

# Cascades Mill Uses Atomized $\text{ClO}_2$ to Oxidize TRS, Optimize NCG Treatment

TRS is being reduced by atomizing a fresh solution of 10-g/l  $\text{ClO}_2$  directly into the kraft mill's NCG duct, significantly reducing odorous emissions.

By ANDRÉ NORMANDIN, LUC BELLEY, AND JACQUES LÉVESQUÉ

The characteristic odor of an operating kraft pulp mill is due to the total reduced sulfur (TRS) in non-condensable gases (NCG) that emanate from various pulping equipment vents. Digesters, blow tanks, and evaporators produce NCG with high concentrations of TRS, whereas mechanically ventilated equipment such as brown stock washers, vibrating screens, and foam tanks produce NCG with low concentrations of TRS (usually the largest volume of gases produced).

Traditional NCG treatment involves oxidation of TRS using heat, either by injecting the gases into the lime kiln, recovery boiler, or dedicated incinerator. However, incinerating these gases has several drawbacks, such as the risk of inhaling toxic fumes (air tightness of existing boilers), risks of explosion, personnel reluctance, complexity of security systems required to ensure the injection of such gases in the ovens or process boilers, and high boiler operation and modification costs.<sup>1,2</sup>

Also, because NCG incineration costs can be relatively high, alternate methods were developed by some mills in the early 1970s<sup>3</sup> as well as several equipment manufacturers who specialized in industrial emissions treatment<sup>4,6</sup> and research centers such as Paprican.<sup>5</sup> These methods involve chemical oxidation of contaminants in the NCG stream using powerful oxidizers such as sodium hypochlorite or chlorine dioxide, readily available at mills with onsite pulp bleach plants.

Such a technique, for example, was successfully implemented at the Nexfor Fraser Paper mill in Thurso, PQ, Canada.<sup>7</sup> At this mill, NCG gases to be treated are mixed with gases coming from the bleach plant washer

vent, in order to use the residual oxidizer present in these gases to oxidize contaminants in the gas phase.

This article describes an innovative TRS chemical oxidizing technique involving chlorine dioxide atomization that was recently implemented at the Cascades Fjordcell mill in Jonquière, PQ, Canada. Working with Mesar/Environair Inc., the Fjordcell mill designed a program to optimize its existing NCG treatment system and reduce emissions coming from its sewer mixing box, even though such processes are not yet under the sulfate pulp plant regulations of the Québec province.<sup>8</sup>

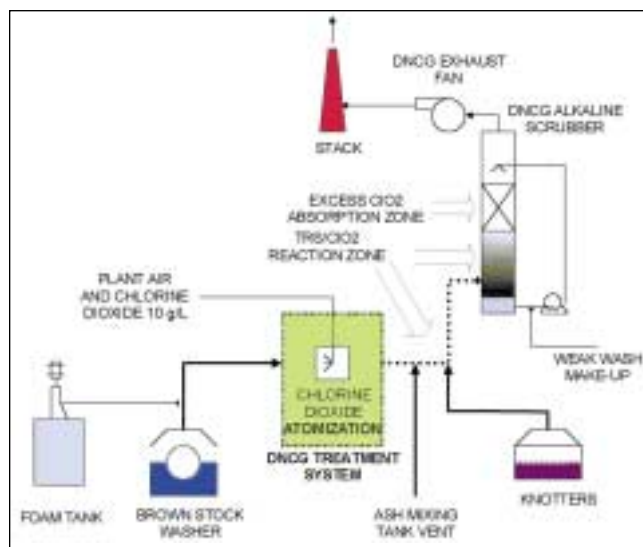
This article demonstrates the simplicity and low cost of such an approach compared with the traditional method of TRS treatment for kraft pulp mills having integrated bleaching processes.

## Diluted NCG System

Fjordcell's process involves oxidation of TRS contained in diluted NCG coming from the mill. Four vents in particular are covered by the regulations on sulfate pulp plants, and the diluted NCG produced by these vents is atomized with a solution of 10 g/l of chlorine dioxide (see Figure 1).

Originally, the diluted NCG system was an alkaline scrubber using E<sub>o</sub>P effluent coming from the bleaching process, which contained residual peroxide. Recently, the capacity of the diluted NCG system was increased, as the amount of TRS coming from the process had increased as well, and there had been modifications to the system (DNCG fiber filter).

Four NCG sources are treated—vents from the vibrating screens, from the foam tank, from the ash mixing tank, and from the brown stock washers.



**Figure 1.** Process diagram of TRS-diluted NCG collection, transport, and oxidation system for the Cascades Fjordcell kraft mill, in Jonquière.

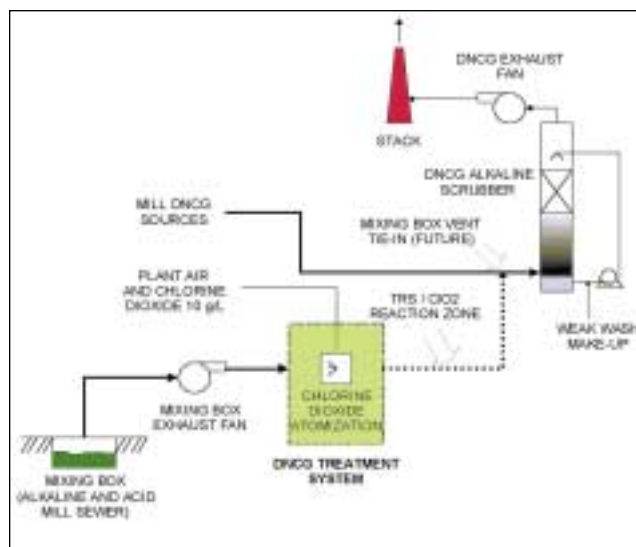
The duct that is common to the vents from the washer, from the foam tank, and from the ash mixing tank is connected to vents from the vibrating screens. The duct that is then common to all four sources is connected to the existing diluted NCG scrubber. The connecting point for the injection of chlorine dioxide has been installed as far away as possible from the entry point of the NCG scrubber, and the scrubber has been modified to optimize contacting time of the chlorine dioxide.

The spraying as such is done using a compressed air nozzle. Such a nozzle can spray a solution in fine droplets of a diameter as small as 5 to 50 microns. Chlorine dioxide is injected when a vacuum confirmation signal is sent along the diluted NCG duct. The vacuum is necessary to ensure that there are no dioxide emissions leaking into this sector of the plant

### NCG from Sewer Mixing Box

Figure 2 illustrates the piping that was added for the oxidation tests on NCG emanating from the sewer mixing box, except for the existing connection to the NCG scrubber. The tie-in to the scrubber will be performed when a permanent chlorine dioxide injection system is installed on that vent.

For the trials, a nozzle was mounted on a 175-ft-long 12-in.-dia temporary duct installed at the discharge point of the existing fan in order to allow sufficient contacting time between the vent gases and the oxidizer.



**Figure 2.** Diagram of the TRS collection, transport, and oxidation system process from the sewer mixing box vent.

For the trials, the diluted NCG injection system was bypassed so that an experimental nozzle could be fed to obtain the minimal required data to size a permanent treatment system

### Materials, Method

During the trials, an external firm took samples of TRS at the outlet point of the modified NCG scrubber. This was done using an impinger and a heated gauge, following the EPA 16A method.

Sampled gases were continuously analyzed using an NDUV Bovar series 900 (TRS>10 ppmv) and an analyzer Monitor Lab 8850 (TRS<10 ppmv). A gas cylinder containing hydrogen sulfide (9.9 ppmv), provided by Air Liquide, was used for the calibration of the analyzers.

Chlorine dioxide residual concentrations were measured by an external firm. The total chlorine was measured using the NCASI No. 520 method.

One essential condition for success when using chlorine dioxide is the stability as well as the quantity of available reagent for TRS oxidation. Consequently, the first step in evaluating such an approach involves estimating the required amounts of oxidizer to get a clear picture of the economic viability of the treatment process.

However, according to previous work by Paprican<sup>5</sup> and the stoichiometry of the reactions involved, the theoretical amount of oxidizer required to achieve a complete conversion of the TRS depends on the compound to be

oxidized. The molar proportions of required chlorine dioxide are 8:1, 2:1, 1:1, and 2:1, for H<sub>2</sub>S, CH<sub>3</sub>SH, CH<sub>3</sub>SCH<sub>3</sub>, and CH<sub>3</sub>SSCH<sub>3</sub>, respectively. Table 1 illustrates the means to establish the theoretical required quantity of chlorine dioxide as a function of the relative proportion of each compound.

Compound (Basis: 1 lb TRS)	TRS %	Qty mole/hr	ClO <sub>2</sub> required	ClO <sub>2</sub> mole/hr
H <sub>2</sub> S	5	1.47	8:1	11:8
CH <sub>3</sub> SH	10	2.94	2:1	5.9
(CH <sub>3</sub> ) <sub>2</sub> S	70	20.59	1:1	20.6
(CH <sub>3</sub> S) <sub>2</sub>	15	2.21	2:1	4.4
<b>Total (2.9 lb ClO<sub>2</sub>/lb TRS as H<sub>2</sub>S)</b>				<b>42.6</b>

Table 1. Example of estimation for the amount of chlorine dioxide required to oxidize TRS.

### Trial Results—Diluted NCG System

Figure 3 below presents the results obtained before and after chlorine dioxide injection. It should be noted that despite fluctuations in the process, the TRS concentrations remained stable, about 50% below the current norm of 10 ppmv.

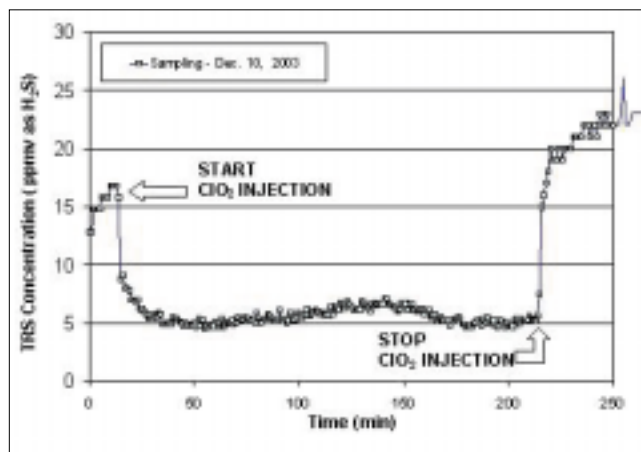


Figure 3. Concentration of TRS in diluted NCG with and without chlorine dioxide treatment.

Table 2 illustrates results of the main trials run with variations in the solution flow. It becomes apparent from this table that TRS conversion is directly proportional to the flow of chlorine dioxide and that destroying 75% of the TRS was enough to comply with the current 10 ppmv norm.

Trials	Flow ClO <sub>2</sub> (l/min)	TRS (ppmv)	Conversion (% mole)
<i>Diluted NCG System</i>			
<b>Trial No. 1</b>	10.4	5.0	75
<b>Trial No. 2</b>	8.5	11.3	55
<b>Trial No. 3</b>	4.8	15.0	32
<i>Sewer Mixing Box Vent</i>			
<b>Trial No. 4</b>	4.7	92.0	73

Table 2. Concentration and conversion of TRS as a function of the chlorine dioxide solution flow at 10 g/l.

It should be noted that the relationship between the flow of chlorine dioxide and the final TRS concentration (and the molar conversion) is linear. The objective in reducing TRS at Jonquière was not to obtain 100% conversion, but rather to conform to established norms and to reduce malodorous emissions.

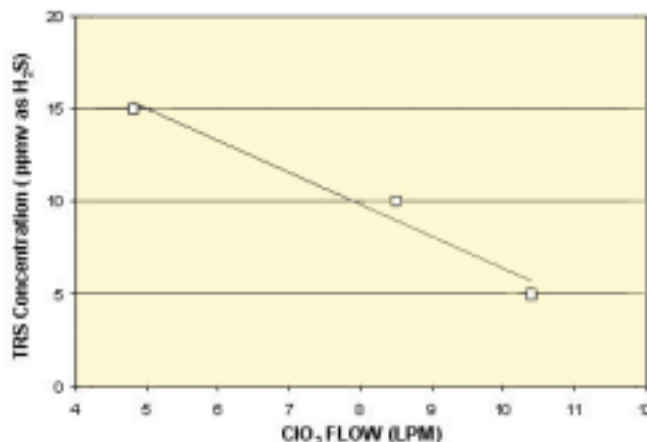


Figure 4. Concentration of TRS in the diluted NCGs as a function of the flow of injected ClO<sub>2</sub>.

### Trial Results—Mixing Box Vent

Figure 5 shows results obtained after injecting chlorine dioxide in the sewer mixing box vent. There is a significant impact, with the TRS concentration going from 320 to 92 ppmv in less than 3 min, which represents a 73% drop in TRS.

As a reminder, the trials on the sewer mixing box vent were not intended to optimize the process, but to obtain minimal design data in order to size a permanent installation for the treatment of these gases. Further, it was observed that the reagent consumption was 2.5 lb of ClO<sub>2</sub>/lb of TRS, or 15% less than the theoretical predic-

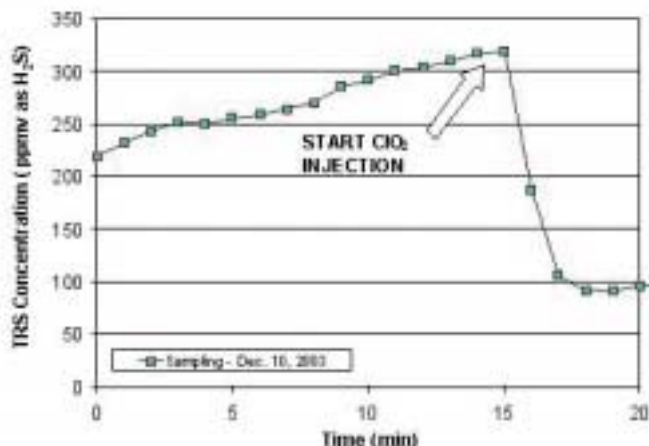


Figure 5. Concentration of TRS in the NCG emanating from the sewer mixing box.

tion. This can be explained by taking into account the dominant presence of DMS in the gases. Each mole of this compound only requires a single mole of oxidizer.

### Conclusion

TRS chemical oxidation treatment of a diluted NCG system was successfully implemented at the Cascades Fjordcell plant in Jonquière. The treatment system, which involves injecting a fresh solution of chlorine dioxide in the contaminated gases, has very low operating costs compared with the traditional incineration approach, as shown in Figure 6.

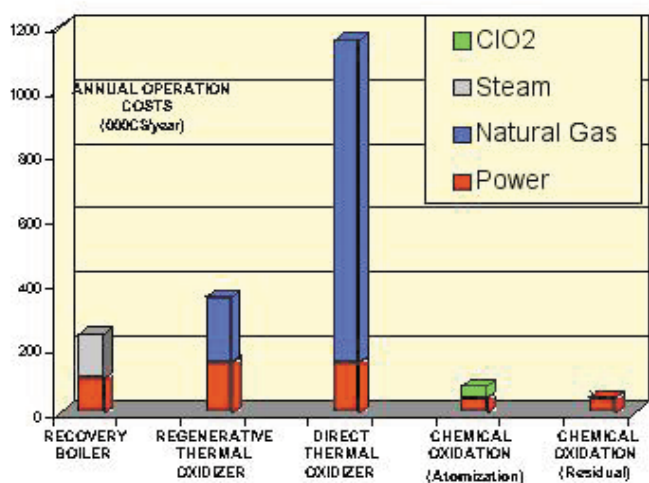


Figure 6. Comparison of required annual operating costs to treat 30,000 scfm of TRS in diluted NCG.

The biggest expense is fuel in the case of dedicated incinerators. Vapor costs are second in importance, as vapor is necessary to condition the gases before introducing them in the recovery boiler. The main proportion of capital investment is in piping connections, because significant costs are necessary when modifying the boiler to incinerate the contaminated gases, or worse, when the mill is forced to acquire a dedicated incinerator.

Conditions favorable to the implementation of such new technology include the presence of a bleaching process on the mill site, which is the case for many mills, as well as the presence of a bleaching alkaline scrubber, which allows the capture of residual oxidizer vapors in the chemically treated gases.

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