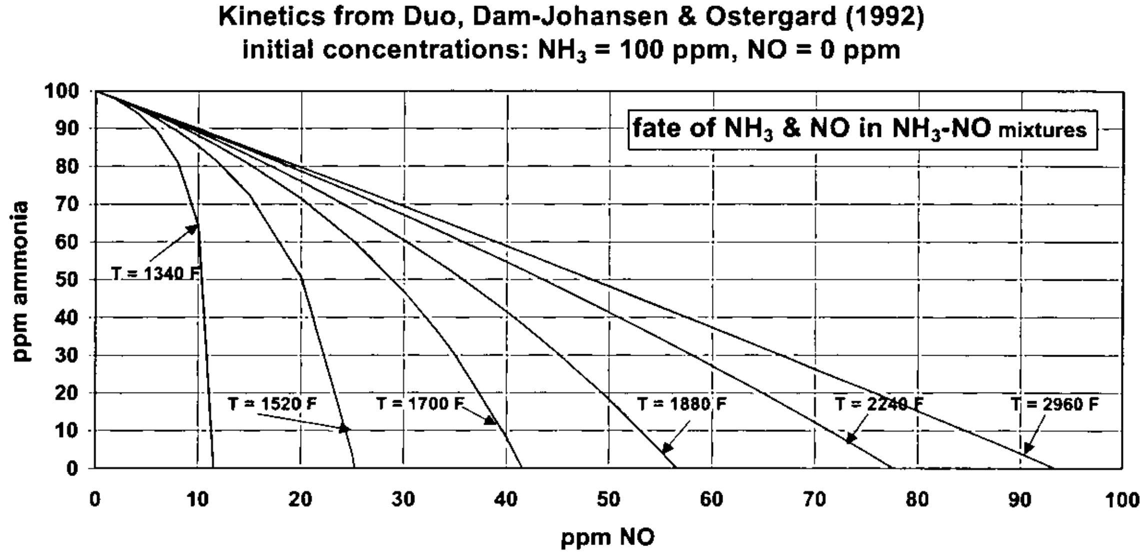

Kinetics from Duo, Dam-Johansen & Ostergard (1992)
initial concentrations: NH_3 = 100 ppm, NO = 0 ppm

Figure 4.2 Removal of Ammonia in Ammonia-NO-O_2 Gas Mixtures

Figure 4.3 combines Figures 4.1 and 4.2 and shows the simultaneous removal of NH_3 and generation of NO for temperatures ranging from 1340 to 2960°F in this gas mixture. The simplified kinetics between NH_3, NO, and O_2 shown in Figures 4.1 to 4.3 support the earlier observation that about one-half of the ammonia volatilized from the liquor droplets during pyrolysis oxidizes to NO, the rest being presumed to reduce to N_2. However, this fraction is dependent on the temperature profile existing in the region where the NH_3-to-NO oxidation takes place within the furnace.



Kinetics from Duo, Dam-Johansen & Ostergard (1992)
initial concentrations: NH_3 = 100 ppm, NO = 0 ppm

Figure 4.3 Removal of Ammonia and Generation of Nitric Oxide in NH_3-NO-O_2 Gas Mixtures

5.0 CONTROL OF NO_X EMISSIONS FROM KRAFT RECOVERY FURNACES

The highest temperatures measured in the recovery furnace, usually in the lower furnace region, typically range from about 2,100 to 2,500°F. Acoustic temperature measurements in a recovery furnace showed peak temperatures in the range of 2,191 to 2,398°F (Whitten et al. 1989). The rate of formation of thermal NO_x is significant only at temperatures exceeding about 2,800°F. Hence, factors that generally aid in reducing peak gas temperatures in the lower furnace, such as the firing of lower solids content liquors, reducing combustion air temperature and pressure, instituting changes in burner design and position, and reducing liquor feed temperature, are all expected to play a role in controlling NO_x formation only by the fuel NO_x pathway. The contributions to total NO_x by prompt NO_x, which is most prevalent in rich flames, have been shown by many investigators to be small for stationary combustors (Yuan 1999). Thus, fuel NO_x is expected to make the greatest contribution to the total NO_x emissions from kraft recovery furnaces, especially when the nitrogen content in the fuel is high.

In 1992, NCASI conducted a detailed investigation into the origins of kraft recovery furnace NO_x emissions and related parameters and concluded that black liquor N content was perhaps the most important factor affecting NO_x emissions from kraft recovery furnaces (NCASI 1992). Excess oxygen in the zone where the bulk of liquor combustion takes place was considered the second most important factor for NO_x formation. The report concluded that while very little can be done to affect the liquor nitrogen content, maximizing staged air combustion, a concept that is already integral to the operation of most existing recovery furnaces, is perhaps the best strategy for minimizing NO_x formation. The precise distribution of combustion air between primary, secondary and, if relevant, tertiary or quaternary air levels, is most likely quite furnace-specific (NCASI 1992). However, this investigation did not look into the effect of reducing lower furnace temperatures on fuel NO_x formation. The currently proposed mechanisms of liquor N volatilizing as NH_3 and the NH_3 subsequently oxidizing to NO were not developed at that time.

The 1992 NCASI report on recovery furnace NO_x emissions also contained long-term continuous emissions monitoring data for NO_x emissions from several kraft recovery furnaces. These data showed that NO_x emissions fell within a fairly narrow band for each furnace, in spite of apparent, significant day-to-day fluctuations in furnace operating behavior as indicated by the widely fluctuating emissions simultaneously measured for SO_2 and CO. This lack of significant variability in the NO_x emission pattern of a given recovery furnace was further evidence of the absence of NO_x formation by the thermal NO_x pathway and also suggested that most furnaces already utilize the concept of staged combustion quite efficiently. The differences observed between one furnace's NO_x emissions and another's is mainly a result of the differences between the N contents of the black liquors fired. Another factor that must be considered when effecting a change in operating conditions in a given kraft recovery furnace is the resulting impact this could have on emissions of other compounds such as reduced sulfur compounds, CO, SO_2, and volatile organic compounds (VOCs). These latter emissions often respond more readily when, for example, reconfiguring the distribution of the furnace combustion air.

5.1 In-Furnace Control of NO_x Formation by Staged Air Combustion

Early trials with two techniques for minimizing NO_x emissions at a full-scale recovery furnace, viz., staged combustion and firing with low excess air, were reported to have limited effectiveness (Prouty, Stuart, and Caron 1993). However, this furnace was equipped with only three stages of combustion air (normal configuration in most furnaces). NO_x emissions increased from about 0.64 lb/tBLS to about 0.95 lb/tBLS as secondary air was decreased and the percent of air fed through the tertiary ports increased from 16 to 31%. Corresponding temperatures measured using a radiometer (E^2Technology) at the liquor gun level also surprisingly increased from about 1820°F to about 2650°F. This increase in temperature was explained by an increase in the destruction of organics at the gun level. In Section 4.0, it was seen that the fraction of ammonia oxidized to NO increased with increasing temperatures. Thus, considering that the current mechanisms of black liquor fuel NO_x formation involve the volatilization of liquor N as NH_3 which then oxidizes to NO, these results appear to be explained by a temperature effect on fuel NO_x rather than on thermal NO_x. A second set of trials, which consisted of reducing the total amount of combustion air while maintaining the same proportion of air to each of the three air levels, showed NO_x emissions dropped by almost 30% as the excess O_2 in the combustion gas was reduced from 1.7 to 1.0%. However, emissions of CO increased almost fivefold from 20 to 100 ppm. TRS emissions also increased marginally from about 4 to 5 ppm.

As previously described, using both laboratory experiments and kinetic modeling studies, Forssén, Kilpinen, and Hupa (2000) examined the influence of various operating conditions on NO formation in the recovery furnace. They concluded that NO is formed from the oxidation of ammonia produced during liquor droplet devolatilization, and this oxidation is strongly dependent on the temperature and number of stages in which the air is mixed with the devolatilized gases. The authors implied that additional air feed levels in the upper furnace could aid in minimizing NO_x formation, although no full-scale test results were presented to support this conclusion.

Janka et al. (1998) compared field experiments with three NO_x reduction methods: air staging, the SNCR method, and a recently developed scrubber method. The SNCR method and scrubber technology are discussed later in Section 5.2. The authors provide limited field evidence of NO_x reduction by "air staging" in a large Scandinavian furnace. In this furnace, the final air was fed to the upper part of the furnace using an additional air register (quaternary air). As a result, the conditions in the furnace remained reducing up to the upper furnace. Furthermore, the temperature was somewhat lower in the upper furnace. The efficiency of this method is affected by a) the elevation of the fourth register (the amount of additional volume in a reducing atmosphere) and b) the portion of the air fed through the fourth register (the air ratio in the reducing zone). Quaternary air ports were installed at 12 m and 20 m above the liquor guns, and tests were performed to determine the efficiency of the quaternary air, with different air splits between the tertiary and quaternary air registers. The boiler load was also varied between 70 and 100% of its nominal maximum. The relative air distribution between the primary, secondary, and upper (tertiary and quaternary) air registers was kept constant except at the lowest loads, when the portion of upper air was decreased in order to maintain stable operating conditions. Based upon the tests results, the following relationship was developed:

$$C_{NOx} = C_0 + Bq + Al \tag{8}$$

where C_{NOx} = NO_x concentration in ppm; q = relative quaternary air feed (compared to total air feed); l = relative boiler load (compared to nominal maximum); C_0, B, and A are constants obtained from best fits (C_0 = 23.7 ppm, B = -143.8 ppm, A = 85.5 ppm).

The authors concluded that while the results were based on runs with just one furnace operated with one liquor and run according to one philosophy, nevertheless, 20% quaternary air yields nearly 30% NO_x reduction, and a load decrease from 100 to 75% leads to a 20% reduction in NO_x. The dependence of NO_x emissions on load has two plausible reasons: a) the lower furnace is cooler at low loads, and the release of nitrogen compounds from the black liquor droplets fed to the furnace is slower under cooler conditions, and also the cooler furnace tends to convert the released N compounds to N_2 rather than NO; and b) a lower load provides longer residence times in the reducing lower furnace atmosphere.

Arakawa et al. (2003) conducted laboratory and field tests to study the impact of using quaternary air for maximizing "in-furnace" NO_x reduction. In the laboratory tests, black liquor was continuously fed from the top onto a ceramic crucible within an electric tube furnace (first stage) with combustion air introduced from below (primary air) and above (secondary air) the ceramic crucible and in the upper part (tertiary air) of the vertical ceramic reaction tube. The combustion gas from the first stage furnace was then introduced to a second-stage horizontal combustion furnace where the combustion was completed by introducing quaternary air. The laboratory results showed that a) NO_x levels were reduced with decreasing air-to-fuel ratios in the first stage combustion furnace even as the furnace temperature increased, b) there existed an optimum ratio for this reduction in the first-stage combustion, and c) NO_x levels were reduced up to 30% as the fraction of total air flow directed to the quaternary air was increased (up to 16%). The field tests were conducted on a large Mitsubishi single-drum recovery furnace (1,775 t BLS/d) with primary, secondary, tertiary, and quaternary air ports. Up to 8% of total air was used as quaternary air, resulting in up to a 30% NO_x reduction from baseline (about 100 ppm). The location of the quaternary air ports was also varied to evaluate the impact of residence time of combustion gas on NO_x reduction. NO_x emissions decreased as the gas residence time up to the quaternary air port level was increased. This furnace was also equipped with urea injection for post combustion NO_x reduction, but only as a backup for peak reduction of NO_x emissions. Test results using this SNCR method are discussed in Section 5.2. Arakawa et al. (2003) also reported that a new furnace (1,900 t BLS/d) with quaternary air was designed and successfully operated. Quaternary air was injected through five nozzles on both the front and rear walls in this furnace. A 30% NO_x reduction from baseline was obtained with a 16% quaternary air ratio (baseline NO_x level unknown).

Recently, in 2003, two kraft pulp mills in the U.S. informed NCASI they had installed a fourth stage air system in a large recovery furnace at each mill. In the first case, short-term test data for NO_x emissions were developed using an NO_x continuous emissions monitor (CEM). NO_x emissions historically close to 100 ppm dropped to almost 60 ppm due to the fourth stage air, resulting in about a 40% reduction in NO_x. In the second case, NO_x emissions as measured by the mill's CEM dropped from about 1.75 lb/ton BLS (roughly 95 ppm) to about 1.38 lb/ton BLS, or about a 20% drop. It should be noted that both of these mills have only limited experience with the installation of quaternary air ports, and the long-term impacts of such a modification on emissions of other pollutants (such as SO_2, CO, and total reduced sulfur), and on other furnace operational characteristics, are unknown. For example, it is commonly understood that operating the lower furnace colder results in higher emissions of SO_2, and one way to cool the lower furnace is by shifting the primary air to higher levels of air introduction. Section 6.0 deals with responses to a few brief questions posed by NCASI to several U.S. mills that have continuous emission monitors for NO_x installed on their kraft recovery furnaces in order to gain further insights into potential factors affecting NO_x emissions. One mill indicated that they routinely shift air from primary to secondary ports, which results in a colder bed and thus lower NO_x emissions (Mill C in Appendix A). Although the SO_2 emissions rise as a result, this furnace is always operated with residual SO_2 in the stack to assist in purging chlorides. Another mill indicated that NO_x is typically controlled in its furnace by having CO "spike" occasionally (Mill E in Appendix A). CO spikes are typically brought about by decreasing the lower furnace temperatures. Another mill (Mill F in Appendix A) stated "One day we would be at the top on NO_x and the next day we would have high SO_2. We found that for us it was better to control the bed temperature on the high side. The higher bed temperature does result in higher NO_x, but we are able to control that well within our permit limit. We run basically zero on SO_2 emissions."

5.2 Post-Combustion Control of NO_x Emissions

Over a decade ago, a two-week test run using the SNCR technology (NOxOUT process with urea injection) was conducted on a Swedish furnace and the results reported by Lovblad et al. (1991). Nearly 60% NO_x reduction was reported to be observed during this short duration run. Small amounts of ammonia were detected in the economizer and ESP ashes. The ammonia concentrations in the stack gas increased from about 3 mg/m^{3}n during baseline tests to about 8 mg/m^{3}n when urea was injected (or from 4.2 ppm to 11.3 ppm). However, another source of information (NCASI File Information) which could not be confirmed, suggested the furnace may have been equipped with an ESP followed by a flue gas scrubber. Thus, ammonia slip for furnaces without scrubbers (normal situation) could potentially be higher. The authors stated that no negative effects were observed in the chemical recovery cycle during the two-week short duration test runs. NCASI has learned the furnace on which these tests were conducted was decommissioned shortly thereafter. A new furnace built at the same mill does not currently incorporate the SNCR technology for NO_x control.

As mentioned in Section 5.1, Janka et al. (1998) compared field experiments with three NO_x reduction methods: air staging, the SNCR method, and an oxidation-reduction (O-R) scrubber. The only experience they quote for the use of the SNCR method is that provided earlier by Lovblad et al. (1991). Janka et al. (1998) concluded that although the SNCR method offered an efficient solution achieving about a 60% reduction, the storing, feeding, and control systems for the SNCR agent required an investment of several million dollars. In addition, the use of urea may lead to unwanted emissions of ammonia and also increase the potential for fouling and corrosion from ammonia salts. Relative to removal of NO_x by scrubbing, the authors stated that pilot- and full-scale tests had demonstrated the effectiveness of an NO_x scrubber, although no details were provided. They claimed a 66% NO_x removal efficiency was obtained in a full-scale recovery furnace scrubber that used a ClO_2 feed. Estimated costs would depend greatly on a) whether a flue gas scrubber made from corrosion-resistant material already exists and b) whether an NCG treatment system, which produces Na_2SO_3, is available. The operating costs are dependent upon the manufacturing costs of the ClO_2 solution in the mill.

Two other kraft mills in Sweden have reportedly conducted tests with NH_3 injection (De-NO_x process) in their recovery furnaces, although details are lacking (NCASI File Information). Ammonia was injected into the furnaces at a location near the superheater entrance. While positive results were obtained in terms of NO_x reduction during the tests, the mills did not continue practicing this technology because of high capital and maintenance costs. As mentioned earlier in section 5.1, Arakawa et al. (2003) reported on the installation of the SNCR technology with urea injection at two kraft recovery furnaces in Japan. However, both these systems were designed for "emergency peak cut use" only. Information made available to NCASI indicates both of these furnaces could generally meet their respective NO_x limits (110 ppm at 4% O_2 for Mill 1 and 100 ppm for Mill 2) by either improving the combustion air distribution in the lower furnace (Mill 1) or by optimizing the use of a quaternary air system (Mill 2). Only a three-week trial was conducted to examine the performance of the SNCR system at Mill 1. Thus, long-term effects of the urea injection SNCR process are not known. Arakawa et al. (2003) report that around 30% NO_x reduction was observed in the Mill 1 trials at an NH_3 to NO molar ratio of 1.0, with corresponding ammonia slip of less than 5 ppm at the stack. They also report that a maximum NO_x reduction of about 70% could be achieved with NH_3 to NO molar ratios of 2.5 to 3.0. However, although not reported by them, this would no doubt result in much higher levels of NH_3 slip, and the impact of excess ammonia on fouling and corrosion by ammonia salts is of concern.

5.3 Summary of NO_x Emissions Control in Kraft Recovery Furnaces

Staged combustion appears to be the only viable "in-furnace" NO_x reduction technique applicable to kraft recovery furnaces. Other techniques that result in reduced temperatures in the lower furnace could perhaps also lead to lower NO_x emissions. However, the concomitant effect on other furnace emissions (such as SO_2 and CO) and furnace operational characteristics are unknown. The staged combustion principle is optimally exploited within an existing furnace by using "quaternary air ports" to perhaps obtain up to 30% reduction in prevailing NO_x emissions. However, the furnace has to be large and capable of accommodating a fourth stage of combustion air feed. Marginal NO_x reduction by installing quaternary air ports appears to be a technologically feasible alternative in full-scale furnaces at the present time. However, in each case, the impact on emissions of other compounds such as CO and TRS needs to be investigated on a longer time scale than the short-term experience currently available. In a summary assessment of control technologies for reducing nitrogen oxide emissions from non-utility point sources and major area sources, EPA stated "NO_x emissions from recovery boilers do not generally result from thermal oxidation of nitrogen in the air. Oxidation of fuel nitrogen, which appears to be the dominant mechanism for recovery boiler NO_x formation, can be sensitive to furnace temperature, however. Changes in the process, such as low excess air and air staging, may reduce NO_x emissions in some cases. SNCR may be applicable as a post-process reduction technique. It should be noted, though, that most recovery furnaces already operate with relatively low excess air with little room for significant improvement. While some gains can be achieved in the newer (larger) furnaces, the use of these techniques may also result in increases in SO_2 and CO emissions and can foul and plug the convection passes, increase acid deposition, and result in production losses" (USEPA 1998).

In principle, the efficacy of the SNCR technology in reducing NO_x emissions from a kraft recovery furnace will be lesser than, for example, in a fossil fuel-fired utility boiler. This is mainly because of the large variation in flue gas temperature at the superheater entrance, this being the most suitable location for injecting ammonia or urea into the furnace. Besides repeatedly fluctuating loads by virtue of the furnace being interconnected with pulp mill and evaporation area operations, as-fired black liquor is not as uniform as fossil fuels; its composition, heating value, and combustion behavior are affected greatly by mill operations, and these properties change considerably with time. Once an SNCR system is installed, the locations for NH_3/urea injection are fixed. Targeted NO_x reductions require a narrow optimum temperature window, and it would be difficult to obtain this window in a furnace at all times. At locations near the superheater entrance, it is not uncommon to have a flue gas temperature of 1750 ± 250°F. The gas temperature change is particularly large when there is a load change in the lower furnace, or when a nearby soot blower is activated, blowing high pressure steam to remove deposits from superheater tube surfaces. Such large temperature ranges may exceed the optimum temperature range required for effective SNCR, resulting in a low NO_x reduction efficiency.

The injected ammonia/urea also needs to have sufficient residence time in order to react with the NO_x within the optimum temperature window. In this regard, a small furnace has less residence time than a large one; thus, efficiency of NO_x removal by the SNCR system is expected to decrease with furnace size. The long-term use of NH_3 or urea in a recovery furnace has not been studied. The indirect effect of NH_3 on fireside deposit buildup on heat exchanger tube surfaces in the upper furnace needs to be evaluated. It is known that the rate of deposit accumulation increases with an increase in chloride content in the as-fired black liquor (Tran 1997). The presence of NH_3 in the gas would prevent Cl from being purged from the furnace through the stack. Chlorides accumulate in the chemical recovery system if they are not purged. The majority of the chloride is purged from the mill system through hydrogen chloride emissions from the recovery furnace stack. HCl is formed as a reaction between NaCl, sulfur oxides, and water:

$$2\,NaCl + SO_2 + \tfrac{1}{2}\,O_2 + H_2O \Rightarrow Na_2SO_4 + 2\,HCl \qquad (9)$$

If NH_3 is present in the flue gas, it will react with HCl and SO_3 when the gas temperature is cooled below 660°F to form ammonium chloride (NH_4Cl) and ammonium sulfate [$(NH_4)_2SO_4$] particulate, which will mix with the precipitator dust. In the black liquor mix tank, where the pH is high, the acidic NH_4Cl and $(NH_4)_2SO_4$ in the recycled dust will be neutralized to form alkali chloride and sulfate and gaseous ammonia according to the following reactions:

$$NH_4Cl + NaOH \Rightarrow NaCl + NH_3 + H_2O \qquad (10)$$

$$(NH_4)_2SO_4 + 2\,NaOH \Rightarrow Na_2SO_4 + 2\,NH_3 + H_2O \qquad (11)$$

As a result of the particulate formation and neutralization reactions, Cl will remain within the kraft liquor cycle and will gradually be enriched in the as-fired black liquor and deposits with time. Most of the unreacted ammonia injected during the SNCR process will not be lost through the recovery furnace stack, but rather will be lost as NH_3 emissions around the black liquor mix tank and dissolving tank. A small amount may ultimately end up in the liquor cycle, gradually increasing the nitrogen content of the liquor.

Thus, a long-term SNCR operation has the potential to increase the chloride and nitrogen content of kraft liquors, leading to higher NO_x emissions with time and aggravated fouling and plugging conditions in the furnace due to high chloride deposits. These effects are expected to be more pronounced for furnaces that burn high sulfidity liquors and/or for furnaces which operate at low bed temperatures. In such furnaces, the concentration of SO_2/SO_3 in the flue gas is high. A large amount of ammonium bisulfate (NH_4HSO_4) may form based upon the following reactions:

$$NH_3 + SO_3 + H_2O \Rightarrow NH_4HSO_4 \qquad (12)$$

$$(NH_4)_2SO_4 + SO_3 + H_2O \Rightarrow 2\,NH_4HSO_4 \qquad (13)$$

NH_4HSO_4 is acidic and melts at 297°F. Consequently, it is likely to be present as a molten phase at temperatures prevailing in the precipitator. This may lead to severe corrosion and/or massive deposit in the precipitator.

Relative to flue gas treatment by selective catalytic reduction or SCR, this option has never been demonstrated to be applicable to kraft recovery furnaces. Kravett and Hanson (1994) concluded that SCR is not technologically feasible for kraft recovery furnaces. The technological limitations include a) the potential for plugging and fouling of the SCR catalyst, b) the potential for fouling of the ESP, c) the handling of ammonia and ammonia slip, d) the potential for increased particulate emissions, e) the creation of a new hazardous waste (spent catalyst), and f) the potential for significant energy penalty.

The SCR catalyst may be sensitive to fine dust particles prevalent in kraft recovery furnace emissions. Since the optimum temperature for most catalysts is between 450 and 750°F, an SCR system will need to be installed in the economizer region of a recovery furnace. However, in this region, the flue gas is laden with a massive amount of dust particles (typically about 5 wt% of the total black liquor solids burned in the furnace), which would quickly cover the catalyst surface, making the catalyst inactive. SCR catalyst poisoning by soluble alkali metals is also a well known phenomenon.

SCR may be installed after the ESP to minimize the effect of dust on catalysts. However, in such a case, a flue gas reheating system would be required to bring the gas temperature within the optimum range. This would be very expensive and perhaps impractical.

6.0 MILL-PROVIDED INFORMATION ON FACTORS AFFECTING NO_X EMISSIONS

CEMSs for NO_x have been installed on numerous kraft recovery furnaces. NCASI contacted approximately 25 mills with NO_x CEMS on non-direct contact evaporator (NDCE) type furnaces to see if the monitoring data provided any useful insights into factors affecting NO_x emissions. Three specific questions were posed to each mill. These were:

Q#1. Have you had to deal with issues of NO_x control (quaternary air, SNCR, etc.) on this furnace in the past and if so, in what way?

Q#2. In your (or the mill's) opinion, what governs the level of NO_x emissions from this furnace the most (if you know)?

Q#3. Have you noticed that NO_x emissions change with liquor quality (type of wood pulped, percent liquor solids, etc.) or other furnace operational parameter?

Mill personnel were also asked to identify other factors that, in their opinion, could influence NO_x emissions from their furnace.

Information provided by nine of the 25 mills has been summarized in Table 6.1. Detailed responses are given in Appendix A.

Table 6.1 Summary of Mill-Provided Information on Factors Affecting Kraft Recovery Furnace NO_x Emissions

Mill Code	NO_x lb/tBLS[a]	Q #1	Q #2	Q #3	Additional Information
A	1.28	Switching black liquor nozzles reduced NO_x, CO and PM carryover. Meeting CO limit as well as NO_x limit requires careful balancing.	Tertiary air	Primary factor seems to be Btu content of BLS; higher Btu liquors results in more NO_x.	Furnace rebuilt in 2001; NO_x emissions now higher than in 2000, currently averaging 1.70 lb/ton BLS.
B	0.64	Not had to deal with NO_x limits on the furnace until recently; Furnace rebuilt in 2003.	Possibly secondary air ratio - not sure	Too early to tell.	New superheater, economizer and tri level air in May 2003.
C	1.35	80 ppm 30 d limit; also have a 24 hr avg lb/hr limit; furnace approaches NO_x limit often, especially lb/hr limit.	Routinely shift air from primary to secondary – results in colder bed which lowers NO_x – mill operates furnace with residual SO_2 to purge chlorides.	When % solids creeps up (72 to 73%), it is brought down (if NO_x is a problem); not sure if it is the % slds or the changed air flow that affects NO_x at such times.	Load burners above tertiary air ports sometimes used as "quasi" quaternary air ports – believe this helps polish NO_x emissions.
D	1.50	Went through PSD permitting during furnace rebuild – current limit is 140 ppm at 8% O_2.		80 to 90 ppm on softwood liquor, 100 to 110 ppm on hardwood liquor	NCG incinerator feeds to same stack, biasing NO_x levels upwards.
E	1.71	Recently installed a quaternary air system – learning to operate the furnace based on this change – NO_x levels are falling - anticipated to drop to 1.38 lb/ton BLS	Not sure why NO_x varies at similar firing rates – more issues with NO_x than CO - control of NO_x is to spike CO occasionally	Use primary, secondary and/or tertiary air system to control NO_x.	Tampella, high solids furnace (80 to 82% slds) – current limit is 110 ppm and 100.7 lb/hr; typically operating in the mid 90s – have to take a few gpm off at times to meet #/hr limit.

Table 6.1 Continued

Mill Code	NO_x lb/tBLS[a]	Q #1	Q #2	Q #3	Additional Information
F	1.85	Initial work done with air flows (when monitors were installed) suggested bed temperature was the biggest factor – temperature controlled by adjusting primary & secondary air flows.	Not sure about impact of liquor quality or solids		Run bed temperature hot to get essentially zero SO_2 emissions – NO_x levels could be high as a result, but within permit limit.
G	1.16	Conducted BACT-type reviews for furnace, including evaluation of SNCR – required to maintain good combustion practices/controls.	Mass emissions (lb/hr) directly proportional to boiler load; other factors appear insignificant.	Bulk of operation is with mixed liquors – thus, impact of type of liquor unknown.	Error in reporting in 2000[a]; actual emissions in 2001 and 2002 were 1.5 & 1.86 lb/ton BLS.
H	1.45	Have not had to deal with NO_x control other than "proper combustion"; typically constant level of NO_x, usually 60-65 ppm at 8% O_2.	Higher NO_x emissions with higher bed temperatures, which result from liquor with higher Btu value and fired at higher rates	Proper distribution of P & S air to control bed temperature; large liquor droplets that dry, swell & burn as they hit the bed.	NO_x can range from 45 to about 80 ppm, depending on liquor HHV, bed temperature and furnace firing rate.
I	1.89	After measuring high NO_x levels during tests in 1999, mill considered installing a quaternary air system (but did not); SNCR was never considered feasible.	Hdwd to sftwd liquor ratio; more hardwood ⇒ higher NO_x; also, NO_x related to the BLS firing rate and amount and placement of combustion air[b].	Besides the hdwd to sftwd ratio, % solids, liquor T, droplet size and liquor droplet distribution in furnace can impact NO_x.	CEM gave reliable data only after 11/17/00; 2002 emission estimates - 1.58 lb NO_x/ton BLS, more in line with industry averages.

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[a] average emission rate reported in 2000 – rate obtained from NCASI survey for calendar year 2000 SO_2 and NO_x emissions; survey yielded an average NO_x emission of 1.5 lb/ton BLS for NDCE furnaces

[b] e.g. excess air must be kept to an absolute minimum; just enough primary air needs to be applied to keep the smelt bed in control and the balance of the air should be moved to secondary and tertiary levels; primary air ports must be able to supply a strong directional jet of air toward the smelt bed; a "lazy" jet of air will not work; short term spikes occur when reducing the black liquor firing rate and not reducing air flow rates; NO_x emissions are higher at reduced firing rate

7.0 IMPACT OF BURNING SOGS IN FURNACES ON NOX EMISSIONS

In the U. S., low volume high concentration (LVHC) non-condensible gases (NCGs) from kraft pulping and recovery operations (also called concentrated NCGs or CNCGs) and stripper off-gases (SOGs) from foul condensate stripping operations are typically burned in lime kilns, boilers, or thermal oxidizers. The safety concerns associated with burning these moisture-laden gases in kraft recovery furnaces precluded most mills from burning them in such furnaces. More recently, these concerns have begun to be successfully dealt with, and the burning of CNCGs and SOGs in kraft recovery furnaces is gaining increasing acceptance. In a recent report *Recommended Good Practice Thermal Oxidation of Waste Streams in Black Liquor Recovery Boilers* (BLRBAC 2002), the Black Liquor Recovery Boiler Advisory Committee states the following:

> "The burning of dilute and/or concentrated non-condensible gases or other waste streams in the kraft black liquor recovery boiler adds complexity and potential hazards to the operation. Recognizing this, BLRBAC does not encourage the practice. However, if non-condensible gases or any waste stream are burned in the recovery boiler this *Recommended Good Practice* should be followed to assist in minimizing the potential for accidents."

Relative to introducing the CNCGs and SOGs into the recovery furnace the report states

> "A dedicated burner should be used for thermal oxidation of CNCG and SOG in the recovery boiler. The burner should be equipped with a continuous igniter and igniter flame scanner. This arrangement will provide more stable and safer firing of the gases than arrangements that depend on the heat from black liquor combustion to sustain the thermal oxidation of the NCG. This arrangement further considers that there is not a reliable means of detecting a loss of black liquor flame to shut off the NCG flows to the recovery boiler.
>
> It is possible that the dedicated burner would also be used to thermally oxidize methanol and turpentine in the recovery furnace. A future activity of the Waste Streams Subcommittee is to consider the guidelines for introducing these into the recovery furnace."

The ability of kraft recovery furnaces to capture and recover sulfur compounds present in CNCGs and SOGs, recover their heat content, and act as a buffer to temper the load fluctuations typical of these gases are described as some of the main advantages over burning them in kilns, boilers, or thermal oxidizers. However, the impact of burning SOGs in kraft recovery furnaces on the resulting NO_x emissions could potentially be of concern because SOGs can contain high levels of ammonia (up to 9 vol %) which could potentially oxidize to NO. The burning of CNCGs in recovery furnaces is not expected to have an impact on NO_x emissions since they typically contain negligible levels of ammonia.

7.1 Published Literature

Janka and Tamminen (1999) reported on measurements for NO_x from burning SOGs containing ammonia in kraft recovery furnaces. At one furnace, NO_x levels which typically ranged from about 400 to 600 mg NO_x/m^3n should have increased by 100 to 200 mg NO_x/m^3n when the SOGs were burned if all the ammonia in the SOGs were converted to NO_x. However, the measurements indicated no increase in NO_x emissions when the burner was located at the secondary air level. The authors mention that similar results had been obtained in other furnaces where the SOG burner was installed below the liquor guns. The authors explain this result by a so-called "reburning effect," caused by reactions between the nitrogen species originated from liquor and SOG. The nitrogen released from the liquor in the lower furnace is mainly as NH_3. Consequently, even though the SOG burner oxidizes most of the NH_3 in SOGs to NO, the ammonia released from the liquor reacts with this NO to yield molecular N_2 and water. At a second furnace, the SOG burner was installed above the liquor guns, and NO_x emissions increased. The authors explain that in this case, the majority of the ammonia that originated from the black liquor would have been oxidized above the liquor guns and thus unavailable to reduce NO_x resulting from oxidation of the NH_3 in the SOG burner. However, when the burner air ratio was kept low (~0.5), this increase in NO_x was mostly compensated for by the reduction effect of unburned gases from the burner. The authors concluded that feeding the SOG directly (without a burner) into the furnace or operating the burner at sub-stoichiometric air ratios nearly compensated for the additional NO_x from SOG ammonia.

In a follow-up paper, Janka et al. (2001) discussed ways of minimizing NO_x emissions during the burning of SOGs in recovery furnaces by comparing the experimental results obtained in their earlier field work (Janka and Tamminen 1999) to results from two kinds of theoretical calculations, a detailed kinetic NO_x chemistry model and a global reaction mechanism implemented to a 3-D CFD model. However, they concluded that the simplified NO_x models did not give satisfactory results in estimating NO_x emissions from kraft recovery furnaces because a) the NO_x reaction concept itself was too simplified, and b) the mixing models did not give satisfactory realistic mixing rates for the reacting compounds. In a practical furnace, all the relevant circumstances (temperature, flow, concentrations, etc.) are highly inhomogeneous, and for that reason, the detailed chemistry concept is difficult to utilize reliably.

7.2 Mill Experience

Although the BLRBAC recommendation gave guarded approval for the burning of CNCGs and SOGs in kraft recovery furnaces (BLRBAC 2002), very few mills in the U.S. burn CNCGs and even fewer burn SOGs in their furnaces. NCASI's Year 2000 NO_x/SO_x summary (NCASI 2002) indicated that seven mills burned CNCGs in the kraft recovery furnace and four burned SOGs (three of the four also burned CNCGs). These mills were contacted to learn about their experience with the NO_x emission impact of burning CNCGs and/or SOGs in the furnace. Of the seven that burned CNCGs, one mill (which also burned SOGs) is no longer in operation and one indicated that due to the Cluster Rule the CNCGs were presently being burned in the lime kiln instead. Four of the five remaining mills that burned CNCGs in the furnace did not know its impact on NO_x emissions since their furnaces were not equipped with an NO_x monitor. Of the three remaining mills that indicated they burned SOGs in the furnace, one reported that the SOGs were condensed without a rectifier and the condensate (with < 40% methanol concentration) was blended with the black liquor just before it was fired in the furnace. The NO_x emission impact of such a practice was not known since the furnace did not have an NO_x CEM. CEM NO_x data for a three-month period in 2002 for one of the remaining two kraft recovery furnaces in the U.S. that indicated they burned SOGs and CNCGs in the furnace were obtained by NCASI for analysis of the impact of burning SOGs on NO_x emissions from this furnace. At the time the data were obtained (2001), the furnace had just recently been installed (in 2001) and was firing a substantial amount of natural gas (nearly 20% of heat input). The SOGs were injected through dedicated burners with continuous igniters in accordance with the BLRBAC recommendation. The burners were located at the secondary air level. Three periods of SOG burning were identified in these data with adjacent periods when the SOGs were removed from the furnace and the NO_x emissions from the two situations compared. The data presented in Figures 7.1, 7.2, and 7.3 appear to indicate that SOG burning increased NO_x emissions from this furnace, at least during the time periods for which the data were analyzed.

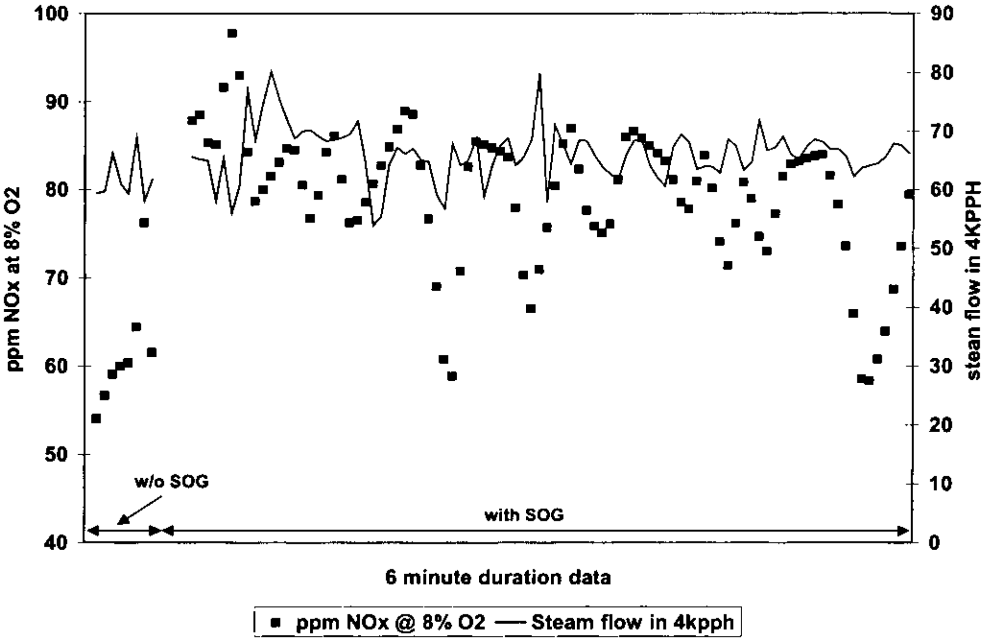

Figure 7.1 Kraft Recovery Furnace NO_x – Impact of SOG Burning – Period I
Average ppm NO_x = 61.5 (w/o SOG); 79.4 (w/SOG)

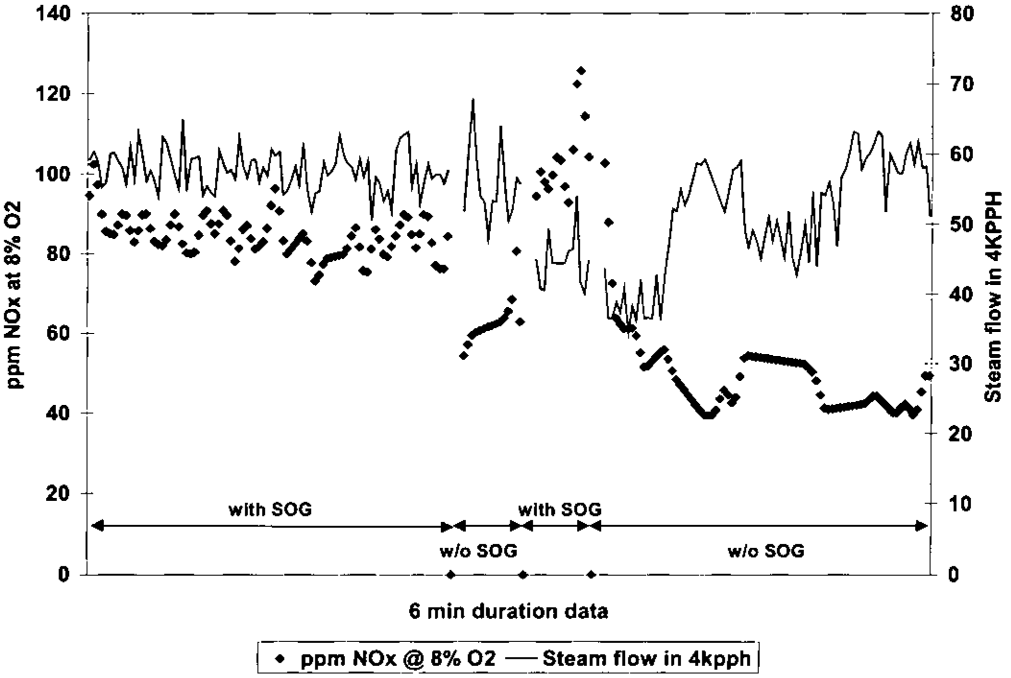

Figure 7.2 Kraft Recovery Furnace NO_x – Impact of SOG Burning – Period II
Average ppm NO_x = 84.4 (w/SOG); 62.9 (w/o SOG); 104.3 (w/SOG); 49.3 (w/o SOG)

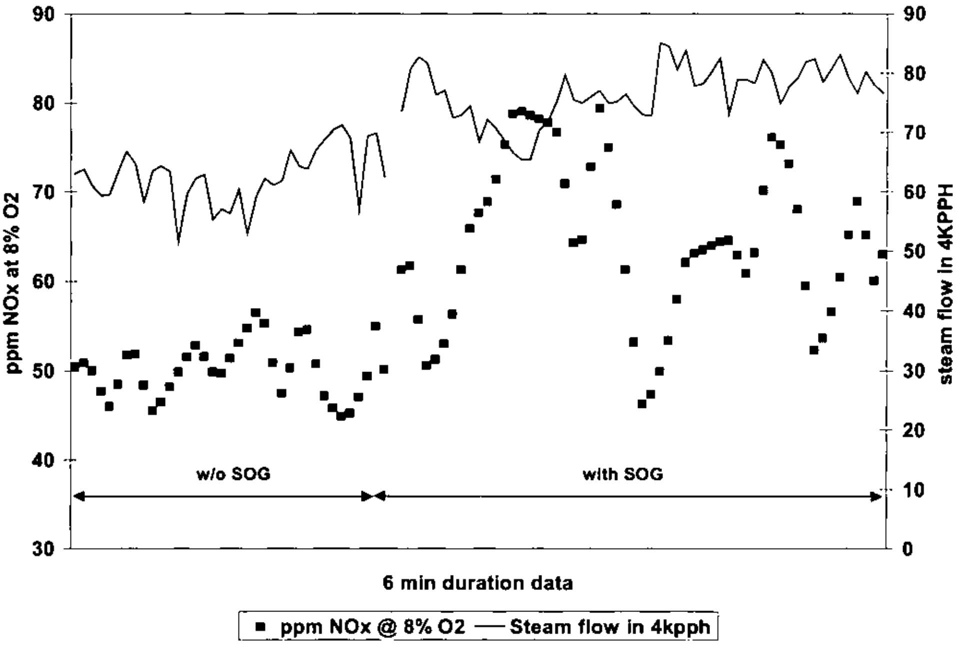

Figure 7.3 Kraft Recovery Furnace NO_x – Impact of SOG Burning – Period III
Average ppm NO_x = 50.1 (w/o SOG); 64.4 (w/SOG)

8.0 NOX EMISSIONS FROM KRAFT SMELT DISSOLVING TANKS

NCASI's first compilation of emission factors for NO_x, SO_2, and VOCs for boilers, kraft pulp mills, and bleach plants (NCASI 1993) summarized selective NO_x emission data for ten smelt dissolving tank (SDT) vents from available test reports. NO_x emissions from SDTs are not expected since no combustion takes place in such operations and the smelt-water explosion that occurs is not expected to generate any oxides of nitrogen. Nevertheless, while the bulk of the NO_x emissions recorded in the ten SDT vents were quite low (less than 12 ppm), there were two cases with rather high NO_x concentrations, ranging from ND to 95 ppm (0.23 lb NO_x/ton BLS). The NCASI report (NCASI 1993) suggested two possible reasons for these values: a) in-leakage of combustion gases from the lower portions of the kraft recovery furnace; or b) thermal NO_x formation from air oxidation in the smelt tank. Other flue gas characteristics (moisture content, CO, SO_2, and VOC) measured concurrently suggest in-leakage may not have been occurring. NO_x formation by the thermal NO_x pathway would require a substantial amount of the gases in the SDT to be subjected to a temperature exceeding 2800°F, which appears highly improbable.

An alternative explanation for the varying levels of NO_x detected in SDT vent gases may lie in the measurement methods. Ammonia is known to be present in SDT vent gases. The chemiluminescent analyzer typically used to measure NO_x in source vent gases contains a catalytic converter which reduces all the NO_2 in the sample gas to NO at elevated temperatures. The NO in the gas (including the NO from reduced NO_2) is then made to react with ozone, generating NO_2 in an excited state, and the analyzer then measures the intensity of the chemiluminescence resulting when this NO_2 returns to the ground state. The catalytic converter may also oxidize any NH_3 present to NO.

There are two types of converters, one a thermal reaction converter that decomposes NO_2 at 600-800°C and the second a chemical reaction converter that uses graphite carbon, molybdenum, tungsten, metal-impregnated carbon or some similar carbon to reduce NO_2 at 100-400°C (http:// nett21.unep .or.jp/CTT_DATA/index_amon.html). When the temperature rises to 400°C or more, ammonia is oxidized. This generates NO, which causes an interference effect. For this reason, the chemical reaction converters, which use a carbonaceous substance at 300°C or less, are predominantly used today for NO_x measurements.

Thermal decomposition of NO_2 to NO is complete at about 540°C (1100°F). Older models of NO_x analyzers used a stainless steel converter, usually a length of coiled stainless steel tubing heated to about 700°C (1300°F), providing sufficient residence time at a sample flow rate of 10 scfh for essentially complete conversion of NO_2 to NO. Gordana and Miroljub (1997) studied the influence of the stainless steel converter temperature on the conversion of NO_2 and NH_3 to NO in a Scott Model 125 chemiluminescent NO/NO_x analyzer. They found that the conversion level of NH_3 to NO ranged from 20 to 40% for gas streams with 22 to 110 ppm NH_3 between the temperatures of 550 and 700°C. They concluded that ammonia is partially oxidized to NO and must be eliminated from the air sample before measurement for NO.

A study was conducted by the University of California, Riverside to quantify sources of error in NO_x measurement methods applied to low-NO_x and new-technology emission sources (Fitz and Welch 2001). This study states "a problem with the chemiluminescent method is that the converters used to reduce NO_2 to NO can also oxidize ammonia (NH_3) to NO. The extent of ammonia conversion depends on many factors such as converter age, water content and matrix composition. With molybdenum-based converters, for example, the ammonia bias is typically a few percent of concentration, although the formation of molybdenum trioxide as the converter ages raises this conversion rate. NH_3, therefore, causes a positive interference. Evaluating this interference is particularly important when the sampled stream uses ammonia injection to reduce NO_x emissions." Working with three types of converters (stainless steel converter, molybdenum, and molybdate carbon), the authors concluded that "only the NO_x analyzer with the stainless steel converter responded significantly to ammonia and the ammonia response from the stainless steel converter increased with increasing water input."

Ammonia has been found in kraft SDT, slaker and causticizer vents and reported in NCASI Technical Bulletin No. 789 (NCASI 1999). NH_3 emissions from 14 SDT vents ranged from 0.02 to 3.80 lb/ton BLS, with a mean of 0.51 and median of 0.04 lb/ton BLS. Thus, even if only 10% of the NH_3 in a SDT vent gas with about 0.51 lb NH_3/ton BLS converts to NO due to the oxidizing effect of the high-temperature stainless steel converter in an NO_x analyzer, this would result in about 0.14 lb/ton BLS being erroneously reported as NO_x emissions from the SDT [0.50 x 0.10 x (46/17)].

9.0 SUMMARY

Compared to coal- or residual oil-fired boilers of similar capacity, NO_x emissions from kraft recovery furnaces are generally quite low, typically in the 60 to 100 ppm range. Further, these emissions, on average, are lower from DCE as compared to NDCE furnaces (1.1 vs. 1.6 lb/ton BLS). The reasons for this latter observation are unclear, beyond the fact that generally less robust combustion is expected in the older DCE furnaces. The lower NO_x emissions from kraft recovery furnaces are due to several factors which include a) low nitrogen concentrations in most "as-fired" black liquor solids (around 0.1%), b) recovery furnace NO_x formation resulting predominantly from fuel NO_x mechanisms (insufficient temperatures for thermal NO_x formation), c) low overall conversions of liquor N to NO_x (around 20 to 35%), and d) existence of sodium fumes that might participate in "in-furnace" NO_x reduction or removal.

Researchers have concluded that nearly three-fourths of the liquor N is released during pyrolysis or devolatilization, partly as NH_3 and partly as N_2, the rest remaining with the smelt product most likely as a reduced N species. The latter is believed to be the origin of the ammonia released from smelt dissolving tank vents, slaker vents and other causticizing area operations that use fresh water or clean condensates. The ammonia released from the black liquor during pyrolysis partly oxidizes to NO and partly reduces to N_2. An NCASI review of the theoretical kinetics governing the reactions between NH_3, NO, and O_2 suggests that in the presence of excess O_2, a decrease in temperature decreases the degree of oxidation of NH_3 to NO, thus implying that fuel NO_x generation during black liquor combustion is more temperature-dependent than originally thought. Researchers have also concluded that to the extent that "staged combustion" is allowed to take place during the oxidation of NH_3 to NO, the conversion of the ammonia to NO can be minimized. Limited short-term experience after installing quaternary air ports on two U.S. furnaces has shown that a 20 to 40% reduction in baseline NO_x levels is feasible using such air staging.

Most of the NO is formed by oxidation of the NH_3 volatilized during pyrolysis of the liquor droplets. Very little NO is formed by the char bed. In certain instances, where the liquor droplet dries completely before reaching the char bed, additional NO can be formed during "in-flight" char combustion of the liquor droplet. The use of liquor sprays resulting in larger droplet sizes avoids the problem of additional NO contribution from char burning. The anomalous results observed by Prouty, Stuart, and Caron (1993), viz., NO_x emissions rising as a result of increasing tertiary air while reducing secondary air, may be explained partly by the fact that such a change in combustion air feed patterns resulted in increased temperatures at the liquor gun levels, which in turn increased conversion of NH_3 to NO, and partly from potential "in-flight" char burning of liquor droplets. The observations during field tests by Jones and Anderson (1993) that NO_x emissions increased when firing liquors with increasing liquor solids contents and later similar observations by Jones and Nagel (1998) may have had less to do with thermal NO_x or an "in-furnace" capability of alkali fume to capture NO_x as suggested by these respective authors, but more to do with a possible effect on increased conversion of ammonia to NO within the furnace due to an increase in lower furnace temperatures resulting from firing higher solids liquors.

At the current time, there is no published information on the extended use of SNCR on an operating kraft recovery furnace. Short-term tests with the SNCR technology have been reported on furnaces in Japan and Sweden. There are a number of unresolved critical issues surrounding the use of urea or ammonia injection in a kraft recovery furnace for NO_x control over a long-term basis. Kraft recovery furnaces are designed to effectively recover chemicals from spent pulping liquors in a safe and reliable operation. Although steam is generated from liquor combustion, certain chemical reactions have to be accomplished inside the furnace. It is not known whether the long-term injection of NO_x-reducing chemicals into the furnace would have deleterious effects on the kraft liquor chemical cycle. Long-term tests would be needed to address this important issue. In addition, factors such as the impact of large variations in flue gas temperatures at the superheater entrance due to fluctuating load and liquor quality, limited residence times for the NO_x-NH_3 reactions available in smaller furnaces, impact on fireside deposit buildup due to reduced chloride purging from long-term NH_3/urea use and resulting impact on tube corrosion and fouling, potential for significant NH_3 slip and plume opacity problems due to NH_4Cl emissions, etc., need to be investigated thoroughly.

The use of SCR on a kraft recovery furnace has never been demonstrated, even on a short-term basis. The impact of high particulate matter concentrations in the economizer region and fine dust particles on catalyst effectiveness is a major concern. Catalyst poisoning by soluble alkali metals in the gas stream is also a concern. In the case of SCRs installed after the ESP, additional energy use for reheating the flue gas would be a major drawback.

Optimization of the staged combustion principle within a large, existing kraft recovery furnace to obtain perhaps 20 to 30% reduction in prevailing NO_x emissions might be the only technologically feasible option at the present time for NO_x reduction. However, the effect of such air staging on emissions of other pollutants, chiefly SO_2, CO, and TRS, and other furnace operational characteristics needs to be examined with longer-term data on U.S. furnaces. Ultimately, the liquor nitrogen content, which is dependent on the types of wood pulped, is the dominant factor affecting the level of NO_x emissions from black liquor combustion in a recovery furnace.

The NO_x emission impact of burning ammonia-rich stripper off-gases in kraft recovery furnaces is currently unclear. Some researchers have suggested that the impact is minimal if the SOGs are introduced into the furnace below the liquor guns, whereas introduction above the liquor guns could result in increased NO_x levels. A "reburning effect" is believed responsible in the case of the former.

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APPENDIX A

RESPONSE TO NCASI SURVEY ON FACTORS AFFECTING KRAFT RECOVERY FURNACE NO_X EMISSIONS – MILLS WITH NO_X CEMSS

From the data provided to generate the 2000 NO_x/SO_x summary for pulp and paper mills (NCASI 2002), mills that operated kraft recovery furnaces equipped with continuous emission monitoring systems (CEMSs) for NO_x were identified. A preliminary email questionnaire was sent out by NCASI to about 25 such mills (all of which had NDCE furnaces equipped with NO_x CEMSs) in order to summarize the mill environmental personnel's views and experience on what governed NO_x emissions from their furnace and what issues relative to NO_x control the mill may have had to deal with in recent times. Mill personnel were provided with the estimated year 2000 average NO_x emissions rate obtained earlier by NCASI from the mill for the furnace equipped with a NO_x CEMS. A NO_x/SO_x survey similar to the one conducted in 2000 was conducted in 1995 (NCASI 1997) and this survey yielded an average NO_x emission rate for NDCE furnaces of about 1.50 lb/ton BLS. When a significant difference between this estimate and the mill's estimate was indicated, the mill was asked to explain this if possible. The questionnaire also asked three specific questions relative to kraft recovery furnace NO_x emissions in order to gather the collective experience of U.S. mills in this regard. Nearly one-third of the mills (nine out of 25) responded, and these responses are summarized below.

Mill A - NDCE Furnace (Mid-West)

249 tons NO_x emitted in year 2000 based upon 389,000 tons of BLS fired - 1.28 lb NO_x/ton BLS

General Comments by Mill – The recovery furnace was rebuilt in 2001. The current average emission rate is 1.69 lb/ton BLS.

Answers to Specific Questions

1. Have you had to deal with issues of NO_x control (quaternary air, SNCR, etc.) on this furnace in the past and if so, in what way?

Yes. We have had to balance the NO_x & CO limits, for both of which we have CEMs. We have recently switched black liquor nozzles to the Andritz Can nozzle type that has helped with CO, NO_x and carryover.

2. In your (or the mill's) opinion, what governs the level of NO_x emissions from this furnace the most (if you know)?

Tertiary air

3. Have you noticed NO_x emissions to change with liquor quality (type of wood pulped, percent liquor solids, etc.) or other furnace operational parameters?

Yes, primarily associated with Btu content of the fuel, i.e. soap burning.

Mill B - NDCE Furnace (Northwest)

302 tons NO_x emitted in year 2000 based upon 939,000 tons of BLS fired – 0.64 lb NO_x/ton BLS.

General Comments by Mill - The current No. 3 furnace has been rebuilt - new superheater, economizer and tri-level air have just been installed. The current limit for NO_x is 115 ppm. Up until the rebuild, we were meeting it.

Answers to Specific Questions

1. Have you had to deal with issues of NO_x control (quaternary air, SNCR, etc.) on this furnace in the past and if so, in what way?

We have not had NO_x limits on the No. 3 recovery furnace until recently.

2. In your (or the mill's) opinion, what governs the level of NO_x emissions from this furnace the most (if you know)?

It is still too early to tell. My guess would be secondary air ratio, but I will check with the superintendent before I send you the official reply.

3. Have you noticed NO_x emissions to change with liquor quality (type of wood pulped, percent liquor solids, etc.) or other furnace operational parameters?

It is still too early to tell, but I will get a good idea by the end of next month.

Mill C - NDCE Furnace (Northeast)

546 tons NO_x emitted in year 2000 based upon 809,000 tons of BLS fired - 1.35 lb NO_x/ton BLS.

General Comments by Mill – The furnace has an 80 ppm 30 d avg limit; it also has a 24 hr avg lb/hr limit; the furnace NO_x approaches the lb/hr limit quite often.

Answers to Specific Questions

1. Have you had to deal with issues of NO_x control (quaternary air, SNCR, etc.) on this furnace in the past and if so, in what way?

Yes, bed temperature is controlled to control NO_x (see below) – also, load burners on this furnace situated above the tertiary air ports are sometimes used as "quasi" quaternary air ports to help polish NO_x emissions.

2. In your (or the mill's) opinion, what governs the level of NO_x emissions from this furnace the most (if you know)?

To control the lb/hr NO_x emission rate, we routinely shift air from primary to secondary ports which results in a colder bed and thus lower NO_x emission – also, this furnace is always operated with residual SO_2 in the stack to assist in purging chlorides – excess SO_2 causes problems with sticky ash.

3. Have you noticed NO_x emissions to change with liquor quality (type of wood pulped, % liquor solids, etc.) or other furnace operational parameters?

At times, when the percent solids in the liquor creeps up to about 72 to 73%, the percent solids is brought down if NO_x is a problem – do not know if percent solids or changed air flow patterns lead to the lower NO_x emissions at such times.

Mill D - NDCE Furnace (Northwest)

559 tons NO_x emitted in year 2000 based upon 785,600 tons of BLS fired - 1.50 lb NO_x/ton BLS.

General Comments by Mill – We had the benefit of going through PSD permitting for a furnace rebuild after another mill in the region had gotten stuck with an impossibly tight NO_x limit. Our limit is 140 ppm @ 8% O_2. We typically run very steadily and consistently at about 80-90 ppm when our Kamyr has been on softwood, and about 100-110 ppm after hardwood runs in the digester. Our NCG incinerator goes to the same stack and biases the value upwards, especially during boiler startup and shutdown.

Mill E - NDCE Furnace (Northeast)

323 tons NO_x emitted in year 2000 based upon 430,300 tons of BLS fired - 1.71 lb NO_x/ton BLS.

General Comments by Mill – Our 2001/2002 recovery NO_x average emission estimate was 1.73 and 1.75 lbs/ton BLS, respectively. We have a Tampella high solids furnace (80 to 82% solids). We have been operating the furnace fairly close to the edge of its steaming capacity for the last several years. We have a 30-day rolling average for NO_x in terms of ppm and lbs/hr (110 ppm & 100.7 lbs/hr). We operate typically in the mid 90s for both concentration and mass emissions and use our EMS to operate accordingly. There are times we have to take a few GPM of liquor off to reduce our daily and rolling average for NO_x.

Answers to Specific Questions

1. Have you had to deal with issues of NO_x control (quaternary air, SNCR, etc.) on this furnace in the past and if so, in what way?

We recently installed a quaternary air system (during the May 03 shutdown). We are learning to operate the furnace now based on this change. We have seen a NO_x drop and anticipate it dropping down to a 1.38 lb/ton of BLS – we are already approaching that.

2. In your (or the mill's) opinion, what governs the level of NO_x emissions from this furnace the most (if you know)?

I am not sure why NO_x increases slightly from one time to another at similar firing rates, but perhaps fuel NO_x is responsible. We typically have more emission management issues with NO_x than CO. CO spikes around typically 300 ppm limit, daily avg., but the control for NO_x is to have CO spike occasionally. The furnace operates best in that way. We use the primary/secondary/tertiary air system to accomplish this control.

Mill F - NDCE Furnace (Southeast)

338 tons NO_x emitted in year 2000 based upon 335,600 tons of BLS fired - 1.85 lb NO_x/ton BLS.

General Comments by Mill – I am not surprised that our NO_x is a little higher than the average. We also have an SO_2 monitor on our recovery furnace. When we installed the monitors several years ago, we initially had compliance issues as we were learning to operate the furnace with the new monitors. One day we would be at the top on NO_x and the next day we would have high SO_2. We found that for us it was better to control the bed temperature on the high side. The higher bed temperature does result in higher NO_x, but we are able to control that well within our permit limit. We run basically zero on SO_2 emissions.

Answers to Specific Questions

1. In your (or the mill's) opinion, what governs the level of NO_x emissions from this furnace the most (if you know)?

There was a lot of work done with air flows when we first installed the monitors, but from what we were able to tell, bed temperature was the big factor. From what I could find, we controlled the bed temperature by adjusting boiler primary and secondary air flows. There are statements that increasing the bed temperature increased NO_x and decreased SO_2, but no data.

2. Have you noticed NO_x emissions to change with liquor quality (type of wood pulped, percent liquor solids, etc.) or other furnace operational parameters?

As far as whether NO_x emissions change due to liquor quality or solids, it is hard to be sure about that. We have been receiving some outside black liquor for the past several months and have at the same time increased our liquor solids. NO_x emissions are a little lower than average for this time period, but I do not have enough information to answer that question with any level of confidence.

Mill G - NDCE Furnace (Northeast)

356.8 tons NO_x emitted in year 2000 based upon 613,700 tons of BLS fired - 1.16 lb NO_x/ton BLS.

General Comments by Mill – In 2001, we discovered an error in our calculation of NO_x lb/hr emissions from the recovery furnace, which has been corrected. Prior to 2001, we were understating our NO_x emissions. NO_x emissions reported for years 2001 and 2002 are higher than previous years. NO_x emissions for 2001 were approximately 452.3 tons, firing 616,391tons of "as-fired" black liquor solids, for an emission rate of approximately 1.5 lb/ton. In 2002, NO_x emissions were 520.2 tons, firing 558,251 tons of "as-fired" black liquor solids, for an emission rate of 1.86 lb/ton. This puts us at or above the industry average for NDCE recovery furnaces.

Answers to Specific Questions

1. Have you had to deal with issues of NO_x control (quaternary air, SNCR, etc.) on this furnace in the past and if so, in what way?

We have conducted BACT type reviews for the recovery furnace, including the evaluation of SNCR. We currently do not have any NO_x pollution control equipment on the furnace. We are required to maintain good combustion practices/controls.

2. In your (or the mill's) opinion, what governs the level of NO_x emissions from this furnace the most (if you know)?

Mass emissions of NO_x (lb/hr) are directly proportional to boiler load. NO_x emissions increase with increased liquor firing. Other operating factors seem to be insignificant. I do not have any information regarding variations in boiler combustion temperatures, combustion air, or other operating parameters. We have not had reason to further study NO_x emissions relative to boiler operating conditions or other parameters, since emissions are relatively consistent.

3. Have you noticed NO_x emissions to change with liquor quality (type of wood pulped, percent liquor solids, etc.) or other furnace operational parameters?

Due to the mill configuration, I do not have any extended data that would allow us to evaluate the effect of the different species on NO_x emissions. We do not operate for extended periods of time with only one side of the pulping operating on-line. Since there is a common weak liquor tank, there is rarely a time when only the liquor from one species would be fired.

Mill H – NDCE Furnace (Northwest)

361 tons NO_x emitted in year 2000 based upon 498,000 tons of BLS fired - 1.45 lb NO_x/ton BLS.

General Comments by Mill – In 2001, we fired 496,046 tons of BLS and emitted 308 tons of NO_x for a ratio of 1.24 lb NO_x per ton BLS. In 2002, we fired 553,694 tons BLS and emitted 393 tons NO_x for a ratio of 1.42 lb NO_x per ton BLS. This unit runs very consistent in terms of NO_x emissions, usually around 60-65 ppm, corrected to 8% oxygen. It is, of course, very dependent upon bed temperature and will run lower NO_x at low firing rates or during those times when the black liquor HHV drops due to increases in the inorganic to organic ratio. We have seen NO_x 3 hour averages as low as 45 ppm and as high as 80 ppm, corrected to 8% oxygen. Yield increases in the pulp mill due to use of pulping additives like AQ are one example of this. Another aspect of bed temperature decreasing is that sodium fuming also decreases and we see increases in SO_2 emissions.

Answers to Specific Questions

1. Have you had to deal with issues of NO_x control (quaternary air, SNCR, etc.) on this furnace in the past and if so, in what way?

We have not had to deal with NO_x control, other than "proper combustion."

2. In your (or the mill's) opinion, what governs the level of NO_x emissions from this furnace the most (if you know)?

I believe that we have higher NO_x emissions when we have higher bed temperatures, which occurs when the unit fires liquor with good fuel value and at higher rates.

3. Have you noticed NO_x emissions to change with liquor quality (type of wood pulped, percent liquor solids, etc.) or other furnace operational parameters?

Proper distribution of primary and secondary air is critical for bed shaping and bed temperature. Also influencing this is the size of the spray droplets. They need to be large enough so that they just dry, swell and start burning as they hit the bed. A good bed is also important for maximizing the reduction efficiency to reduce the sodium sulfate dead-load throughout the digesting and recovery process.

Mill I – NDCE Furnace (Southeast)

593 tons NO_x emitted in year 2000 based upon 627,000 tons of BLS fired - 1.89 lb NO_x/ton BLS.

The mill did a round of emissions testing on all emitting units in September of 1999 in preparation for Title V. The only problem we discovered was the NO_x emissions from the recovery furnace. The three run test indicated emissions were slightly above the permitted NO_x limit (mass and concentration). NO_x emissions for 2000 were estimated based on the mass limit of 139.5 lb/hr x operating hours = 593 tons. This estimate is very close to actual emissions for that year. The CEM was installed and began generating reliable data on 11/17/00.

Emission estimates for 2002 are based on CEM data - 489 ton NO_x /yr x 2000 lb/ton/619,141 ton BLS/yr = 1.58 lb NO_x/ton BLS. This is more in line with the average you quoted.

Answers to Specific Questions

1. Have you had to deal with issues of NO_x control (quaternary air, SNCR, etc.) on this furnace in the past and if so, in what way?

After discovering we had a problem, we seriously considered installing a quaternary air system. However, it was not installed. SNCR was never considered to be feasible.

2. In your (or the mill's) opinion, what governs the level of NO_x emissions from this furnace the most (if you know)?

According to the pulp mill superintendent, it is mostly controlled by the hardwood to softwood liquor ratio. More hardwood equals higher NO_x. In 2000, unbleached hardwood pulp was 76.5% and in 2002 it was 74.2% of production, with the balance being softwood. However, I would say it is related more to the black liquor firing rate and the amount and placement of combustion air, e.g., excess air must be kept to an absolute minimum, just enough primary air needs to be applied to keep the smelt bed in control, and the balance of the air should be moved to secondary and tertiary levels. Primary air ports must be able to supply a strong directional jet of air toward the smelt bed. A "lazy" jet of air will not work. Short term spikes occur when reducing the black liquor firing rate and not reducing air flow rates. We have experienced instances when NO_x emissions are higher at reduced firing rates.

3. Have you noticed NO_x emissions to change with liquor quality (type of wood pulped, percent liquor solids, etc.) or other furnace operational parameters?

Yes, it is very possible that our higher than average NO_x emissions are caused by our higher than average hardwood content in our liquor. I believe that percent solids, liquor temperature, droplet size and liquor distribution into the furnace can all impact NO_x emissions. Many factors contribute to NO_x emissions from a recovery furnace. There is not a single one that absolutely controls.

ATTACHMENT D
Response to Question N.2

APPENDIX D-1 SELECTIVE CATALYTIC REDUCTION (SCR) COSTS FOR NO. 4 RECOVERY BOILER

The following calculations have been used to estimate the costs to install and operate an SCR system for the Palatka Mill's No. 4 Recovery Boiler. The average flue gas temperature exiting the No. 4 Recovery Furnace is about 425 °F. Since an SCR system has an optimum temperature window of 700 °F, the temperature of the furnace exhaust must be raised from 425 °F to 700 °F in order for the SCR catalyst to work effectively. The actual average volumetric flow rate from the furnace is about 447,000 acfm. The energy required to heat the flue gas from 425 °F to 700 °F can be calculated as shown below:

$H = m\,C_p\,(t_2\text{-}t_1)$ Where: H = heat input, Btu/hr

m = mass flow rate of flue gas, lbs/hr

C_p = specific heat of flue gas, Btu/lb-°F

$t_2\text{-}t_1 = 700\text{-}425 = 275$ °F

Assume: From Figure 3-12 of Perry's Chemical Engineers Handbook, 5th Edition,

$C_p = 0.25$ Btu/lb-°F

Mass flow rate of flue gas can be calculated using the Ideal Gas Law equation:

$PV = nRT$ where P = pressure, atm = 1.0 (assumed)

V = volumetric flue gas flow rate, ft^3/min = 447,000

Assume that mol. wt. of flue gas ~ 29.0 lb/lb-n for any combustion device

n = moles of flue gas = mass flue gas/molecular weight flue gas = mass of flue gas (lb/hr) / 29.0 lb/lb-mole = mass/29.0

R = ideal gas law constant, atm-ft^3/lb-°R = 0.7302

T = temperature, °F + 460 = °R = 425 + 460 = 885 °R

Solving for mass rate lbs/hr: lbs/hr = 1 atm x 447,000 ft^3/min x 60 min/hr x 29 lbs/lb-m / (0.7302 atm-ft^3/lb-°R) x 885 = 1,203,570 lbs/hr

H = 1,203,570 lb/hr x 0.25 Btu/lb- °F x 275 °F = 82,745,438 Btu/hr

Assuming a cost for natural gas (average for 2004) of $6.44/MM Btu, the annual cost for heating the flue gas to 700 °F = $6.44/MM Btu x 82.745 MM Btu/hr = $532.88/hr x 8,760 hr/yr = $4,668,009/yr.

ATTACHMENT D-2 SELECTIVE CATALYTIC REDUCTION (SCR) COSTS (CON'T)

The capital, operating, and maintenance (O & M) costs of adding an SCR system to the Recovery Furnace are estimated based on the costs in EPA's Cost Control Manual, January 2002. The capital costs for retrofitting a SCR system are given as \$10,000/MM Btu/hr or higher for a large coal-fired boiler. Assuming that the cost estimates for a coal-fired boiler can be applied for a recovery furnace, the following calculations can be made to conservatively estimate the SCR costs:

Capital Costs:

1,346 MM Btu/hr heat input for No. 1 Recovery Furnace x \$10,000/MM Btu = \$13,460,000

The O & M cost for the SCR system components is equal to \$0.001/Kw-hr which equates to \$3,454,751 per year. The annual cost for heating the flue gas from 425 °F to 700 °F equals \$4,668,009. The annualized cost estimate at 7% interest over 20 years is \$8,283,990 per year as shown in Table D-2.

The average (based on 2003-2004 calendar years) NO_x emission rate for the No. 4 Recovery Boiler was 425.4 tons/yr (see Attachment B). Assuming a 90% reduction in emissions, the controlled option emissions rate will be 10% of 425.4 ton/yr or 42.5 ton/yr.

The average cost effectiveness in dollars per ton of NO_x removed is equal to:

$$\frac{\text{Control option annualized cost}}{\text{Average emissions rate} - \text{Control option emissions rate}}$$

$$\frac{\$8{,}283{,}990}{425.4 - 42.5 = 382.9 \text{ tons/yr}} = \$8{,}283{,}990/382.9 = \$21{,}635/\text{ton}$$

ATTACHMENT E

Response to Question S.1

(Reference: Page 12 of "Guidance for Reporting Sulfuric Acid (acid aerosols including mists, vapors, gas, fog, and other airborne forms of any particle size)", EPA-745-R-97-007, November 1997).

A copy of the reference for this information is included as part of this submittal. (See next pages).

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Att. E

gas are separated by special filters and determined by measurement of the acid content.

Regeneration of Spent Sulfuric Acid

The regeneration of spent sulfuric acid normally comprises two major steps, concentration to the highest feasible level and decomposition of the spent acid (1). Water is essentially the only substance evaporated (other than volatile organic impurities) in concentrating the acid to <75% H_2SO_4. Vapors evolved during the concentration of spent sulfuric acid to a more highly concentrated state (93-98% H_2SO_4) contain significant quantities of gaseous sulfuric acid (1). The formation of this gaseous sulfuric acid contributes to the manufacturing threshold of sulfuric acid aerosols for reporting under section 313 of EPCRA. Spent sulfuric acid may be concentrated in either vacuum or drum concentrators. While vacuum concentrators yield negligible emissions, those from drum concentrators contain acid mist. Exit gas is passed through scrubbers before being vented to the atmosphere. Emissions from acid drum concentrators operating at 55, 73, and 100% of capacity are reported to be 7034, 2401, and 2334 metric ton/day (12).

Acid Aerosol Emissions

Nearly all the sulfuric acid aerosols emitted from sulfuric acid manufacturing plants come from the absorber exit gases. The exit gas contains small amounts of SO_2, even smaller amounts of SO_3, and sulfuric acid vapor and mist. Even with efficient gas drying, mist formation is impossible to eliminate completely. Once formed, these aerosols are of such a fine particle size and so stable that only a small amount can be removed in the absorber. Sulfuric acid is normally combined with SO_3 in determining an emission factor because SO_3 reacts so rapidly with water vapor. The emission factor for SO_3 is calculated as 100% H_2SO_4 and added to the H_2SO_4 value.

Sulfuric acid mists are always formed when sulfur trioxide combines with water vapor at temperatures below the dew point of sulfur trioxide. The dew point is a function of gas composition and pressure and is generally around 140-170°C. Equations are available that predict the dewpoint for different concentrations of H_2O and H_2SO_4 (4). Examples are given in Section 3.1.5 in Tables 6 and 8 for coal and fuel oil combustion.

Use of Sulfuric Acid Emission Monitoring Data

Some sulfuric acid manufacturing facilities may have sulfuric acid emission monitoring data available that can be used to estimate emissions for sulfuric acid mist under the Clean Air Act New Source Performance Standards (NSPS). Sulfuric acid plants constructed or modified after August 17, 1971, are subject to a sulfuric acid mist emissions limit of 0.15 pounds of sulfuric acid per ton of 100% sulfuric acid produced (see Part 60 Subpart H of Title 40 of the Code of Federal Regulations). If such information is available, it is preferable to use such data for estimating uncontrolled emissions of sulfuric acid, rather than published emission factors since monitoring data should be the best available data. If the measured data available is for controlled emissions, then the amount of sulfuric acid generated prior to emission controls should be calculated based on the average actual

ATTACHMENT F

Response to Question M.1

Q.M. 1. On page A-39 (Section F1) of the application, potential benzene emissions were listed as "296.1 TPY". Please correct and submit the revised pages.

Answer: The Revised page is included in Attachment "F".

Please replace the page in the permit application booklet in your possession with this new page.

SEE NEXT PAGE.

I. APPLICATION INFORMATION

EMISSIONS UNIT INFORMATION
Section [1] of [1]
No. 4 Recovery Boiler

POLLUTANT DETAIL INFORMATION
Page [19] of [41]
Benzene

F1. EMISSIONS UNIT POLLUTANT DETAIL INFORMATION – POTENTIAL/ESTIMATED FUGITIVE EMISSIONS

(Optional for unregulated emissions units.)

Potential/Estimated Fugitive Emissions

Complete for each pollutant identified in Subsection E if applying for an air construction permit or concurrent processing of an air construction permit and a revised or renewal Title V permit. Complete for each emissions-limited pollutant identified in Subsection E if applying for an air operation permit.

1. Pollutant Emitted: **H017**	2. Total Percent Efficiency of Control: **0.0**
3. Potential Emissions: **2.6** lb/hour **11.5** tons/year	4. Synthetically Limited? ☐ Yes ☒ No
5. Range of Estimated Fugitive Emissions (as applicable): to tons/year	
6. Emission Factor: **0.025 lb/ton BLS** Reference: **NCASI TB No. 858, Table 14A**	7. Emissions Method Code: **5**

8. Calculation of Emissions:

(hourly) = 0.025 lb/ton BLS x 105 ton BLS/hr = 2.6 lb/hr

(annual) = 2.6 lb/hr x 8,760 hr/yr / 2,000 lb/ton = 11.5 ton/yr

9. Pollutant Potential/Estimated Fugitive Emissions Comment:

ATTACHMENT G
Response to Question M.2

Q.M. 2 We are still reviewing the modeling and will ask any questions that arise by December 21 of next week.

Answer: On December 28, 2005 GP received Cleve Holladay's December 20th letter regarding the Federal Land Manager's (FLM) comments on the modeling for haze in Class 1 areas. Based on those comments and other input from DEP and the FLM office; GP's consultant, Golder Associates, conducted revised modeling studies. A response to the December 20th letter and the results of the revised modeling are attached in Attachment "G".

Please replace **Table C-38** in the permit application booklet in your possession with this new page.

Responses to Comments from the U.S. Fish and Wildlife Service
(PDF Memorandum, attached, dated 12/19/2005
from Meredith Bond, FWS, to Cleve Holladay and Bruce Mitchell, FDEP)
RE: GP Palatka – Modification to No.4 Recovery Boiler Application

1. All PSD Class I air modeling files will be provided to the FWS.

2. The regional haze analysis submitted with the application was performed Method 2 (i.e., MVISBK = 2) and RHMAX = 95 percent. The results for that analysis were provided in Table C-38 and indicated that 11 days were predicted to exceed the Federal Land Manager's recommended visibility criteria of 5 percent. Per the FWS' request, a second air modeling analysis was performed using Method 2 and the FLAG RHMAX default value of 98 percent. The results for that analysis are included in a revised Table C-38 (attached) and indicate that 23 days are predicted to exceed the visibility criteria. The additional CALPOST air modeling files for this analysis are being provided to Cleve Holladay of the FDEP.

3. Because the application analysis was performed using Method 2 with RHMAX = 95 percent, an additional analysis was performed using Method 6. Monthly relative humidity factors (f(RH)) were obtained from the document "Guidance for Estimating Natural Visibility Conditions Under the Regional Haze Rule (EPA, September, 2003)", In this document, monthly f(RH) values are presented for each mandatory federal Class I area in Tables A-2 and A-3. The f(RH) values in Table A-3 were based on centroid locations for each area, while the f(RH) values presented in Table A-2 are based on IMPROVE locations. Presently, it is not certain which set of f(RH) values will be used for the BART modeling. For this reason, the higher f(RH) factors in Table A-3 were used to provide conservative estimates of visibility impairment.

   The results for the Method 6 analysis are included in revised Table C-38 and indicate that no days are predicted to exceed the 5 percent visibility impairment criteria at any of the PSD Class I areas. The additional CALPOST air modeling files for the Method 6 analysis are being provided to the FDEP.

TABLE C-38 (revised 1/5/06)

MAXIMUM 24-HOUR AVERAGE VISIBILITY IMPAIRMENT PREDICTED FOR THE PROPOSED GP AND CONTEMPORANEOUS PROJECTS EMISSIONS AT THE OKEFENOKEE, WOLF ISLAND AND CHASSAHOWITZKA NWA PSD CLASS I AREAS

Area	Visibility Impairment (%) [a]			Visibility Impairment Criteria (%)
	1990	1992	1996	
BACKGROUND EXTINCTION CALCULATIONS: METHOD 6 WITH MONTHLY F(RH) FACTORS				
Okefenokee NWA	4.67	4.70	4.02	5.0
Wolf Island NWA	2.77	2.68	1.78	5.0
Chassahowitzka NWA	3.36	4.35	4.87	5.0
BACKGROUND EXTINCTION CALCULATIONS: METHOD 2 WITH RHMAX = 95 PERCENT				
Okefenokee NWA	5.89 (1)	5.92 (4)	8.21 (2)	5.0
Wolf Island NWA	3.22	5.41 (1)	3.08	5.0
Chassahowitzka NWA	4.01	7.92 (2)	8.49 (1)	5.0
BACKGROUND EXTINCTION CALCULATIONS: METHOD 2 WITH RHMAX = 98 PERCENT				
Okefenokee NWA	7.23 (2)	8.84 (5)	12.41 (10)	5.0
Wolf Island NWA	5.04 (1)	8.81 (1)	4.07	5.0
Chassahowitzka NWA	5.65 (1)	10.80 (2)	12.28 (1)	5.0

[a] Concentrations are highest predicted using CALPUFF model and CALMET wind fields for N. FL-S. GA, 1990, 1992 and 1996.

Background extinctions calculated using FLAG Document (December 2000) and stated method

NWA = National Wilderness Area

( ) = Number of Predicted Days > 5 %

ATTACHMENT H

Revisions to PSD Application Pages

Attached are revised pages: Introduction – P. 3-3, A-35, A-36, B-40, B-43, and Table 4-3 of the PSD Permit Application. They were revised to correct an oversight regarding the RB TRS limits.

GP is voluntarily agreeing to an annual average TRS limit of 5ppm at 8% O_2 for TRS. The current 12-hour average limit of 11.2 ppm was not intended to be changed.

Please replace these pages in the permit application booklet in your possession with these new pages.

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vendor quotations for this work, including suggested scope. As such, the exact scope of this work is not available at this time. The current cost estimate is less than $2 million.

Crystallizer

A third project involves a modification to the black liquor evaporation system (No. 4 Evaporator Set). This change will increase the solids concentration of the black liquor to the Recovery Boiler from 65 percent solids to approximately 75 percent solids. When the new system is operational, the liquor from the concentrator will pass through a Crystallizer vessel to raise the temperature of the liquor. The liquor will then enter a storage/flash tank at lower pressure where the moisture will "flash off". The "flash" vapors will then be routed to the existing evaporator system and collected as part of the existing non-condensible gas (NCG) collection system. The purpose of the project is to increase Boiler efficiency by reducing the amount of water entering the Boiler with the liquor solids. By reducing the amount of water vaporization being performed by the Boiler, less supplemental fuel will be required to process the same amount of black liquor solids (BLS). Furthermore, the increase in solids will improve the efficiency of the Boiler for steam production per pound of BLS, thus reducing the amount of steam produced from oil firing in the other boilers. The estimated cost of this work is in the range of $5 to $6 million.

Concentrators

Finally, the Mill is considering the removal of some internal baffles and resizing some downcomer piping in the existing concentrators. The unit currently has scaling problems, leading to frequent "boil outs". The proposed changes will improve liquor circulation and increase velocity through the tubes, which should reduce scaling and fouling. This will increase the time between "boil outs". In addition, an external heat exchanger will be added to the existing concentrators to preheat the liquor with steam prior to entry into the concentrators. This will allow for increased evaporation surface, providing for a capability that more closely matches the capacity of the Recovery Boiler.

3.3 Requested Emission Limits

The Mill is not proposing to increase the throughput that has been established in past permitting actions for the Recovery Boiler. In fact, in order to avoid PSD review for sulfur dioxide, the Mill is requesting an annual limit of 12 parts per million by volume (ppmv) (at 8% oxygen). This is a significant reduction over the current limit that is based on 37.5 ppmv. The Mill is also proposing to reduce the maximum sulfur content of fuel oil from 2.35% to 2.1%. As discussed further in Section 5.2, there is a possibility that the addition of the crystallizer will lead to an increase in the maximum hourly throughput level for the Recovery Boiler, causing the unit to become subject to federal New Source Performance Standards. As such, an annual average of 5 ppmv (at 8% oxygen) is proposed for total reduced sulfur (TRS) compounds.

For sulfur dioxide, a request was submitted to the FDEP in April 2004 to modify the short-term (3-hour and 24-hour average) emission rates for the Recovery Boiler. As explained in that submittal, the Mill's Recovery Boiler has been subject to a number of permitting activities in the past and the history can be traced back to permits that were issued in the early- and mid-1980s. Varying sulfur dioxide emission limits have been imposed over time.

Air Operating Permit AO54-54072, dated June 1982, specified allowable sulfur dioxide emission rates for the Recovery Boiler of 277.5 lbs/hour and 1,189 tpy. Subsequently, Air Operating Permit AO54-131787, dated May 1987, specified allowable sulfur dioxide emission limits of

F1. EMISSIONS UNIT POLLUTANT DETAIL INFORMATION – POTENTIAL/ESTIMATED FUGITIVE EMISSIONS

(Optional for unregulated emissions units.)

Potential/Estimated Fugitive Emissions

Complete for each pollutant identified in Subsection E if applying for an air construction permit or concurrent processing of an air construction permit and a revised or renewal Title V permit. Complete for each emissions-limited pollutant identified in Subsection E if applying for an air operation permit.

1. Pollutant Emitted: **TRS**	2. Total Percent Efficiency of Control: **0.0**
3. Potential Emissions: **7.8 lb/hr and 34.2 tons/year**	4. Synthetically Limited? ☐ Yes ☒ No
5. Range of Estimated Fugitive Emissions (as applicable): to tons/year	
6. Emission Factor: **5.0 ppmv @ 8 % oxygen annual average** Reference: **Voluntary limit to avoid PSD**	7. Emissions Method Code: **5**

10. Calculation of Emissions: **See Attachment B of PSD Application**

TRS (annual average) = (5 $ft^3/10^6 ft^3$) x 294,000 dscf/min x 2,116.8 lb/ft^2 x 1 lb-n-°R/1,545.6 ft-lb x 1/528 °R x 34 lb-lb-n x 60 min/hr = 7.8 lb/hr

TRS (annual) = 7.8 lb/hr x 8,760 hr/yr / 2,000 lb/ton = 34.2 ton/yr

9. Pollutant Potential/Estimated Fugitive Emissions Comment:

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F2. EMISSIONS UNIT POLLUTANT DETAIL INFORMATION - ALLOWABLE EMISSIONS

Complete if the pollutant identified in Subsection F1 is or would be subject to a numerical emissions limitation.

Allowable Emissions Allowable Emissions 1 of 1

1. Basis for Allowable Emissions Code: **RULE**	2. Future Effective Date of Allowable Emissions:
3. Allowable Emissions and Units: **7.8 lb/hr (annual avg.) and 34.2 tons/year**	4. Equivalent Allowable Emissions: lb/hour
5. Method of Compliance: **Stack testing must be performed once per fiscal year**	
6. Allowable Emissions Comment (Description of Operating Method): **Based on taking voluntary restriction of TRS emissions to avoid PSD**	

Allowable Emissions Allowable Emissions _____ of _____

1. Basis for Allowable Emissions Code:	2. Future Effective Date of Allowable Emissions:
3. Allowable Emissions and Units:	4. Equivalent Allowable Emissions: lb/hour tons/year
5. Method of Compliance:	
6. Allowable Emissions Comment (Description of Operating Method):	

Allowable Emissions Allowable Emissions _____ of _____

1. Basis for Allowable Emissions Code:	2. Future Effective Date of Allowable Emissions:
3. Allowable Emissions and Units:	4. Equivalent Allowable Emissions: lb/hour tons/year
5. Method of Compliance:	
6. Allowable Emissions Comment (Description of Operating Method):	

No. 4 Recovery Boiler- Emissions Unit ID # 018 - Rated capacity of 210,000 lb/hr of BLS or 5.04 MM lb BLS/day. Maximum dry standard cubic feet per minute (dscfm) at 2.8% oxygen = 210,000 dscfm = 294,000 dscfm @ 8% oxygen. Maximum CaO = 38,889 lb/hr or 170,334 ton CaO/yr.

	Current Title V Limits 1070005-029-AV		**Proposed Title V Limits**	
Pollutant	**lb/hr**	**TPY**	**lb/hr**	**TPY**
PM	75.6	331.1	75.6	331.1
PM_{10}	-	-	56.7	248.3
VOC	31.5	138.0		
SO_2	109.9	481.4	439.4 (3-hr) 109.9 (24-hr) 35.1 (annual)	153.9
SAM	3.2	14.2	3.6	15.9
CO	1,025.4 (3-hr) 512.7 (24-hr)	2,245.6 (24-hr)	1,025.4 (3-hr) 512.7 (24-hr)	2,245.6 (24-hr)
TRS	10.9 (12-mo) 17.5 (12-hr)	47.7 (12-mo)	7.8 (annual average)	34.2
Lead	-	-	0.0033	0.014
Be	$6x10^{-4}$	$2.8x10^{-3}$	$6x10^{-4}$	$2.8x10^{-3}$

Oxygen correction from 210,000 dscfm at 2.8% oxygen to 8% oxygen is shown in the calculations below.

$$\text{Correction Factor} = \text{Actual}\left[\frac{(21-8)}{(21-2.8)}\right] = \text{Actual}(1.4)$$

$$\text{Corrected Oxygen} = 210{,}000\,\text{dscfm}(1.4) = 294{,}000\,\text{dscfm at 8\% oxygen}$$

Particulate Matter Emissions - 75.6 lb/hr and 331.1 TPY - Current Title V Permit Limits (Section III Subsection E.4).

$$\text{PM(hourly)} = \left(\frac{0.03\text{ grains}}{\text{dscf}}\right)\left(\frac{294{,}000\text{ dscf}}{\text{min}}\right)\left(\frac{1\text{ lb}}{7{,}000\text{ grains}}\right)\left(\frac{60\text{ min}}{\text{hr}}\right) = 75.6\frac{\text{lb}}{\text{hr}}$$

$$\text{PM(annual)} = \left(75.6\frac{\text{lb}}{\text{hr}}\right)\left(\frac{8{,}760\text{ hr}}{\text{yr}}\right)\left(\frac{\text{ton}}{2{,}000\text{ lb}}\right) = 331.1\text{TPY}$$

Proposed PM_{10} limits of 56.7 lb/hr and 248.3 TPY based on PM_{10} as 75% of PM from AP-42, Table 10.2-3 (9/90).

$$PM_{10}\text{(hourly)} = 0.75\left(75.6\frac{\text{lb}}{\text{hr}}\right) = 56.7\frac{\text{lb}}{\text{hr}}$$

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Hourly average:

$$\mathrm{TRS\,(hourly\,)} =$$

$$\left(\frac{5\,\mathrm{ft}^3}{10^6\,\mathrm{ft}^3}(\mathrm{ppmvd})\right)\left(\frac{294{,}000\ \mathrm{dscf}}{\mathrm{min}}\right)\left(\frac{2{,}116.8\,\mathrm{lb}}{\mathrm{ft}^2}\right)\left(\frac{\mathrm{lb-mole-R}}{1{,}545.6\,\mathrm{ft-lb_f}}\right)\left(\frac{1}{528\ \mathrm{R}}\right)\left(\frac{34\ \mathrm{lb}}{\mathrm{lb-mole}}\right)\left(\frac{60\,\mathrm{min}}{\mathrm{hr}}\right)=7.8\frac{\mathrm{lb}}{\mathrm{hr}}$$

Annual average:

$$\mathrm{TRS(annual)}=\left(7.8\frac{\mathrm{lb}}{\mathrm{hr}}\right)\left(\frac{8{,}760\,\mathrm{hr}}{\mathrm{yr}}\right)\left(\frac{\mathrm{ton}}{2{,}000\,\mathrm{lb}}\right)=34.2\,\mathrm{TPY}$$

Lead Emissions – Proposed Title V permit limits of 0.0033 lb/hr and 0.014 TPY based on emission factor for BLS firing of 31.3 lb/MM ton BLS from NCASI TB # 701, Tables 12 C & 12 D.

$$\mathrm{Pb(hourly)}=\left(31.3\frac{\mathrm{lb}}{\mathrm{MMton}}\right)\left(\frac{\mathrm{MMton}}{10^6\,\mathrm{ton}}\right)\left(\frac{210{,}000\,\mathrm{lb\,BLS}}{\mathrm{hr}}\right)\left(\frac{\mathrm{ton}}{2{,}000\,\mathrm{lb}}\right)=0.0033\frac{\mathrm{lb}}{\mathrm{hr}}$$

$$\mathrm{Pb(annual)}=\left(0.0033\frac{\mathrm{lb}}{\mathrm{hr}}\right)\left(\frac{8{,}760\,\mathrm{hr}}{\mathrm{yr}}\right)\left(\frac{\mathrm{ton}}{2{,}000\,\mathrm{lb}}\right)=0.014\,\mathrm{TPY}$$

Beryllium Emissions - 0.5 lb/10^{12} Btu or $6.4\mathrm{x}10^{-4}$ lb/hr and $2.8\mathrm{x}10^{-3}$ TPY - Current Title V Permit Limits (Section III Subsection E.12).

$$\mathrm{Be(hourly)}=\left(\frac{0.5\,\mathrm{lb}}{10^{12}\,\mathrm{Btu}}\right)\left(\frac{210{,}000\,\mathrm{lb\,BLS}}{\mathrm{hr}}\right)\left(\frac{6{,}084\,\mathrm{Btu}}{\mathrm{lb}}\right)=6.4\mathrm{x}10^{-4}\,\frac{\mathrm{lb}}{\mathrm{hr}}$$

$$\mathrm{Be(annual)}=\left(6.4\mathrm{x}10^{-4}\,\frac{\mathrm{lb}}{\mathrm{hr}}\right)\left(\frac{8{,}760\,\mathrm{hr}}{\mathrm{yr}}\right)\left(\frac{\mathrm{ton}}{2{,}000\,\mathrm{lb}}\right)=2.8\mathrm{x}10^{-3}\,\mathrm{TPY}$$

Mercury Emissions: Emission factor of $1.8\mathrm{x}10^{-7}$ lb/ton BLS from NCASI TB 858, Table 14B.

$$\mathrm{Hg(hourly)}=1.8\mathrm{x}10^{-7}\,\frac{\mathrm{lb}}{\mathrm{ton}}\left(\frac{210{,}000\,\mathrm{lb}}{\mathrm{hr}}\right)\left(\frac{\mathrm{ton}}{2{,}000\,\mathrm{lb}}\right)=1.9\mathrm{x}10^{-5}\,\frac{\mathrm{lb}}{\mathrm{hr}}$$

$$\mathrm{Hg(annual)}=\left(1.9\mathrm{x}10^{-5}\,\frac{\mathrm{lb}}{\mathrm{hr}}\right)\left(\frac{8{,}760\,\mathrm{hr}}{\mathrm{yr}}\right)\left(\frac{\mathrm{ton}}{2{,}000\,\mathrm{lb}}\right)=8.3\mathrm{x}10^{-5}\,\mathrm{TPY}$$

Other HAP emission estimates are contained in Attachment A of this application.

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TABLE 4-3
POTENTIAL EMISSION RATES-LB/HR

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EMISSIONS UNIT ID	EMISSIONS UNIT DESCRIPTION	POTENTIAL POLLUTANT EMISSION RATES-LB/HR								
		PM	PM$_{10}$	SO$_2$	NO$_x$	CO	VOCs	Pb	TRS	SAM
018	# 4 Recovery Boiler-Annual	75.6	56.7	35.1	126.4	512.7	31.5	3.30E-03	7.8	3.6
018	# 4 Recovery Boiler-24-hr	---	---	219.7	---	---	---	---	---	---
018	# 4 Recovery Boiler-3-hr	---	---	439.4	---	1,025.4	---	---	---	---
019	# 4 Smelt Dissolving Tanks	12.6	11.3	7.7	15.9	2.6	26.3	2.90E-03	3.4	0
017	# 4 Lime Kiln	29.70	29.70	34.50	97.50	16.3	9.4	5.60E-02	3.7	1.5
	Lime (White Liquor) Slakers	0.60	0.60	---	---	---	0.8	---	0.875	---
	White Liquor Storage Tanks	---	---	---	---	---	0.1	---	---	---
	White Liquor Clarifiers (East and West)	---	---	---	---	---	0.1	---	---	---
	Lime Mud Washer Tanks	---	---	---	---	---	1.7	---	0.04	---
	Lime Mud Splitter Box Tank	---	---	---	---	---	1.7	---	0.04	---
	Causticizer Tanks (Nos. 1A, 1B, 2, 3)	---	---	---	---	---	0.016	---	0.4	---
	North & South Precipitator Tanks	---	---	---	---	---	0.3	---	0.4	---
	Salt Cake Mix Tank	---	---	---	---	---	0.3	---	0.4	---
	Green Liquor Clarifier	---	---	---	---	---	1.3	---	0.012	---
	Green Liquor Tanks (North, South, & 280,000 gal Units)	---	---	---	---	---	1.3	---	0.0016	---
	TOTALS (worst-case operation)	**119**	**98**	**736**	**240**	**1,557**	**75**	**6.22E-02**	**17**	**5**

Note: all boilers and the lime kiln will be limited to a sulfur content of 2.1% (wt.) when burning No. 6 fuel oil

ATTACHMENT I

Revisions to PSD Application – Attachment D

This section of the PSD application was updated to reflect GP's response to RAI Question C.1.

Please replace these pages in the permit application booklet in your possession with these new pages.

ATTACHED TO HARD COPY ONLY

ATTACHMENT D
BEST AVAILABLE CONTROL TECHNOLOGY (BACT) REVIEW FOR NO. 4 RECOVERY BOILER

PROJECT DESCRIPTION

The Recovery Boiler is at the heart of the Kraft chemical recovery process. It fulfills the following essential functions:

(1) Evaporates residual moisture from the black liquor solids.
(2) Burns the organic constituents.
(3) Supplies heat for steam generation.
(4) Reduces oxidized sulfur compounds to sulfide.
(5) Recovers inorganic chemicals in molten form.
(6) Conditions the products of combustion to minimize chemical carryover.

Heavy black liquor from the pulping process is sprayed directly into the Boiler. The liquor droplets dry and partially paralyze before falling onto the char bed. Incomplete combustion in the porous char bed causes carbon and carbon monoxide to act as reducing agents, thus converting sulfate and thiosulfate to sulfide. The heat is sufficient to melt the sodium salts, which filter through the char bed to the floor of the Boiler. The "smelt" then flows by gravity through water-cooled spouts to the No. 4 Smelt Dissolving Tanks.

The No. 4 Recovery Boiler (Emission Unit 018) was originally constructed in the mid-1970s. The current, permitted capacity of the Boiler is 210,000 pounds per hour (lbs/hour) of black liquor solids (BLS) and 5.04 million pounds (MM lbs) of BLS per day. The Boiler is also permitted to combust natural gas, No. 6 fuel oil with a sulfur content not to exceed 2.35% by weight and on-spec used oil as start-up fuels. As part of this permitting action, the Mill is requesting that the allowable sulfur content of the fuel oil be lowered from the current 2.35% to 2.1%. The Recovery Boiler is equipped with an electrostatic precipitator (ESP) for particulate matter control.

This PSD application is being submitted to implement several projects for the No. 4 Recovery Boiler and associated evaporators. First, the Mill plans to replace a large percentage of the tubes in the Recovery Boiler. This includes tubes in the superheater, economizer, and generating banks of the Boiler. This major tube work is estimated to commence in May 2006 and conclude in 2008. The total cost of this work is estimated to be in the range of $24 million.

Although still in the preliminary engineering phase, the Mill is also considering replacement of, or changes to, the combustion air system for the Boiler. The objective of this part of the project is to lower peak furnace exit gas temperature and velocity into the superheater in an effort to reduce the potential for corrosion and pluggage of the superheater in the future. The new air system is also expected to reduce carry over and fouling in the Boiler convection banks. Through the staging of air, it is anticipated that emissions of some pollutants (*e.g.*, total reduced sulfur (TRS) compounds and carbon monoxide (CO)) will be more consistently controlled and/or reduced. At the same time, by reducing TRS and CO and increasing boiler efficiency, nitrogen oxide (NO_x) emissions are expected to increase slightly. The Mill is in the process of receiving vendor quotations for this work, including suggested scope. As such, the exact scope of this work is not available at this time.

A third project involves a modification to the black liquor evaporation system (No. 4 Evaporator Set). This change would increase the solids concentration of the black liquor to the Recovery Boiler from 65 percent solids to approximately 75 percent solids. When the new system is operational, the liquor from the concentrator will pass through a Crystallizer vessel to raise the temperature of the liquor. The liquor will then enter a storage/flash tank at lower pressure where the moisture will "flash off". The "flash" vapors will then be routed to the existing evaporator system and collected as part of the existing non-condensible gas (NCG) collection system. The purpose of the project is to increase Boiler efficiency by reducing the amount of water entering the Boiler with the liquor solids. By reducing the amount of water vaporization being performed by the Boiler, less supplemental fuel will be required to process the same amount of BLS. Furthermore, the increase in solids will improve the efficiency of the Boiler for steam production per pound of BLS, thus reducing the amount of steam produced from oil in the other boilers.

Finally, the Mill is considering the removal of some internal baffles and resizing some downcomer piping in the existing concentrators. The unit currently has scaling problems, leading to frequent "boil outs". The proposed changes will improve liquor circulation and increase velocity through the tubes, which should reduce scaling and fouling. This will increase the time between "boil outs". In addition, an external heat exchanger will be added to the existing concentrators to preheat the liquor with steam prior to entry into the concentrators. This will allow for increased evaporation surface, providing for a capability that more closely matches the capacity of the Recovery Boiler.

APPLICABILITY

The following pollutants are subject to PSD review as shown in Table 5-1 of the main text of this application package and are therefore subject to the BACT review for this project:

- Particulate matter (PM), including particulate matter less than 10 micrometers in aerodynamic diameter (PM_{10})
- Nitrogen oxides (NO_x)
- Carbon monoxide (CO)
- Sulfuric acid mist (SAM)
- Ozone (based on a significant increase in volatile organic compounds (VOCs))

Each of these pollutants is addressed in turn in the following section.

BACT ANALYSIS FOR THE NO. 4 RECOVERY BOILER

Particulate Matter (PM/PM_{10})

Step 1a-Identification of Control Technologies-Typical Technologies in Use in the United States

Emission control equipment that may be selected to control particulate matter emissions from recovery boilers includes ESPs, baghouses, and high efficiency wet scrubbers. Each of these types of control equipment, described more fully below, is capable of significantly reducing particulate matter emissions.

Electrostatic Precipitators(ESPs)

ESPs use electrical energy to charge and collect particles with very high removal efficiencies. The classification of ESPs may be as wet or dry systems and/or single-stage or two-stage systems. Dry systems are the predominant type used in industrial applications. Wet systems are gaining in use today since they eliminate the possibility of fires, which can sometimes occur in dry systems.

The principal components of an ESP include the housing, discharge and collection electrodes, power source, cleaning mechanism, and solids handling systems. The housing is gas-tight, weatherproof, and grounded for safety. Dust particles entering the housing are charged by ions from the discharge electrodes. Dust is collected on the collection electrodes. The collection electrodes are also referred to as plates. The system voltage and the distance between the discharge and collection electrodes govern the electric field strength and the amount of charge on the particles. ESPs are most effective at collecting coarse, larger particles above the 1 micron (μm) size. Particles smaller than this are difficult to remove because they can inhibit the generation of the charging corona in the inlet field, thereby reducing collection efficiency. Rappers and liquid washdown serve as the cleaning mechanisms for dry and wet ESPs, respectively. Dust hoppers collect the precipitated particles from a dry ESP. Wet sluicing is used to remove wet particles. Dry dust is removed continuously or periodically from the hopper and stored in a container until final disposition. Wet solids must be continuously removed and sent to a holding pond or to a wastewater treatment system.

ESPs are the predominant type of particulate matter control device used on recovery boilers in the U.S. today. ESPs can achieve particulate matter removal efficiencies as high as 99.9%. Some of their advantages over other types of particulate matter control devices are listed below:

- Low power requirements and associated electrical energy costs
- Capable of removing very small particles, even those not removable by other treatment technologies
- Dry dust collection often used, which may be useful for byproduct recovery
- Temperature changes very small with dry systems
- Small pressure drops (in the range of 1-2 inches water column (w.c.) pressure)
- Low maintenance due to few moving parts
- System tolerant of high temperatures
- System capacity can easily be expanded with the addition of partitions

Some of the disadvantages of using an ESP over other particulate matter control devices are listed below:

- High capital cost
- Space requirements large
- Gaseous wastes are not controlled
- Safety is a concern due to high voltage
- Wet systems produce sludges that may require dewatering before disposal

Baghouses

A baghouse, or fabric filter, is one of the most efficient devices for removing particulate matter. Baghouses have the capability of maintaining collection efficiencies above 99% for particles down to 0.3 μm in size. The basic components of a fabric filter unit consist of woven or felted fabric, usually in the form of bags that are suspended in a housing structure (baghouse), an induced draft or forced draft fan, a blow-back or reverse air fan for cleaning the bags, or a pulse-jet fan or a mechanical shaking mechanism for cleaning the bags. The emission stream is distributed by means of specially designed entry and exit plenum chambers, providing equal gas flow through the filtration medium. The particle collection mechanism for fabric filters includes inertial impaction, Brownian diffusion, gravity settling, and electrostatic attraction. The particles are collected in dry form on a cake of dust supported by the fabric or on the fabric itself. The process occurs with a relatively low-pressure drop requirement (usually within the range of 2-6 inches w.c.). Periodically, most of the cake dust is removed for disposal. Cake dust is removed by the use of a mechanical shaking or "rapping" system, with the use of reverse air, or with the use of a pulse-jet of air. Dust is collected in a hopper at the bottom of the baghouse and is removed through a valve and dumped into a storage container. Usually, the dust is disposed of at an industrial landfill.

Some of the advantages of using baghouses over other types of particulate matter control devices are listed below:

- High collection efficiency down to small particle sizes (99% control down to 0.3 μm)
- Relatively low capital cost
- Dry dust collection may be useful for byproduct recovery

- Low pressure drop

Some of the disadvantages of using baghouses compared to other types of particulate matter control devices are listed below:

- High maintenance costs due to the presence of many moving parts
- Maximum operating temperatures of about 550 degrees Fahrenheit (°F)
- Gaseous wastes are not controlled
- Space requirements large
- Cannot operate with saturated (wet) gas streams

Wet Scrubbers

Wet scrubbers are collection devices that trap wet particles in order to remove them from a gas stream. They utilize inertial impaction and/or Brownian diffusion as the particle collection mechanism. Wet scrubbers generally use water as the cleaning liquid. Water usage and wastewater disposal requirements are important factors in the evaluation of a scrubber alternative. Types of scrubbers include spray scrubbers, cyclone scrubbers, packed-bed scrubbers, plate scrubbers, and venturi scrubbers. The most common particulate matter removal scrubber is the venturi scrubber because of its simplicity (*e.g.*, no moving parts) and high collection efficiency. In this type of scrubber, a gas stream is passed through a venturi section, before which, a low-pressure liquid (usually water) is added to the throat. The liquid is atomized by the turbulence in the throat and begins to collect particles impacting the liquid as a result of differing velocities for the gas stream and atomized droplets. A separator is used to remove the particles or liquid from the gas stream. The most important design consideration is the pressure drop across the venturi. Generally, the higher the pressure drop, the higher the removal efficiency.

Advantages of using a wet scrubber compared to other particulate matter control devices are listed below:

- Adsorbs gas phase emissions, as well as particulate matter as long as proper scrubbing media is used
- Compact size
- Efficient through wide loading range
- Insensitive to moisture content
- Venturi – no moving parts

Disadvantages of using a wet scrubber compared to other particulate matter control devices are listed below:

- Inefficient with high-temperature gases
- Requires high power input to create large pressure drop and high collection efficiency
- Waste scrubber liquid handling required

Step 1b-Identification of Control Technologies-Review of RACT/BACT/LAER Clearinghouse (RBLC)

Searches of the RBLC were conducted to identify control technologies for the control of PM/PM_{10} emissions from recovery boilers.

The specific categories searched are listed below:

- External Combustion-Other-11.999
- Kraft Pulp Mills-30.002

- Pulp & Paper Production Other than Kraft-30.004
- Other Wood Products Industry Sources-30.999

The results of the search are listed in Table D-1a. As can be seen in Table D-1a, all of the entries, with just a few exceptions, indicate the use of ESPs to control PM/PM_{10} emissions from recovery boilers.

Step 1c-Identification of Control Technologies-Review of Technologies in Use at Georgia-Pacific Corporation Facilities

Georgia-Pacific operates numerous pulp and paper mills in the United States, with many of these employing Kraft recovery boilers. All of the recovery boilers at these facilities use ESPs to control PM/PM_{10} emissions. One facility, located in Camas, Washington (listed in the RBLC as James River Corporation, but now owned by GP), has two recovery boilers equipped with both ESPs and wet scrubbers. The wet scrubbers were installed to recover heat and make hot process water for use in the Mill. The wet scrubbers were not installed to control particulate matter emissions, which is accomplished by the ESPs.

Step 2-Technical Feasibility Analysis-Eliminate Technically Infeasible Options

While baghouses can achieve high levels of particulate matter control, the exhaust gas streams from the recovery boilers have relatively high moisture contents (25 to 30%) that cause the particulate matter to be hydroscopic in nature. These characteristics will cause the bag filters in the baghouse to "blind-up" and plug. These problems indicate that a baghouse is not an appropriate technology for recovery boilers. Therefore, baghouses are not considered further as part of this BACT analysis.

ESPs and wet scrubbers are feasible technologies for reducing particulate matter emissions from recovery boilers.

Step 3-Ranking the Technically Feasible Control Alternatives to Establish a Control Hierarchy

ESPs are most effective in controlling fine particulate matter emissions from recovery boilers. As discussed above, ESPs are the predominant particulate matter control device listed in EPA's RBLC for Kraft recovery boilers. ESPs control particulate matter from recovery boilers at levels that exceed 99+%.

Wet scrubbers will not have any problem with the high moisture content in recovery boiler exhaust gas streams. However, the particulate matter control efficiency for a scrubber will be approximately 98% versus a control efficiency of 99+% attained by an ESP.

Step 4-Control Effectiveness Evaluation

This step of the BACT analysis is only necessary when the top control technology from Step 3 is not selected as BACT. Since the Mill already uses an ESP to collect particulate matter emissions, which is the top control technology, a control effectiveness evaluation is not necessary.

Nearly all recovery boilers in the United States employ ESPs as the particulate matter control technology. This is validated by the RBLC listings in Table D-1a, which indicate the predominant use of ESPs as BACT.

Since an ESP is the most effective technology for removing particulate matter from the No. 4 Recovery Boiler, and since the unit already utilizes an ESP to control particulate matter emissions, no additional controls are proposed.

Step 5-Select BACT

The NSPS (40 CFR 60, Subpart BB) for particulate matter from Kraft recovery boilers is 0.044 grain per dry standard cubic foot (grain/dscf) at 8% oxygen (O_2). The Maximum Achievable Control Technology (MACT) rule, promulgated in January 2001, also specifies a particulate matter emission limit of 0.044 grain/dscf at 8% oxygen. However, the No. 4 Recovery Boiler already has a Title V Permit limit of 0.03 grain/dscf at 8% O_2, which is more stringent than either the NSPS or MACT standards.

The limits listed for other recovery boilers in Table D-1a range from 0.021 grain/dscf to 0.15 grain/dscf. Therefore, BACT for the No. 4 Recovery Boiler should be the use of an ESP with a limit set equal to the current Prevention of Significant Deterioration (PSD) and Title V Permit limit of 0.03 grain/dscf at 8% O_2. This is at the low end of the limits contained in Table D-1a.

Nitrogen Oxides (NO_x)

Step 1a-Identification of Control Technologies-Typical Technologies in Use in the United States

NO_x is formed during combustion processes by the thermal oxidation of nitrogen in the combustion air (*i.e.*, thermal NO_x) and the oxidation of nitrogen in the fuel (*i.e.*, fuel-bound NO_x). In a recovery boiler, black liquor nitrogen content, or fuel NO_x, is the most important factor affecting NO_x formation. Fuel properties, temperature, and the stoichiometric conditions present during combustion are additional variables that affect NO_x formation. Excess oxygen in the zone where the bulk of black liquor combustion takes place is also an important factor for NO_x formation.

There are two main approaches that can be used to reduce nitrogen oxides emissions from boilers. The first is combustion modification and the second is post-combustion controls.

Combustion Modification Techniques

There are a number of combustion modification techniques available for reducing NO_x emissions. These include:

- Staged combustion using overfire air in burners (20-50% reduction)
- Addition of levels of staged air combustion (percent reduction dependent upon the number of existing levels and number of levels added)
- Low-NO_x burners (20-50% reduction)
- Flue gas recirculation (15-20% reduction)
- Low excess air (0-30% reduction)

The combustion modification techniques listed above all reduce NO_x by minimizing its formation in the combustion chamber of the Boiler by using less oxygen than is stoichiometrically required for complete combustion of the fuel. This lowers the temperature in the combustion chamber, thus reducing the amount of thermal NO_x that is formed. To complete the combustion process, excess air is added later in the combustion process. Each of these modifications requires additional equipment, such as new fans or burners, as well as controls, to operate properly.

Post-Combustion Controls

The technologies for post-combustion control include:

- Selective non-catalytic reduction (SNCR) (25-70% reduction)
- Selective catalytic reduction (SCR) (up to 90% reduction)

Post-combustion technologies work by several different methods as explained in the following sections.

SNCR systems work by injecting ammonia or urea into the combustion chamber of the boiler, thereby converting NO_x to elemental nitrogen, carbon dioxide, and water vapor. The reaction must take place between specific temperature ranges or more NO_x will be formed instead of less NO_x. The optimum temperature range for a system that uses ammonia is 1,600 to 2,000 °F and for a system that uses urea, the optimum temperature range is 1,650 to 2,100 °F. Increasing the residence time available for mass transfer and chemical reactions generally increases NO_x removal. Variations in boiler steam load or flue gas temperature make the design and operation of an SNCR system more difficult.

SCR systems work by passing the contaminated exhaust gas stream through a catalyst bed and injecting aqueous or anhydrous ammonia just in front of the catalyst bed. This system also converts NO_x to elemental nitrogen, carbon dioxide, and water vapor, similar to an SNCR system. This reaction also has an optimum temperature range to work efficiently. The optimum temperature range for the catalyst to work efficiently is 550 to 1,000 °F (best temperature window is between 700 and 750 °F). Since the optimum temperature window for the SCR process is less than that for the SNCR process, reaction of NO_x is designed to take place downstream of the combustion chamber, as opposed to inside the combustion chamber as is the case for an SNCR system. Most designs install the reaction chamber downstream of the economizer, but upstream of the air pre-heater, where the metal oxide-based catalyst works best. Reheating of the flue gas is required for reaction chambers located downstream of the air pre-heater.

Most of the operating parameters discussed above for an SNCR system are valid for an SCR system as well, except for catalyst management. Catalysts can lose their activity over time for a number of reasons as discussed below:

> *Poisoning*-certain fuel constituents released during the combustion process can act as catalyst poisons. Catalyst poisons include calcium and magnesium oxides, potassium, sodium, arsenic, chlorine, fluorine, and lead. These constituents deactivate the catalyst by diffusing into active pore sites and occupying them irreversibly.
>
> *Thermal Sintering*-high flue gas temperatures cause sintering (*i.e.*, a permanent loss of catalyst activity due to a change in pore structure of the catalyst). Thermal sintering can occur at temperatures as low as 450 °F. The amount of sintering that occurs is dependent upon the composition and structure of the catalyst.
>
> *Binding/Plugging/Fouling*-ammonia salts, fly ash, and other particulate matter in the flue gas can cause binding, plugging, and/or fouling of the catalyst. The particulate matter deposits in the active pore sites of the catalyst, which results in a decrease in the number of sites available for NO_x reduction and an increase in flue gas pressure loss across the catalyst bed.
>
> *Erosion and Aging*-catalysts with hardened leading edges or increased structural strength are less susceptible to erosion. Increasing catalyst strength by hardening reduces the number of active pore sites. Catalyst aging occurs over a period of time, which changes the physical and chemical properties of the catalyst.

There are methods available to minimize the possibility of the catalyst from deactivating over time (because of the reasons listed above). These include the use of soot blowers to dislodge deposits of particulate matter on the catalyst, turning vanes and rectifier grids to remove some of the particulate matter from the flue gas before it reaches the catalyst, and replacing the catalyst on a routine basis before it becomes poisoned or deactivated. Catalyst replacement can be a significant part of the operating costs for an SCR system

Similar to an SNCR system, an SCR system requires an aqueous or anhydrous ammonia or urea storage, feed, and control system, to operate properly.

Step 1b-Identification of Control Technologies-Review of RACT/BACT/LAER Clearinghouse

Searches of the RBLC were conducted to identify control technologies for the control of NO_x emissions from recovery boilers.

The specific categories searched are listed below:

- External Combustion-Other-11.999
- Kraft Pulp Mills-30.002
- Pulp & Paper Production Other than Kraft-30.004
- Other Wood Products Industry Sources-30.999

The results of the searches are listed in Table D-1b and are summarized below:

- No controls feasible
- Boiler design and good combustion practices
- Low-NO_x burner for natural gas combustion
- Proper combustion techniques and operating practices
- Staged combustion
- Boiler design and operation
- Combustion control
- Addition of 4th level of air

Step 1c-Identification of Control Technologies-Review of Technologies in Use at Georgia-Pacific Corporation Facilities

Some of the recovery boilers located at GP mills utilize four levels of staged combustion control, some of the boilers utilize three levels of staged combustion control, and some of the boilers utilize only two levels of staged combustion control. None of the boilers use any type of add-on control, such as SCR, to control NO_x emissions. Average NO_x emission rates during normal operations from GP's recovery boilers range from 70-150 parts per million by volume (ppmv).

Step 2-Technical Feasibility Analysis-Eliminate Technically Infeasible Options

Combustion modification techniques as a control option are technically feasible for recovery boilers and most recovery boilers employ one type of combustion technique or another. Probably the most widely used combustion technique is staged combustion where there are two to four different stages of combustion air supplied to the boiler at successively higher points in the body of the boiler.

Relative to flue gas treatment as a control option, SNCR is not considered technically feasible for Kraft recovery boilers based on the fact that a recovery boiler is a complete, chemical reaction system and any disruption of the delicate chemistry could potentially damage the boiler, impact the quality of the product, or otherwise unacceptably affect the system. The injection of a urea solution or ammonia gas would have a detrimental effect upon the chemistry inside of a recovery boiler. For these reasons, SNCR is considered technically infeasible for a recovery boiler and it is not considered further in this BACT analysis.

It is questionable if an SCR system is technically feasible for the treatment of flue gases generated by a recovery boiler. The toxic metals present in the flue gas exhaust, even after passing through the ESP, are of sufficient quantity to build-up on the surface of the catalyst bed and poison the catalyst within relatively short periods of time. Additionally, the flue gas exhaust would need to be heated from a temperature of about 425

°F to at least 700 °F in order for the catalyst to work efficiently. This will add significant cost for a duct burner combusting natural gas, as well as add NO_x emissions back into the environment.

To verify that an SCR system is not economically feasible for a recovery boiler, a cost estimate for the installation and operation of an SCR system is presented under Step 4 of this section (see below), even though an SCR system is probably not suitable because of the likelihood of catalyst poisoning.

Low-NO_x burners represent a method for lowering NO_x emissions for the combustion of fossil fuels in a recovery boiler, however, the Mill only burns No. 6 fuel oil in the No. 4 Recovery Boiler for periods of start-up and shut-down, and not during normal operations. Natural gas is only burned to fuel a pilot light which in turn is used to light the No. 6 fuel oil. It would not be practical to use low-NO_x burners for short periods of time that are not representative of normal operation for the boiler.

Step 3-Ranking the Technically Feasible Control Alternatives to Establish a Control Hierarchy

SNCR was eliminated due to technical infeasibility. SCR and combustion modification techniques are the only remaining control technologies to be evaluated. As stated earlier, SCR control systems can reduce NO_x emissions by as much as 90%. Combustion modification techniques can reduce NO_x emissions by varying amounts, depending upon the technology selected and the baseline emission rate. Each of these technologies is discussed under Step 4 below.

Step 4-Control Effectiveness Evaluation

A cost effectiveness evaluation for installation of an SCR system for the No. 4 Recovery Boiler is presented in Table D-2. The cost data presented in Table D-2 were used with EPA's cost factors contained in EPA's Cost Control Manual to develop the cost effectiveness for an SCR system. Based on the data contained in Table D-2, the overall costs for an SCR system are estimated to be greater than $19,575 per ton of NO_x reduced. This is based on the average 2003-2004 NO_x emission rate of 425.4 tons per year from the Recovery Boiler and an assumed 90% reduction of NO_x emissions with the SCR system. This cost effectiveness value is economically infeasible and cannot be justified for a recovery boiler.

While very little, if anything, can be done to affect black liquor nitrogen content, staged air combustion, which is integral to the operation of most recovery boilers, is the most effective strategy for minimizing NO_x formation in a recovery boiler. The No. 4 Recovery Boiler at the Palatka Mill currently employs staged combustion with primary, secondary, and tertiary combustion air. As part of the project to increase boiler efficiency, the Mill is planning to install a fourth level of combustion air. Since the Mill is installing this technology, a cost effectiveness analysis is not necessary.

Step 5-Select BACT

There is no NSPS limit for NO_x emissions from recovery boilers. As stated earlier, typical NO_x emissions from recovery boilers range from 75 to 150 ppmv, depending upon how many levels of combustion air (and the configuration of the air system in general) are used to control NO_x emissions. Table D-1b provides a listing of the NO_x BACT determinations for recovery boilers, which indicate NO_x permit limits that range from 70 to 210 ppmv. The BACT control technologies listed in Table D-1b include combustion control, staged combustion, boiler design and operation, and process controls. One entry lists low-NO_x burners, but this technology applies to a supplemental burner that fires natural gas. One entry lists the addition of a fourth level of combustion air with a NO_x emission limit of 100 ppmv.

The current Title V and PSD NO_x permit limit for the No. 4 Recovery Boiler is 80 ppmvd @ 8% O_2 and 168.5 pounds per hour

To determine what the NO_x emission rate would be by installing a fourth level of staged air combustion, the Mill obtained proposals from a number of vendors. The guaranteed NO_x emission estimates from the vendors for the addition of a fourth level of air in the No. 4 Recovery Boiler ranged from 78 to 90 ppmv, corrected to 8% oxygen. These emission estimates are based on a black liquor solids content of 75%, which is the expected level after the crystallizer project is implemented. As the result of the project to increase boiler efficiency, TRS and CO emission rates will be reduced. However, this will result in a slight increase in NO_x emissions. To keep the NO_x emission rate from increasing beyond its current level (with only three levels of combustion air), a fourth level of combustion air is necessary.

Based on the emission guarantees from the vendors, the Mill believes that BACT should be equal to a fourth level of combustion air with the same NO_x emission rate 168.1 lbs/hr (equivalent to 80 ppmvd, corrected to 8% oxygen) as contained in the current Title V Permit. The 80 ppmvd value is at the low end of the emission estimates obtained from the vendors.

Carbon Monoxide (CO)

Step 1a-Identification of Control Technologies-Typical Technologies in Use in the United States

CO is generated in a recovery boiler when there is insufficient oxygen present to achieve complete combustion of the black liquor solids in the combustion chamber of the boiler. CO generation is inversely proportional to the generation of NO_x emissions. In other words, if NO_x emissions are minimized through the use of internal combustion modification techniques, it is likely that CO emissions will be increased and vice-versa. Therefore, efforts to minimize CO emissions in a recovery boiler must be balanced so that NO_x emissions are not significantly increased.

There are two approaches that can be used to reduce CO emissions from recovery boilers. The first is combustion modification and the second is post-combustion controls (*e.g.*, oxidation catalysts).

Combustion Control

Minimizing the formation of CO emissions is usually performed by ensuring efficient combustion in the combustion chamber of a boiler. This is achieved by providing sufficient air to the material being combusted, in this case carbon, and providing the air in a manner where it mixes effectively with this material. Providing sufficient air is accomplished by providing excess air in the unit to ensure there is adequate air to complete combustion. The additional air for complete combustion is measured by the oxygen analyzers on the boiler outlet and on the stack. Proper mixing is accomplished by manually adjusting the air to the air zone which is deficient in oxygen. Depending on other operating parameters (TRS, NO_x, Bed Height, Liquor Temperature, etc.) the air can be adjusted in either one or multiple zones (primary, secondary, tertiary, or quaternary) to reduce CO without adversely affecting other operating parameters.

Oxidation Catalysts

Oxidation catalysts can be used as a post-combustion technique to reduce CO emissions by as much as 90% from the uncontrolled emission rate. The catalysts work best when the temperature of the gas stream being oxidized is between 600 and 1,100 °F, with an optimum temperature of 800 °F. If the exhaust gas stream temperature of the boiler in question is lower than the optimum temperature range, then additional heat must be used in order to raise the temperature to the desired level (the Palatka Mill's No. 4 Recovery Boiler exhaust temperature is approximately 425 °F). This may add significant operating costs to the control system since fuel must be combusted in a duct burner in order to supply the additional heat.

Oxidation catalysts are typically only used in combustion applications that use natural gas or light grade fuel oils (*i.e.*, No. 1 and No. 2 fuel oils). This is because oxidation catalysts are sensitive to heavy metals that are contained in higher-grade fuel oils or black liquor. Heavy metals, such as zinc, lead, mercury, copper, potassium, magnesium, arsenic and vanadium, will poison the catalyst once a build up of 0.2% (by weight) accumulates on the surface of the catalyst. Most of the referenced heavy metal contaminants are present in black liquor. When the No. 4 Recovery Boiler is burning black liquor, these contaminants will build-up on the surface of the catalyst, thereby poisoning the catalyst and rendering it useless for reducing CO emissions.

Even after consideration of pollution control equipment to remove particulate matter emissions from the flue gas exhaust from the No. 4 Recovery Boiler, a sufficient quantity of heavy metals will still be present to degrade or even poison the catalyst. For these reasons, it is not technically feasible to use an oxidation catalyst for reducing CO emissions from the No. 4 Recovery Boiler.

Step 1b-Identification of Control Technologies-Review of RACT/BACT/LAER Clearinghouse

Searches of the RBLC were conducted to identify control technologies for the control of CO emissions from recovery boilers.

The specific categories searched are listed below:

- External Combustion-Other-11.999
- Kraft Pulp Mills-30.002
- Pulp & Paper Production Other than Kraft-30.004
- Other Wood Products Industry Sources-30.999

The results of the searches are listed in Table D-1c and are summarized below:

- No controls feasible
- Boiler design and good combustion practices
- Proper combustion techniques and operating practices
- Boiler design and good combustion practices
- Combustion control
- Good combustion control of flame temperature and excess air
- Boiler design and operation
- Efficient operation

Step 1c-Identification of Control Technologies-Review of Technologies in Use at Georgia-Pacific Corporation Facilities

All of the recovery boilers at GP's mills utilize varying degrees of staged combustion controls to balance CO and NO_x emissions. The recovery boilers at GP's mills emit varying quantities of CO emissions during normal operations that range from 60 to 450 ppmv, with the higher values coming from older boilers and/or boilers with fewer than three levels of combustion air, and the lower values coming from newer boilers and/or boilers with three or more levels of combustion air.

Step 2-Technical Feasibility Analysis-Eliminate Technically Infeasible Options

As stated earlier, it is not technically feasible to use an oxidation catalyst to reduce CO emissions due to catalyst poisoning from heavy metal contamination. Combustion control is technically feasible for minimizing CO emissions and is inherent in the design of recovery boilers due to the use of staged combustion techniques.

Step 3-Ranking the Technically Feasible Control Alternatives to Establish a Control Hierarchy

The only remaining control technology is combustion control.

Step 4-Control Effectiveness Evaluation

The most effective control technology for minimizing carbon monoxide emissions from recovery boilers is combustion control through the use of staged combustion. As discussed previously, the Palatka No. 4 Recovery Boiler employs staged combustion with primary, secondary, and tertiary combustion air.

Step 5-Select BACT

There is no NSPS limit for CO emissions from recovery boilers. The existing Title V and PSD permits limit CO emissions to 800 ppmv @ 8% O_2 on a 3-hour average basis and 400 ppmv @ 8% O_2 on a 24-hour and annual average basis.

Based on the entries shown in Table D-1c from the RBLC, CO emission limits for recovery boilers range anywhere from 200 to 3,000 ppmv, depending upon the age of the boiler and the averaging time. As stated earlier, the CO emission rate from a recovery boiler is dependent upon the age of the boiler and its inherent design. The BACT control technologies listed in Table D-1c include combustion control, boiler design and operation, and process controls.

GP is not proposing any changes to the CO emission limits for the No. 4 Recovery Boiler as part of this BACT analysis. GP further proposes that BACT for the No. 4 Recovery Boiler be defined as "Boiler Design and Combustion Control".

Sulfuric Acid Mist (SAM)

Step 1a-Identification of Control Technologies-Typical Technologies in Use in the United States

SAM forms as a byproduct of SO_2 emissions when condensation occurs in the gas stream. The quantity of SAM generated is small compared to the amount of SO_2 generated, usually no more than 2-4% of the SO_2 emissions.

There are three approaches that can be used to reduce SAM emissions from recovery boilers. These include mist eliminators, wet ESPs, and combustion control.

Mist Eliminators

The predominant method for controlling SAM emissions from industrial processes and sources of combustion, other than internal design, is mist eliminators. SAM particles are very small, usually in the submicron range. Mist eliminators are designed to remove fine particles, down to 0.5 micron in size. For example, one type of mesh pad manufactured by Enviro-Chem is advertised to remove 99.9% of all particles greater than 2 microns in size and 70% of particles less than 2 microns in size. This efficiency is achieved with a pressure drop of less than 3 inches w.c. pressure.

Wet ESPs

Wet ESPs may also be used to control SAM emissions from recovery boilers. Wet ESPs work similar to dry ESPs, except that the particles are washed off of the electrodes with water sprays, instead of the use of a rapping system for dry ESPs. Also, wet ESPs must be constructed of materials that are resistant to acids, otherwise, the structure of the ESP would corrode very quickly due to the acidic environment. Wet ESPs will remove 90 to 95% of the inlet SAM emissions.

Combustion Control

Combustion control to reduce SO_2 emissions is inherent in the design of a recovery boiler due to the chemical reactions that take place inside of the combustion chamber when black liquor is combusted. Since SAM emissions make up 2 to 4% of SO_2 emissions, minimizing the generation of SO_2 emissions means that SAM emissions will be minimized as well.

Step 1b-Identification of Control Technologies-Review of RACT/BACT/LAER Clearinghouse

Searches of the RBLC were conducted to identify control technologies for the control of SAM emissions from recovery boilers.

The specific categories searched are listed below:

- External Combustion-Other-11.999
- Kraft Pulp Mills-30.002
- Pulp & Paper Production Other than Kraft-30.004
- Other Wood Products Industry Sources-30.999

The results of the searches are listed in Table D-1d and are summarized below:

- No controls
- Boiler design
- Firing rate and pulp production limits

Step 1c-Identification of Control Technologies-Review of Technologies in Use at Georgia-Pacific Corporation Facilities

All of the recovery boilers in use at GP's mills utilize combustion control to minimize the formation of SO_2 and SAM emissions.

Step 2-Technical Feasibility Analysis-Eliminate Technically Infeasible Options

As stated earlier in this analysis, the average exhaust temperature for the No. 4 Recovery Boiler is about 425 °F. At this temperature, SAM emissions would be in a gaseous state. Mist eliminators are not designed to remove gases, rather, they are designed to remove very small liquid droplets. Therefore, the use of mist eliminators for a recovery boiler is not technically feasible unless the unit already had in place a wet scrubber or other means to condense the sulfuric acid gases into a liquid mist. The No. 4 Recovery Boiler at the Palatka Mill does not have a wet scrubber or other device installed to condense the gases into a liquid mist.

The use of a wet ESP and combustion control are technically feasible options for the control of SAM emissions.

Step 3-Ranking the Technically Feasible Control Alternatives to Establish a Control Hierarchy

Combustion control can reduce SO_2 emissions by 99% or more, which means that SAM emissions can be reduced by a similar amount. Wet ESPs will remove 90-95% of SAM emissions.

Step 4-Control Effectiveness Evaluation

The most effective control technology for reducing SAM emissions from recovery boilers is combustion control. Based on stack test data collected over the 5-year period, 1999 through 2003, SAM emissions are generally less than 1.5 lbs/hour and 0.5 ppmv.

GP is unaware of any recovery boilers in the United States that employ mist eliminators to control SAM emissions.

GP selects the only remaining control technology, combustion control, as BACT.

Step 5-Select BACT

There is no NSPS limit for SAM emissions from recovery boilers. Table D-1d provides a listing of the SAM BACT determinations for recovery boilers. These limits range from 2.2 to 20 pounds per hour. The BACT control technologies listed in Table D-1d include "boiler design" and "no controls".

The current Title V Permit limit for SAM emissions is 0.81 ppmv. Based on recent stack test results (2003-2004), SAM emissions are less than the permit limit. GP proposes that BACT for the No. 4 Recovery Boiler be defined as "Boiler Design and Combustion Control" with an emissions limit of 3.6 lbs/hr, which is equivalent to the current Title V Permit limit of 0.81 ppmv.

Volatile Organic Compounds (VOCs)

Step 1a-Identification of Control Technologies-Typical Technologies In Use in the United States

The VOC emission rate is an inverse function of combustion efficiency. In other words, maintaining high combustion efficiencies will lower the VOC emission rate. This holds true in most combustion-related processes, including recovery boilers.

The same two approaches that can be used to reduce CO emissions from recovery boilers can also be used for reducing VOC emissions. The first approach is combustion control and the second approach is post-combustion controls (*e.g.*, oxidation catalysts):

Combustion Control

Just as efficient combustion will minimize the formation of CO emissions, VOC emissions will also be minimized by ensuring efficient combustion in the combustion chamber of a recovery boiler. As explained in the CO section, this is achieved by having the correct controls in place to assure the proper black liquor solids to combustion air ratio in the combustion chamber of the boiler.

Oxidation Catalysts

Oxidation catalysts that are used as a post-combustion technique to reduce CO emissions will also reduce VOC emissions by as much as 90 to 95% from the uncontrolled emission rate. The catalysts work best when the temperature of the gas stream being oxidized is between 600 and 1,100 °F, with the optimum temperature of 800 °F. If the exhaust gas stream temperature of the boiler in question is lower than the optimum temperature range, then additional heat must be added in order to raise the temperature to the desired level. This may add significant operating costs to the control system since fuel must be combusted in a duct burner in order to supply the additional heat.

Oxidation catalysts are typically only used in combustion applications that use natural gas or light grade fuel oils (*i.e.*, No. 1 and No. 2 fuel oils). This is because oxidation catalysts are sensitive to heavy metals that are contained in higher-grade fuel oils or black liquor. Heavy metals, such as zinc, lead, mercury, copper, potassium, magnesium, arsenic and vanadium, will poison the catalyst once a build up of 0.2% (by weight) accumulates on the surface of the catalyst. Most of the referenced heavy metal contaminants are present in black liquor. When the No. 4 Recovery Boiler is burning black liquor, these contaminants will build-up on the surface of the catalyst, thereby poisoning the catalyst and rendering it useless for reducing VOC emissions.

Even after consideration of pollution control equipment to remove particulate matter emissions from the flue gas exhaust from the No. 4 Recovery Boiler, a sufficient quantity of heavy metals will still be present to degrade or even poison the catalyst. For these reasons, it is not technically feasible to use an oxidation catalyst for reducing VOC emissions from the No. 4 Recovery Boiler.

Step 1b-Identification of Control Technologies-Review of RACT/BACT/LAER Clearinghouse

Searches of the RBLC were conducted to identify control technologies for the control of VOC emissions from recovery boilers.

The specific categories searched are listed below:

- External Combustion-Other-11.999
- Kraft Pulp Mills-30.002
- Pulp & Paper Production Other than Kraft-30.004
- Other Wood Products Industry Sources-30.999

The results of the searches are listed in Table D-1e and are summarized below:

- No controls
- Combustion control
- Boiler design and good combustion practices
- Low odor design

Step 1c-Identification of Control Technologies-Review of Technologies in Use at Georgia-Pacific Corporation Facilities

As described above for CO, the recovery boilers in use at GP facilities utilize varying degrees, or stages, of combustion air to maintain adequate combustion efficiency and low CO emission rates. The same control technique also minimizes VOC emissions.

Step 2-Technical Feasibility Analysis-Eliminate Technically Infeasible Options

As stated earlier in this report, it is not technically feasible to use an oxidation catalyst to reduce VOC emissions due to catalyst poisoning from heavy metal contamination. Combustion control is technically feasible for minimizing VOC emissions and is inherent in the design of recovery boilers due to the use of staged combustion techniques.

Step 3-Ranking the Technically Feasible Control Alternatives to Establish a Control Hierarchy

The only remaining control technology is combustion control.

Step 4-Control Effectiveness Evaluation

The most cost effective control technology for minimizing VOCs from recovery boilers is combustion control through the use of staged combustion. As discussed previously, the No. 4 Recovery Boiler employs staged combustion with primary, secondary and tertiary combustion air.

Step 5-Select BACT

There is no NSPS limit for VOC emissions from recovery boilers. Table D-1e provides a listing of the VOC BACT determinations for recovery boilers. These limits range from 2.8 to 50 ppmv and 3.7 to 233 pounds per hour. The current Title V Permit limit for VOC emissions from the No. 4 Recovery Boiler is 31.5 lbs/hr, which is based on an emission factor of 0.3 lb/ton of black liquor solids. Based on recent stack test results (2003-2004), the No. 4 Recovery Boiler is in compliance with the current Title V Permit limits for VOCs.

GP proposes that BACT for the No. 4 Recovery Boiler be defined as Boiler Design and Combustion Control, with no changes in the current Title V Permit limit.

ATTACHMENT J

Revisions to PSD Application – PE Signature

Several pages of the original PSD Application were changed and the response to DEP's RAI contained various technical answers. Mr. Mark Aguilar, PE has reviewed these responses and a copy of the new signature and PE Stamp page is attached.

The original signature page is being sent to Mr. Koerner in a separate letter.

ATTACHED TO HARD COPY ONLY

Georgia-Pacific

Georgia-Pacific Corporation

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January 12, 2006

Mr. Jeffrey Koerner, PE – Permitting North Administrator
Bureau of Air Regulation
Florida Department of Environmental Protection
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

RE: Modification to the No. 4 Recovery Boiler
Project No.: 1070005-035-AC/PSD-FL-367

Dear Mr. Koerner:

This letter is in response to your Request for Additional Information (RAI-#1), dated December 16, 2005 regarding modification to the No. 4 Recovery Boiler Project No.: 1070005-035-AC/PSD-FL-367. Attached is a Professional Engineer Certification sheet (DEP Form No. 62-210.900(1) that should be used for Georgia-Pacific Corporation's responses to your RAI. The RAI has been submitted to you under separate cover from the Palatka Mill directly.

If you have any questions regarding this matter, please contact Myra Carpenter at (386) 329-0918.

Very truly yours,

Wayne J Galler

Wayne J. Galler
Senior Environmental Consultant – Air

encl.

Professional Engineer Certification

1. Professional Engineer Name: **Mark J. Aguilar**
   Registration Number: **52246**

2. Professional Engineer Mailing Address:
   Organization/Firm: **Georgia-Pacific Corporation**
   Street Address: **133 Peachtree St**
   City: **Atlanta** State: **GA** Zip Code: **30303**

3. Professional Engineer Telephone Numbers...
   Telephone: **(404) 652-4293** ext. Fax: **(404) 654-4706**

4. Professional Engineer Email Address: **mjaguila@gapac.com**

5. Professional Engineer Statement:

I, the undersigned, hereby certify, except as particularly noted herein, that:*

(1) To the best of my knowledge, there is reasonable assurance that the air pollutant emissions unit(s) and the air pollution control equipment described in this application for air permit, when properly operated and maintained, will comply with all applicable standards for control of air pollutant emissions found in the Florida Statutes and rules of the Department of Environmental Protection; and

(2) To the best of my knowledge, any emission estimates reported or relied on in this application are true, accurate, and complete and are either based upon reasonable techniques available for calculating emissions or, for emission estimates of hazardous air pollutants not regulated for an emissions unit addressed in this application, based solely upon the materials, information and calculations submitted with this application.

(3) If the purpose of this application is to obtain a Title V air operation permit (check here ☐, if so), I further certify that each emissions unit described in this application for air permit, when properly operated and maintained, will comply with the applicable requirements identified in this application to which the unit is subject, except those emissions units for which a compliance plan and schedule is submitted with this application.

(4) If the purpose of this application is to obtain an air construction permit (check here ☒, if so) or concurrently process and obtain an air construction permit and a Title V air operation permit revision or renewal for one or more proposed new or modified emissions units (check here ☐, if so), I further certify that the engineering features of each such emissions unit described in this application have been designed or examined by me or individuals under my direct supervision and found to be in conformity with sound engineering principles applicable to the control of emissions of the air pollutants characterized in this application.

(5) If the purpose of this application is to obtain an initial air operation permit or operation permit revision or renewal for one or more newly constructed or modified emissions units (check here ☐, if so), I further certify that, with the exception of any changes detailed as part of this application, each such emissions unit has been constructed or modified in substantial accordance with the information given in the corresponding application for air construction permit and with all provisions contained in such permit.

Signature

Date 1/12/06

(seal)

* Attach any exception to certification statement.

Department of Environmental Protection

Jeb Bush
Governor

Twin Towers Office Building
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Colleen M. Castille
Secretary

December 20, 2005

CERTIFIED MAIL – Return Receipt Requested

Mr. Theodore D. Kennedy
Vice President – Palatka Operations
Georgia-Pacific
Palatka Mill
P.O. Box 919
Palatka, Florida 32178-0919

RE: Modification to the No. 4 Recovery Boiler
Project No.: 1070005-035-AC/PSD-FL-367

Dear Mr. Kennedy:

On November 18, 2005, the Department received your application for an air construction permit to modify the No. 4 Recovery Boiler at the Palatka mill, and we received the modeling files on November 21, 2005. The modeling information is incomplete. In order to continue processing your application, the Department will need the additional information requested below. Should your response to this request require new calculations, please submit the new assumptions, calculations, reference material and appropriate revised pages of the application form.

The Department is forwarding the attached e-mail from the federal land manager to you. The Department has verbally clarified and communicated further information to the federal land manager concerning Comments 1, 2 and the guidance in the next to last paragraph concerning the use of Method 2 and a maximum relative humidity of 95%. However, even with this clarification, the federal land manager does not accept the approach of eliminating potential weather events based upon an hour by hour review. Please provide an explanation of how to remove the problem of 11 days showing visibility impairment above the 5% threshold, and provide the CALPUFF results showing this removal, along with the new emission inputs.

The Department will resume processing this application after receipt of the requested information. If you have any questions regarding this matter, please call me at (850)921-8986.

Sincerely,

Cleve Holladay
Air Permitting North
Bureau of Air Regulation

CGH/ch

Enclosure

cc: Gregg Worley, U.S. EPA, Region 4
Dave McNeal, U.S. EPA, Region 4
Lee Page, U.S. EPA, Region 4
John Bunyak, NPS
Chris Kirts, NED
Myra J. Carpenter, G-PC
Mark J. Aguilar, P.E., G-PC

Holladay, Cleve

From: Meredith_Bond@fws.gov

Sent: Monday, December 19, 2005 9:41 PM

To: Holladay, Cleve; Mitchell, Bruce

Cc: Sandra_V_Silva@fws.gov; Catherine_Collins%FWS@fws.gov; Tim_Allen@fws.gov; Jim_Kraus@fws.gov; Allyne_Askins@fws.gov; George_Constantino@fws.gov; Dee_Morse@nps.gov; krivo.stanley@epa.gov

Subject: Comments regarding Class I Air Quality Analysis - GP/Palatka - No. 4 Recovery Boiler Project

Cleve and Bruce,

The Fish and Wildlife Service - Branch of Air Quality has reviewed the November 2005 permit application for the Georgia-Pacific Corporation, Palatka Mill, No. 4 Recovery Boiler (Florida DEP project number 1070005-035-AC, PSD-FL-367). This facility is located in Palatka, Florida, approximately 108 km south of the Okefenokee National Wilderness Area, 137 km northeast of Chassahowitzka National Wilderness Area, and 186 km south of the Wolf Island National Wilderness Area. All three of these FWS managed lands were designated as Class I areas by Congress and are afforded special Clean Air Act protections.

These comments today address the Class I visibility analysis contained within Attachment C of the document. Consistent with the instructions provided to the applicant in a September 23, 2005, FDEP letter, it appears that the air quality impact analysis contained in this permit application assesses the combined effects of several recent permit actions at this facility. We concur with this approach because it more accurately represents the overall impacts of the group of modifications to the air quality and air quality related values at the FWS Class I areas.

1. The application package did not contain electronic copies of the CALPUFF computer model input and output files. These are needed for our review of the project.

2. Based upon the information provided in section 6.0 of Attachment C to the application, titled "6.0 ADDITIONAL IMPACT ANALYSIS - CLASS I AREAS," it is unclear what "Method" is being used for calculating background visibility; that is, we can not find any documentation of what setting for the "MVISBK" setting in CALPOST was used. For conducting a screening modeling exercise in accordance with the Federal Land Managers' guidelines (FLAG Report, December 2000), the analysis should use Method 2 with a maximum relative humidity of 98% (MVISBK = 2, RHMAX = 98). The applicant needs to list all the "switch" settings used in the modeling analysis, and explain those which are not regulatory defaults. (The listing may be done by means of the electronic files requested in comment 1, above.)

3. The modeling results discussed in the report indicated that, for the three years covered in the analysis, there were a total of 11 days showing visibility impairment above the 5% threshold - seven at Okefenokee NWA, three at Chassahowitzka NWA, and one at Wolf Island NWA. The largest impact was predicted at Chassahowitzka, with a predicted impairment of 8.49% (see table C-39 in application). The applicant then proceeds to look at each of these days and subjectively determine "if natural visibility impairment phenomena existed during [those] days...." The application indicates that weather codes from the Jacksonville International Airport (JAX) surface observations were used to assess Okefenokee and Wolf Island NWA's, and weather codes from the Tampa International Airport (TPA) to assess Chassahowitzka NWA. At this point, the application references information contained in "Appendix B, Tables APPB-1 to APPB-5" - it appears that these tables must be from another source, as they do not appear in the application. (Note that JAX is about 50 km from the nearest boundary of Okefenokee, and nearly 100 km from Wolf Island; TPA is about 75 km from Chassahowitzka.)

The Fish and Wildlife Service Branch of Air Quality does not accept this approach of eliminating potential weather event results based upon an hour by hour review. Should the applicant wish to provide alternative modeling analysis to address potential visibility impairing weather events, there are two approaches that the Federal Land Management agencies (National Park Service, USDA/Forest Service, and FWS) have considered informative to our review. The first is to continue to use "Method 2" (MVISBK=2), but with a maximum relative humidity of 95% (RHMAX = 95). The second is similar to the methodology being utilized by the Regional Planning Organizations and states for modeling in support of the "BART analyses" for the regional haze rule plans, and uses Method 6 (MVISBK=6) with EPA-published monthly relative humidity factors appropriate to each of the specific Class I areas. If the applicant does choose to present an additional modeling analysis, the package also needs to present the standard FLAG screening analysis as well.

Thank you for the opportunity to respond to this application. If you have any questions, please contact either Catherine Collins (303-914-3807) or me.

Happy holidays,

-- Meredith

CDR Meredith Bond, P.E., USPHS
Deputy Chief
U.S. Fish and Wildlife Service
Branch of Air Quality
7333 W Jefferson Ave., Suite 375
Lakewood, CO 80235
303-914-3808
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Meredith_Bond@fws.gov

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Department of Environmental Protection

Jeb Bush
Governor

Twin Towers Office Building
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Colleen M. Castille
Secretary

December 16, 2005

CERTIFIED MAIL – Return Receipt Requested

Mr. Theodore D. Kennedy
Vice President – Palatka Operations
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Palatka, Florida 32178-0919

RE: Modification to the No. 4 Recovery Boiler
Project No.: 1070005-035-AC/PSD-FL-367

Dear Mr. Kennedy:

On November 18, 2005, the Department received your application for an air construction permit to modify the No. 4 Recovery Boiler at the Palatka mill; and, we received the modeling files on November 21, 2005. The application is incomplete. In order to continue processing your application, the Department will need the additional information requested below. Should your response to any of the items below require new calculations, please submit the new calculations, assumptions, reference material and appropriate revised pages of the application form.

Boiler

1. The project will overhaul the recovery boiler with extensive replacement of superheater, economizer, generating bank, and floor tubes as well as replace and/or modify components in the combustion air system. The project will also add a crystallizer and make miscellaneous changes to the concentrators (i.e., baffles, heat exchanger, piping, etc.). The application indicates that construction is planned to commence in April of 2006 and be completed over a variety of outages through 2008. Please identify the various stages of construction and the items that scheduled for completion during each stage.
2. The current permitted capacity of the recovery boiler is 1346 MMBtu/hour of heat input and 210,000 lb BLS/hour (24-hour average). What is the corresponding maximum continuous steam production rate for the boiler? What are the design steam conditions (temperature and pressure)? Will the project increase the boiler capacity?
3. The pulp mill capacity is specified as 118 ADTUP/hour and 1850 ADTUP/day, maximum monthly average. Will the project increase the pulp mill capacity?
4. On page B-40, the application identifies the maximum flow rate at permitted capacity as 210,000 dscfm @ "2.8%" oxygen (dry). Identify the basis for this rate. Actual test data provided in the application does not indicate typical operation at an oxygen level of 2.8%. Does the unit have an oxygen meter? Is the oxygen level continuously recorded? What is the optimum oxygen operating range for the recovery boiler?
5. Please provide an ultimate and proximate fuel analysis for the BLS fired in this recovery boiler.
6. The recovery boiler has been identified as a unit subject to the recently promulgated Best Available Retrofit Technology (BART) provisions. How does the facility propose to comply with the BART requirements for NOx, SO2, and PM/PM10?

CO and VOC Emissions

1. The current standards for CO emissions in the Title V permit are 800 ppmvd @ 8% oxygen (3-hour average) and 400 ppmvd @ 8% oxygen (24-hour average). These limits were established in Air Permit No. PSD-FL-226 based on "combustion controls". The application indicates that there is an optimum operating level for BLS-to-air ratio, which will minimize CO emissions. Identify the range of operation for this parameter and correlate the range to actual test data.

2. Identify the boiler combustion parameters monitored and the operating levels that ensure good operation. Does the current system include any automated combustion controls? Will a new control system be added?

NOx Emissions

1. The current NOx standard in the Title V permit is 80 ppmvd @ 8% oxygen based on an annual stack test. This standard was established in Air Permit No. PSD-FL-226. Will the installation of a 4th level of combustion air be able to achieve lower NOx emissions or more steady NOx emissions? The application indicates that NOx emissions from a recovery boiler will range from 75 to 150 ppmvd depending on the levels of combustion air provided. Estimate the fraction of NOx emissions that are fuel NOx compared to thermal NOx. Are the combustion air requirements manually set for fixed operating levels or is there an automated control system? Describe the parameters that are monitored to ensure effective staged combustion with low NOx levels.

2. Please identify the source of the cost estimate for a cold-side SCR system and provide the supporting information. The application assumes that an SCR system would be installed after the ESP and therefore the exhaust would have to be reheated to provide the proper operating window. Would it be possible to locate an SCR system prior to the ESP to avoid costly reheat? What existing circumstances at the plant would prevent this? Otherwise, please provide a cost estimate for a hot-side SCR system.

3. The application rejects SNCR as a technically infeasible control option. To be effective, SNCR requires the a proper operating temperature window in which to inject ammonia or urea, sufficient residence time for the reaction to take place, and turbulence for mixing. Please provide supporting information based on the actual boiler design and operating condition to support GP's belief that SNCR is not technically feasible. Please provide a cost estimate on installing an SNCR system for the recovery boiler.

PM/PM10 Emissions

1. The application indicates that the PM10 emissions are approximately 75% of the total PM emissions. Please provide emissions data for this recovery boiler to support this statement. Other information suggests that approximately 90% of total PM emissions are PM10 emissions and of the PM10 emissions, approximately 50% is actually about 1 micron in diameter or less (Davis, 2000). Describe the difficulties in controlling particles in this size range with a 2-field ESP. Please identify any improvements to the existing ESP that would result in better performance. Can the existing unit be modified to add a 3rd field?

2. As suggested by the application, 25% of the total PM emissions are greater than PM10 in size. Identify control devices (i.e., settling chambers, cyclones, wet cyclones, etc.) that could be installed prior to the ESP to reduce loading so that the ESP could be tuned to remove additional PM emissions. Provide a cost analysis for feasible add-on controls.

3. The application states that an ESP can achieve greater than 99.9% control and identifies the ESP as the top control. What is the control efficiency of the existing ESP? Have there been any major improvements or overhauls to the ESP within the last 5 years? If so, when did this occur, what work was performed and how much did it cost? Are any future major improvements or overhauls planned?

4. The application indicates that GP operates two recovery boilers in another state (St. James River Corp.), each with a combination of an ESP and wet scrubber. The application states that the wet scrubbers were installed to recover heat and supply hot water to the plant and not reduce PM emissions. Nevertheless, identify the control efficiency of the wet scrubbers for reducing PM emissions. What are the PM emissions standards for these units? What are the actual tested PM emissions from these units? Provide test data for the units operating only with the ESP and with the ESP/wet scrubber combination. What is the calculated PM removal efficiency of these wet scrubbers? Does the wet scrubber also remove SO2, TRS and HCl emissions? Provide a cost analysis for a similar wet scrubber.

5. The RACT/BACT/LAER Clearinghouse shows several recovery boilers with PM BACT limits of 0.021 grains/dscf. Much of the recent test data shows that the existing ESP could also achieve this level of control. However, test data collected during 2000/2001 shows much higher emission levels. Identify the cause of the elevated PM emissions. Was the unit undergoing maintenance or about to undergo maintenance? Were both fields of the ESP operating during the tests? Were repairs or corrective actions taken after the tests were conducted? When the existing ESP is properly tuned and operating both fields of the ESP, can the unit achieve a PM emission rate of 0.021 grains/dscf or less?

6. Has any PM10 emissions testing ever been conducted on this RB? If so, please provide the date(s) and a synopsis of the test(s) results.

SAM Emissions

1. The application indicates that SAM emissions are completely in a gaseous form when exiting the stack at 425° F. Stack test data provided indicates that the actual stack exhaust temperature is about 400° F. At what temperature will SAM condense out of the exhaust?
2. Is it possible to reduce the exhaust temperature with a heat exchanger to form SAM droplets that can be removed with mist eliminators? Is this technique used on other recovery boilers? Are mist eliminators installed on other recovery boilers within the pulp and paper industry?

Miscellaneous

1. On page A-39 (Section F1) of the application, potential benzene emissions were listed as "296.1 TPY". Please correct and submit the revised pages.
2. We are still reviewing the modeling and will ask any questions that arise by December 21 of next week.
3. If any response to the above issues affect the application submittal, please correct and/or change the application to reflect the additional analyses and submit.

The Department will resume processing your application after receipt of the requested information. Rule 62-4.050(3), F.A.C., requires that all applications for a Department permit must be certified by a professional engineer registered in the State of Florida. This requirement also applies to responses to Department requests for additional information of an engineering nature. For any material changes to the application, please include a new certification statement by the authorized representative or responsible official. You are reminded that Rule 62-4.055(1), F.A.C. requires applicants to respond to requests for information within 90 days or provide a written request for an additional period of time to submit the information. If you have any questions regarding this matter, please call Bruce Mitchell at (850)413-9198.

Sincerely,

Jeffrey F. Koerner

Jeffrey F. Koerner, P.E.
Permitting North Administrator
Bureau of Air Regulation

JFK/bm

cc: Gregg Worley, U.S. EPA, Region 4
John Bunyak, NPS
David Buff, P.E., GAI
Chris Kirts, NED
Myra J. Carpenter, G-PC

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