

## ODOR CONTROL

### RECOVERY BOILER FURNACE AS CONCENTRATED NCG INCINERATOR

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#### ABSTRACT

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There is increasing pressure to use recovery boilers to reclaim streams in addition to black liquor. Today, quite often, the odor gases from the mill are being treated in the recovery boiler furnace. This paper deals with the influence of strong odor gas combustion on the recovery boiler furnace process. The measurements carried out indicate that the sulfur binding reactions take place prior to the fume formation phase. Further, there are no kinetic limitations of NCG sulfur binding into the dust, if the burner is located at lower furnace level.

The NCG contains considerable amounts of ammonia potential to form  $\text{NO}_x$ . The measurements performed indicates that the NCG ammonia does not increase the  $\text{NO}_x$  level of the boiler, if the burner is located at the secondary air level. If the burner is located below the liquor guns, the  $\text{NO}_x$  level increases. However, sub-stoichiometric combustion of NCG in the burner can mostly compensate for this  $\text{NO}_x$  increase. This indication is explained by a so-called reburning effect.

*Application:* This study helps mills determine the optimum placement of NCG burners for odor and  $\text{NO}_x$  control.

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The trend today is towards an increased closure of the chemical cycles in pulp mills. The driving force for this development is both environmental and economical. The effluent-free and odorless pulp mill is a demanding challenge, which requires constant development and innovative solutions from equipment suppliers. Although the recovery cycle has demands of recovering, in addition to the spent liquor, other streams, such as sulfur containing odorous gases, the simplicity and economy of the total recovery cycle will remain as a definite requirement. For that reason there is an increasing pressure to use the recovery boiler also to recover streams other than the black liquor. Today, quite often, the odor gases from a mill area are being treated in a recovery boiler furnace.

As one of the key components in the recovery of valuable pulping chemicals, a recovery boiler has to be flexible and able to face these new challenges due to the eco-cycle demand.

This paper deals with the influence of strong odor gas combustion on the recovery boiler furnace process. Especially sulfur binding and  $\text{NO}_x$  formation are discussed.

#### THE NONCONDENSIBLE GASES IN THE PULPING PROCESS

The noncondensable gases forming in the chemical wood processing industry are generally divided into strong and weak gases. Typical processes where hazardous noncondensable gases (sulfurous and/or flammable) are collected take place in the digester house, evaporation plant, washing plant and methanol handling. These gases are called strong or concentrated non-condensable gases (CNCG) or low volume and high concentration gases (LVHC). The non-condensable gases collected from tanks, basins, drains and other sources in free contact with the ambient air are called weak or diluted non-condensable gases (DNCG) or low concentration and high volume gases (LCHV). **Table I** shows the main sulfur emission sources of the kraft pulping process

A significant factor to be considered in processing those gases is the instability of their concentration and amount. This means that a considerable over dimensioning of the system is necessary.

Typically the concentrated gases also contain significant concentrations of nitrogen. Stripper off-gas (SOG) contains up to 9 vol-% nitrogen as ammonia. Incineration of SOG or liquid methanol recovered from SOG in standard type incinerators or lime kilns results in high emissions of  $\text{NO}_x$ . The emission is in the range 0.2  $\text{kgNO}_x/\text{ADT}$  or 11...14% of the total  $\text{NO}_x$  emission from the pulp mill. Superconcentrator gases have also been found to contain varying amounts of ammonia. Diluted gases generally contain ammonia less than some thousands ppm /1/.

Åbo Akademi University has recently studied the formation and pathways of ammonia in the recovery cycle/2, 3/. The main result is that the nitrogen species fed to the green liquor with smelt start to convert to ammonia in the green liquor dissolving tank. The ammonia is released to different vent and odor gases in the

recovery cycle before and after the cooking process. The stripper off gas is usually one significant pathway for ammonia.

The pathways of nitrogen species, and the effect of the process conditions on their release to the odorous gases, in different parts of the recovery cycle are today under intensive research work in research organizations and companies.

**Table I.** The main sulfur emission sources of the kraft pulping process.

<b>CNCG's</b>	<b>kgS/ADT</b>	<b>m<sup>3</sup>/ADT</b>
batch cooking blow gases	0.4 -0.8	5 - 15
batch cooking off-gases	0.1 -0.2	1 - 3
continuous cooking gases	0.1 - 0.4	0.5-1.5
evaporator line (hot well)	0.4 -0.8	1 -10
foul condensate stripper	0.5 -1.0	15 - 25
methanol treatment	0.5 - 2.0	1 - 2
black liquor heat treatment	2.0 - 3.0	1.5 - 3.0
superconcentrator off-gases	2.0 - 10	1.5 - 12
<b>CNCG total</b>	<b>1.5 - 12</b>	
<b>DNCG's</b>		
pulp washing off-gases	0.01 -0.1	1 - 1500
tall oil plant	0.5 - 0.2	2000 - 3000
tank venting	0.5 - 0.2	20 - 30
<b>DNCG total</b>	<b>0.5 - 1.0</b>	
<b>Flue gases</b>		
recovery boiler, new	0.01 -0.1 0.1	
recovery boiler, old	1.0 - 14	
lime kiln, new	0.05-0.2	
lime kiln, old	0.04 - 0.5	

### Collection of CNCGs

The CNCGs from cooking, evaporation, foul condensate tank and methanol handling are directed through a water seal tank using steam ejector suction pressure. Stripper off-gas and superconcentrator gas already have high pressure and specific ejectors are not needed. Different gases have separate ducts. The ducting is led below the water seal tank surface level to prevent flow from one line to another. The suction pressure depends on the available steam pressure. Rupture discs are demanded in CNCG lines. Droplet separators can be furnished with two elements to gain maximum efficiency.

## Safety

Since NCG's are corrosive, toxic, and if mixed with air, potentially explosive, great care must be taken in the safety features of these systems. HVLC's are treated below the LEL (lower explosion limit) and LVHC 's are treated above UEL (upper explosion limit) of the gas mixture. Therefore, the CNCG equipment should be designed to prevent ingress of air into the system. Unfortunately, the terms LEL and UEL only explain the situation in theoretical terms. In reality, TRS gases, as emitted, are mixed with air that has most of its oxygen depleted, such that the gases are not explosive. Mixed TRS gases, which also contain other combustibles such as MeOH and turpentine, are flammable over the range of 2 % to 50 % for all combustibles (Table II)/5/. The CNCG system must also be protected against high pressures or vacuum, which may appear during abnormal conditions, especially during start-ups and shutdowns. Under no circumstances should CNCG's be added to DNCG's, especially when DNCG flow contains considerable amounts of turpentine. Support fuel is generally used every time when the CNCGs are burned in the recovery boiler. This is due to process variations which might occur especially in the older recovery boilers and the pulp mill gases themselves. Some mills in Finland have concluded that if the boiler is stable the gases can be burned without any support fuel when the gases are also stable and variations are small. This procedure of operating should be carefully investigated before the use of support fuel is stopped. During startup and at a variable load, the burner must be used with support fuel in any case.

Special interest has to be paid on safety in the treatment of the NCG's in the recovery boiler. In addition to the usual safety devices and design common in all TRS treatment, drains in the system are designed to prevent any water or other condensates getting into the recovery boiler.

**Table II.** CNCG typical analysis during normal operation. The balance of the gas will be nitrogen.

Source	% TRS (Vol)		% O <sub>2</sub> (Vol)			
	Min	Avg	Max	Min	Avg	Max
Batch digester	20	50	70	0.5	2.0	5.0
Continuous digester	12	60	80	1.0	3.0	10.0
Turpentine (batch)	0.1	2.0	10	4.0	12.0	20.0
Evaporator	1.0	60	70	1.0	5.0	8.0
Combined	10	50	65	2.0	3.0	6.0

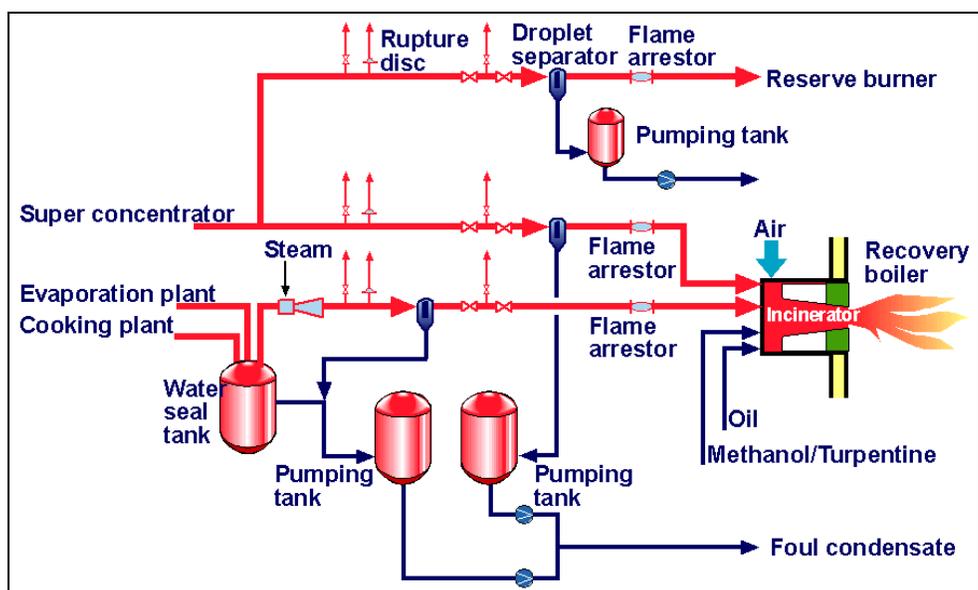
## CONCENTRATED GAS COMBUSTION IN THE RECOVERY BOILER BURNER

Recovery boiler has several advantages to incinerate NCG gases as a side stream. Because the recovery boiler exists anyway, the solution is cost-effective and simple. The NCG sulfur is recovered to the green liquor, as is usually preferred (if there are no considerable SO<sub>2</sub> emissions from the RB stack). Further, the heating value of NCG is recovered to heat and power. An important advantage is also the tolerance of a big furnace to the load variations typical to strong odor gases.

The treatment system based on the recovery boiler burner as the main treatment unit of the non-condensable gases is presented in Fig. 1.

In addition to the proper functioning of the burner itself, the stable and complete combustion of the NCG requires stable combustion and efficient mixing in the boiler furnace. If not fulfilled, TRS emissions in the stack is the first detriment arising. However, a modern recovery boiler with an advanced air feeding and firing system can usually meet these requirements.

The first system was installed in Finland in 1993 /6, 7/. Since that several references have proven that this technology fulfils all the preferences. Based on the basic understanding of the recovery boiler furnace process and on the wide practical experiences, all the changes in boiler performance and emissions can be predicted with a considerable accuracy.



**Figure 1.** Main treatment system of strong odor gases based on the recovery boiler burner.

#### NCG SULFUR BINDING IN RB FURNACE

A recovery boiler burner is worth designing if the fly ash has enough binding capacity for the additional sulfur originating from the gas to be incinerated. If not, the remaining sulfur is contained as  $\text{SO}_2$  in the flue gas. Generally, the  $\text{SO}_2$  emission in a recovery boiler is affected by the sulfur load to the furnace and the furnace temperature, which is mainly influenced by the liquor load and dry solids content. In addition to these basic conditions, the operation model and the performance of the air feeding system have influence on the  $\text{SO}_2$  emission. When NCG is incinerated in the boiler, the respective additional sulfur load should be taken into account. This balance of sulfur and alkalines can be estimated by the concentration and carbonate content of the ESP dust. Practically, the accurate estimation or measurement of NCG flow and sulfur concentration or the dust amount is not so easy.

If the  $\text{SO}_2$  is not buffered, the acidic sulfates can be generated in the dust. Acidic sulfates decrease the sticky temperature of the fly ash and deposits generated in the boiler bank and economizer region /4/.

The  $\text{SO}_2$  generated in a NCG burner flame comes into contact with the alkaline in a part of the furnace different from where sulfur is released from black liquor. A relevant question is if the binding reactions of  $\text{SO}_2$  generated in the NCG burner have any kinetic limitations to prevent the buffering capacity of the dust to be fully utilised. To find answer to this question, the detailed reactions to lead to sulfur binding and dust formation should be understood. However, there is no generally accepted agreement on the sulfur reaction and dust formation pathways in recovery boiler furnace. The main question is if the sulfur is bound by the dust (alkaline carbonates) after the particle formation or if the sulfating of alkalines takes place prior to particle formation - leading further to dust condensation. The possible chemical reactions in these cases are the sulfation of alkaline hydroxide or alkaline carbonate, respectively /8/.

To find out the reaction rates of different reactions leading to sulfur binding, the direct measurements of different sulfur species in the furnace are practically impossible. For this reason an indirect method was used. The method is based on comparison of the content of sulfur species in different size fractions of fume sampled from flue gas before ESP. The size selective sampling of dust is carried out using a low-pressure impactor, which separates particles to different size fractions in the sub-micron size range /9/.

Impactor samples were taken from the flue gas of a big modern recovery boiler burning high dry solids liquor and equipped with a strong odor gas burner. The burner is installed at the upper secondary air register level (below the liquor guns). This burner incinerates the strong odor gases from the cooking plant, evaporator plant, and superconcentrator. The majority of the gases originate from the superconcentrator. **Figure 2** shows the size

distribution of the dust sampled before ESP from the flue gas. **Figure 3** shows the molar ratios of sulfate and alkalines as a function of particle size. This ratio is based on the chemical analysis of the impactor samples for each impactor stages (corresponding to each size range). Figure 3 shows the result for boiler operation without and with odor gas burning. Figure 3 shows that the relative sulfate concentration in the size range appr.  $1\ \mu\text{m}$  is significantly higher than that of lower size ranges. Practically all dust particles smaller than  $1\ \mu\text{m}$  are formed by condensation from vapor phase. The explanation of the dependence of sulfate concentrate on the particle size is based on the following facts: 1) particle formation does not start at the same level of the furnace for all particles. 2) On average, formation of smaller particles has started in the upper part of the furnace (shorter growth time) which is not the case for bigger fume particles. 3) The content of a particle is dependent on the atmosphere where it grows. Because in Fig. 3 the bigger fume particles (started to form at lower levels in the furnace) has the highest sulfate concentrations, it can be concluded that sulfur binding takes place in an early phase of particle formation and growth. This supports the argument that sulfation of alkalines takes place in vapor phase and the resulting alkaline sulfate condensates into particles - at least in these high dry solids firing conditions.

Figure 3. shows that the odor gas burning (additional sulfur feeding) increases the relative sulfate concentration in the size range which has the highest relative sulfate concentration without odor gas burning. The conclusion is that the odor gas sulfur is fed to a lower level than where particle formation starts. As a result, it can be concluded that there cannot be any kinetic limitation of NCG sulfur binding, if the burner is located at this level (below the liquor guns).

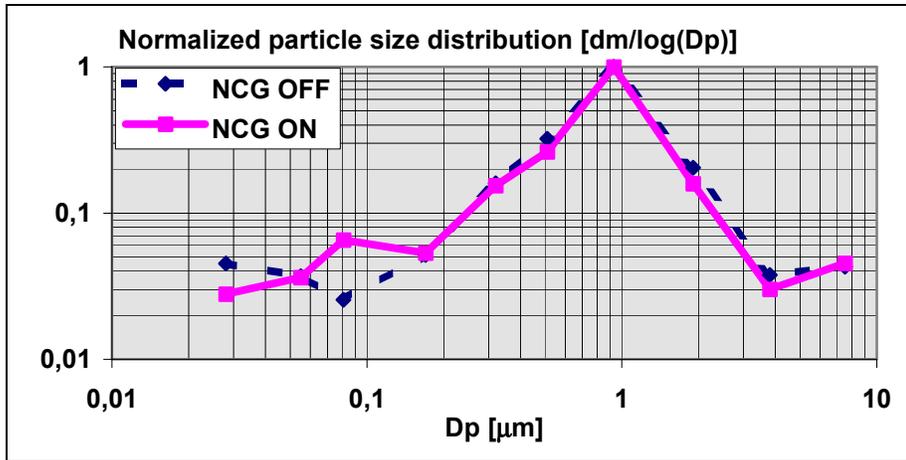
The impactor measurements carried out at another recovery boiler which has a NCG burner installed between the liquor guns and the tertiary air register show the same results as those of the case described above.

#### **NO<sub>x</sub> FORMATION TENDENCY OF NCG IN RECOVERY BOILER FURNACE**

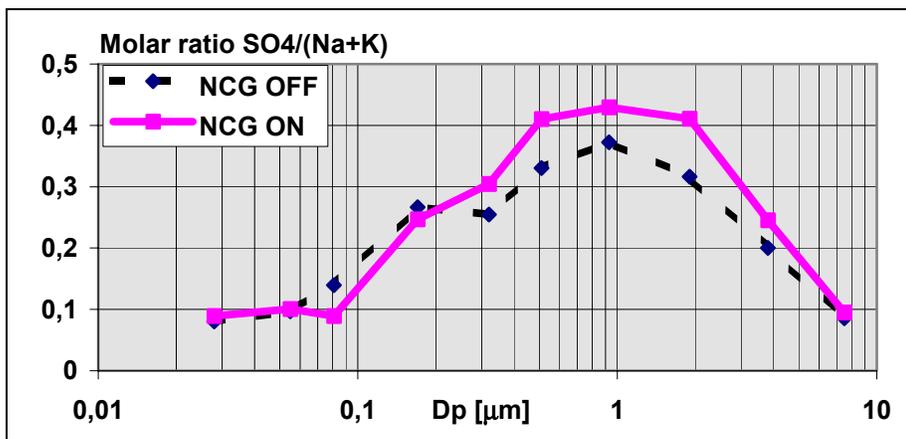
When incinerated, the ammonia in NCG is a potential source of additional NO<sub>x</sub> emission. The basic estimation is that, when NCG is burned in a burner which is installed in the recovery boiler, the ammonia is oxidized to NO<sub>x</sub> and is added to the NO<sub>x</sub> originated from liquor combustion.

The actual effect of NCG combustion on NO<sub>x</sub> emission was measured in a boiler, where an NCG burner is installed at the secondary air level. **Figure 4** shows results of an operation period where the NCG burner was switched OFF (no NCG feed to the burner) for a few hours. The amazing result is that NCG burning has no influence on NO<sub>x</sub> concentration. If the ammonia fed through the NCG burner would be added as NO to the boiler flue gas NO<sub>x</sub>, it should cause an increase of 100–200 mg/m<sup>3</sup>n. The results with other boilers where the NCG burner is installed below the liquor guns are also in agreement with this result.

The probable explanation to the result that NCG ammonia does not increase the RB flue gas NO<sub>x</sub> concentration is the reactions between the nitrogen species originated from liquor and NCG. The nitrogen species in black liquor are released as ammonia from the liquor droplets in the furnace /2/. As a result, the reducing lower furnace contains considerable amounts of ammonia. The NCG burner oxidizes the NCG ammonia mostly to NO. Thus the NCG burner feeds NO to an atmosphere containing ammonia. As is well known, ammonia (NH<sub>3</sub>) and NO can react mutually yielding molecular nitrogen and water. This is known as the “SNCR reaction” applied to reduce NO<sub>x</sub> emission by feeding SNCR reagent (usually ammonia) into the upper furnace. In the case of NCG incineration, the NO from the NCG burner works as a reagent, and ammonia as the compound to be reduced. As a result this “reversal SNCR reaction” can reduce both the NO formed in the NCG burner and the ammonia released from the black liquor. Theoretically, it would be possible to achieve even lower recovery boiler NO<sub>x</sub> emission by incinerating ammonia containing gases than without those gases. Anyway, in the measured case the NCG ammonia is incinerated without any additional NO<sub>x</sub> emission.



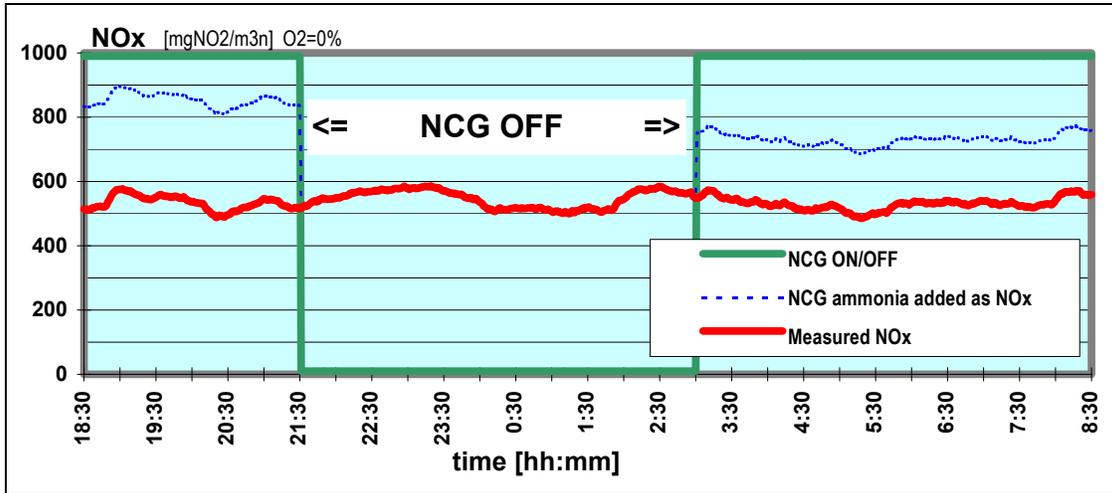
**Figure 2.** The mass size distribution of dust measured before ESP using low pressure impactor in two operation conditions: 1) the NCG burner in operation and 2) The NCG burner not in operation (no NCG feed to the boiler).



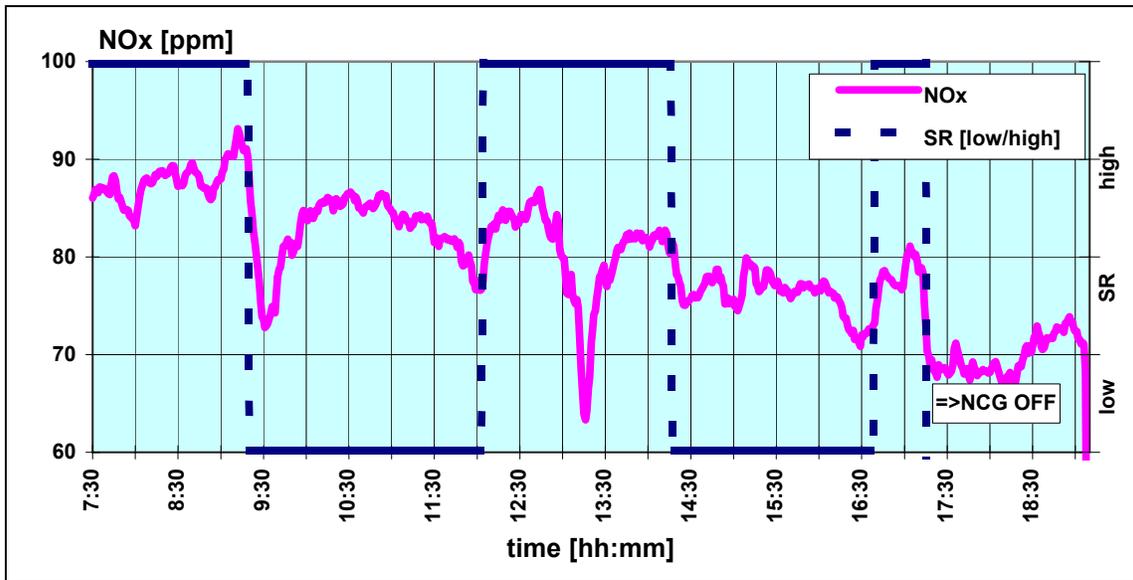
**Figure 3.** The molar ratio of sulfate (SO<sub>4</sub>) and alkalis (Na+K) as a function of particle size based on the analysis of the same impactor samples which were used in the size distribution results in figure 2.

If the burner is installed in an essentially upper position than in the case described above, the circumstances concerning the NCG NO<sub>x</sub> formation tendency are different. The ammonia released from liquor is mostly oxidized at the level where the NO<sub>x</sub> generated in the burner meets the nitrogen species originated from black liquor. Thus the NCG ammonia should be added to the boiler NO<sub>x</sub> emission. However, there is a possibility to use NCG as a “reburning fuel” to decrease the NO<sub>x</sub> emission /10/. Theoretical calculations /11/ show that this method can nearly compensate the additional NO<sub>x</sub> emission caused by typical NCG ammonia concentrations. To find out the effect of NCG as a reburning fuel, experimental trials were carried out at a boiler where NCG burner was installed between the liquor guns and tertiary air register. In normal operation, the air ratio of the burner is >1 and thus no reburning fuel is fed into the furnace from the burner. When stoichiometric air ratio of the burner is switched to a sub-stoichiometric air ratio, the burner feeds unburned gas into the furnace, where the gas is capable to function as a reburning fuel. **Figure 5** shows the result of experimental trials, when the air ratio has been switched between 1.2 and 0.5. The transients in the NO<sub>x</sub> level are weaker in the later part of the period. The reason for this is that the odor gas and the methanol (support fuel) load of the burner is decreased during the experiment. The resulting change in NO<sub>x</sub> concentration is in agreement with the theoretical calculations. At the end of the trial, the burner was switched off by

the control system due to exhausting of the support fuel. This transient shows the influence of the NCG ammonia on the NO<sub>x</sub> emission in this case. As a result, the reburning effect can nearly eliminate the NO<sub>x</sub> increase caused by the additional ammonia load with odor gases.



**Figure 4.** The measured NO<sub>x</sub> concentration in the flue gas of the recovery boiler. The NCG burner is installed at the secondary air level. During the measurement period the NCG burner is switched OFF for 5 hours. The upper curve is calculated by adding the NCG ammonia fed to the furnace as NO<sub>x</sub> to the measured NO<sub>x</sub> values.



**Figure 5.** The measured NO<sub>x</sub> concentration in the flue gas of the recovery boiler. The NCG burner is installed between the liquor guns and the tertiary air level. During the measurement period the stoichiometric air ratio is switched between 1.2 and 0.5. Finally the burner is switched OFF.

## CONCLUSIONS

NCG incineration in a recovery boiler furnace has several advantages: 1) Sulfur is recovered to green liquor, 2) the heating value of NCG is recovered to steam, 3) the big recovery boiler furnace can easily tolerate the changes of the

relatively unstable NCG load, 4) the solution is simple and cost-effective, because the recovery boiler exists in any case.

Sulfur is recovered to ash, if the carbonate amount of ash is sufficient to bind the sulfur in the NCG burned. The measurements show that there are no kinetic limitations of sulfur binding if the burner has been installed at the tertiary air level or lower.

The boiler measurements carried out show as a spin-off result that the sulfation of alkalines in the furnace takes place prior to dust particle formation. This is a relevant result concerning the basic combustion chemistry of black liquor, supporting the argument that the sulfation of vaporized alkali compound initiates dust formation in a recovery boiler furnace.

The NCG gases may contain relative high concentrations of ammonia, having potential to increase the total NO<sub>x</sub> level of the mill when incinerated. If the burner is installed in the lower furnace below the liquor guns, the reaction between the ammonia originated from the liquor and NO formed in the NCG burner reduces the total NO<sub>x</sub> level of the boiler. In the case of the measured boiler, this reduction gives such a result that the odor gas ammonia does not increase the recovery boiler NO<sub>x</sub> concentration at all. Theoretically, it is possible that the odor gas ammonia can even decrease the recovery boiler NO<sub>x</sub> emission compared to the situation with no NCG incineration in the boiler.

If the NCG burner is installed above the liquor guns, the majority of the ammonia originated from black liquor has oxidized and the mutual reaction with the burner NO<sub>x</sub> is not significant any more. Thus, the NO<sub>x</sub> generated in the NCG burner accumulates to the boiler NO<sub>x</sub> emission. However, feeding the NCG directly (without a burner) into the boiler or operating the burner with sub-stoichiometric air ratio decreases the NO<sub>x</sub> level by the reburning effect. In the measured boiler, this reburning effect can nearly compensate for the increase caused by the additional NO<sub>x</sub> from NCG ammonia.

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