

# CHEMICAL OXIDATION OF TRSs USING RESIDUAL CHLORINE DIOXIDE IN A KRAFT PULPING PLANT.

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## RÉSUMÉ

Une technique innovatrice de destruction des sulfures réduits totaux (SRT) a été pilotée par PAPRICAN et adaptée à pleine échelle par MESAR/ENVIRONAIR au traitement des gaz non condensables (GNC) dilués de l'usine de pâte Kraft de Nexfor, à Thurso. Le projet consistait à la collecte, au transport et au traitement des événements de GNC dilués de la pulperie. La réduction des SRT contenus dans les gaz se fait par mélange de ces gaz avec ceux en provenance des événements de l'atelier de blanchiment. Les essais pilotes ont montré que le dioxyde de chlore résiduel contenu dans les gaz du blanchiment était suffisant pour réduire la charge de SRT contenue dans les gaz malodorants de manière à ce que les concentrations de ces contaminants soient conformes à la réglementation. Les conversions de SRT obtenues à pleine échelle ont confirmé ces résultats. Pour couvrir les périodes d'arrêt de l'atelier de blanchiment, un système de relève a de plus été installé.

## ABSTRACT

An innovative technique to oxidise total reduce sulphide (TRS) was conducted by PAPRICAN, and then implemented on full scale basis by MESAR/ENVIRONAIR to treat diluted non-condensable gas (DNCG) at Kraft mill of Nexfor, Thurso. The project was the collection, transport and treatment of vents containing DNCG at pulp mill. The main reduction reaction of TRS contained in gas is performed by gas mixing with those coming from bleach plant vent. Pilot scale trial have shown that residual chlorine dioxide contains in bleach vent was sufficient to reduce SRT load under the regulation requirements. Full scale SRT conversion have confirmed these results. To cover periods where bleach plant is shutdown, a backup system is installed, but results are to be confirmed.

## INTRODUCTION

The total reduced sulfides (TRSs) present in non-condensable gases are partly responsible for the characteristic odour of Kraft pulping plants. These odours mostly originate from the vents associated to pulp production equipment such as digesters, blow tanks and washers, or to the equipment used for the black liquor recovery. Since the early 90's, the Canadian provinces, and more recently the USA<sup>1</sup>, have implemented regulations that force Kraft pulp manufacturers to collect and treat all plant vents containing TRSs.

The traditional approach for treating these gases consists in incinerating them, either in a lime kiln, in the plant boilers, or in a dedicated incinerator. However, thermal incineration of NCGs has several drawbacks, such as the risk of toxic gases inhalation (leakage points on existing boilers due to their age), explosion risks (several cases of boiler explosion following the introduction of TRSs have been reported), reluctance of the operating personnel, complexity of the security devices necessary to ensure safe injection of those gases into kilns or process boilers, high operating costs, and high boiler modification costs. The reader can find additional information about traditional incinerating methods and technologies in more fundamental papers<sup>2,3,4</sup>.

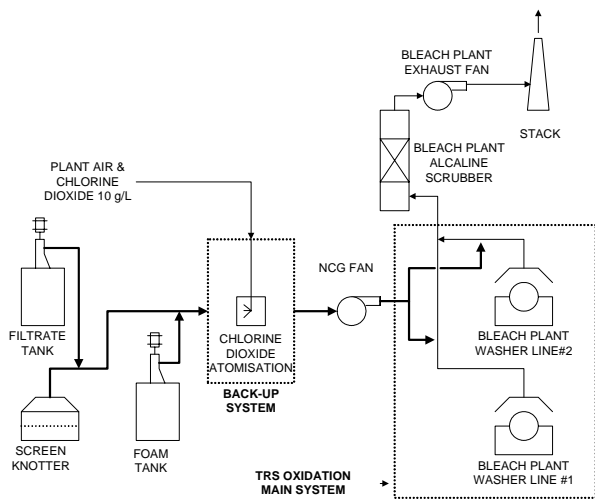
In addition, alternate approaches have been developed by certain equipment manufacturers specialized in the treatment of industrial emissions. These approaches consist in chemically oxidizing the contaminants contained in the NCGs using powerful oxidizers such as sodium hypochlorite or chlorine dioxide, used for pulp bleaching, thus available on site at plants equipped with a bleaching process.

One of these techniques consists in mixing the TRS-laden gases with the gases coming from the bleaching process vents, in order to make use of the residual oxidants contained in the bleaching gases to oxidize the contaminants. The entire process takes place in gas phase. The technical feasibility of this approach was shown by PAPRICAN during pilot tests performed at the Domtar plant in Cornwall, ON in 1999. The technique was then implemented as a full-scale process by MESAR/ENVIRONAIR at the Nexfor Papier Fraser plant in Thurso, QC.

The goal of this article is to describe the oxidation techniques implemented at the Nexfor plant in Thurso, in order to emphasize the simplicity and the low cost of this chemical alternative in comparison to more traditional approaches for treating TRSs, for plants operating a bleaching process.

## DESCRIPTIVE DATA

The problem consists in oxidizing the TRSs present in the diluted NCGs emitted by the plant, that is three vents subject to the local regulation on sulfate pulp plants, by using the residual chlorine dioxide present in the vent gases from the bleaching plant. The process is shown on the process diagram of Fig. 1.



**Figure 1-Process Diagram Showing the Diluted NCG Collection, Transport and Oxidation System at the Nexfor Plant, in Thurso, QC.**

The three NCG sources that must be treated are the vibrating screen vent, a filtrate tank vent and the vent from the plant foam tank.

The vibrating screen and the filtrate tank are connected on a common vent duct. This duct is then connected to the vent duct from the foam tank. This new main vent duct is connected to the existing bleaching ducts, upstream from the alkaline scrubber. The NCG flow was evenly distributed between the two bleaching vents in order to optimize the usage of the residual oxidizer.

In order to minimize the amount of dilution air entering through the knotted hood, the hood was reconfigured and closed around the knotted.

Automatic valves were installed in order to either allow collecting the NCG sources and sending them to the treatment system, or send them directly into the atmosphere, in case of an emergency.

Finally, vacuum breakers were added in order to protect the tanks against a high vacuum, and balancing louvers and pressure gauges were installed to adjust the vacuum level at the sources on system start-ups.

A new NCG fan was installed to transport the gases to the bleaching vent ducts, upstream from the alkaline scrubber. This fan was equipped with a variable frequency drive set to

generate an adequate vacuum on the NCG collection duct. The static pressure at the outlet of the fan is sufficient to allow a homogenous mixing of the NCGs with the bleaching process gases. The tie points on the bleaching ducts are located as far as possible from the inlet flange of the alkaline scrubber so that the residence time of the gases in the duct is sufficient to reach a nearly complete oxidation of the TRSs according to the pilot tests performed by PAPRICAN prior to the installation of the system.

The gas treatment system described above is operational as long as the bleaching process is in operation. When the bleaching process is down, a backup system is activated. The backup system consists in the injection of a fresh chlorine dioxide solution (10 g/L) directly into the duct, at the inlet of the new fan in order to achieve proper mixing. A metering pump is used for the liquid injection and atomization is performed with a compressed air nozzle. This type of nozzle can atomize a solution by producing droplets as small as 5-50 microns in diameter. Chlorine dioxide injection is initiated by a signal confirming that the bleaching process is not operating and remains active until the NCG system receives confirmation that the bleaching process is operating again.

## MATERIAL AND METHOD

For pilot tests, volumes of gas were sampled at the foam tank vent using a 6-mm Teflon tube and put into 10-L Tedlar bags. They were analyzed by a portable chromatograph (PE Photovac, Voyageur GC) equipped with a photoionization detector (PID) for identifying and quantifying individual TRSs. A gas cylinder containing hydrogen sulfide (19.0 ppm), methyl mercaptan (24.1 ppm), DMS (22.9 ppm) and DMDS (20.7 ppm), obtained from Matheson, was used to calibrate the chromatograph.

For full-scale tests, the plant technical services sampled the NCGs at the source vents and at the outlet of the bleaching plant scrubber, using an impinger equipped with a heated probe, according to EPA method 16A. All procedures were duplicated by an external firm which performed the same measurements using the same method.

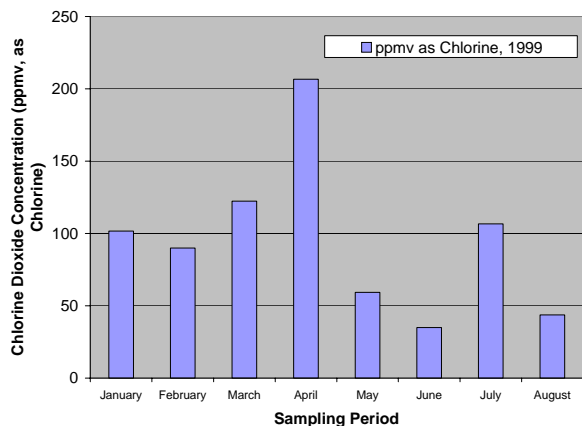
Residual chlorine dioxide concentrations were measured by the plant technical services, along with their routine measurements of the bleaching scrubber efficiency. Total chlorine was measured according to NCASI method #520.

## RESULTS

### *Determination of the Required Amount of Oxidizer*

One essential condition for the success of using residual chlorine dioxide from the bleaching process is the stability and availability of this reagent for the oxidation of the TRSs. Thus, the first step in evaluating this approach consists in analysing the trends in the concentration of chlorine dioxide over a relatively long period of time in order to make sure that there is always a sufficient available excess of this reagent for the reaction.

Figure 2 shows the evolution of the residual chlorine dioxide concentration at the inlet of the bleaching alkaline scrubber between January and August 1999, that is before the system was implemented.



**Figure 2- Residual Concentration of Chlorine Dioxide in the Vent Gases from the Bleaching Plant.**

According to the data illustrated in Figure 2, the average residual chlorine dioxide concentration is around 70 ppmv (90 ppmv as chlorine). The minimal value over the sampling period is around 35 ppmv, which is a third of the average concentration.

Since the gas flow rate from the bleaching process is 31 500 Nm<sup>3</sup>/h, calculations indicate that the molar flow rate of chlorine dioxide is 91 mol/h.

However, according to previous research by PAPRICAN and to the stoichiometry of the reactions involved, the amount of oxidizer theoretically required to achieve complete conversion of the TRSs depends on the compound that must be oxidized. The molar ratios of chlorine dioxide required 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 shows the calculation of the amount of chlorine dioxide required to treat the gases from the foam tank vent. One can infer that to treat the TRSs from the foam tank, 12 ppmv of chlorine dioxide are necessary, which corresponds to one fifth of the total available amount.

**Table 1- Calculation of the Amount of Chlorine Dioxide Required to Chemically Oxidize TRSs.**

Compounds	[SRT] ppmv	Qte mol/h	ClO <sub>2</sub> required	ClO <sub>2</sub> mol/h
H <sub>2</sub> S	3.3	0.24	8:1	1.96
CH <sub>3</sub> SH	15.2	1.13	2:1	2.26
(CH <sub>3</sub> ) <sub>2</sub> S	105	7.79	1:1	7.79
(CH <sub>3</sub> S) <sub>2</sub>	105	7.79	1:1	7.79

### Results of Pilot Tests

Pilot tests were conducted in March 1999 at the Thurso plant in order to confirm the reaction velocities as well as the TRS conversions in the presence of the residual oxidizer contained in the bleaching process vent in the field.

Thus, samples of gases from the foam tank vent and from the bleaching process vent were taken and stored in Tedlar bags before being mixed with one another in volumetric ratios similar to the ratio of the flow rates of the gases to be mixed in continuous process.

Table 2 shows the results of the three tests.

**Table 2- Pilot Tests for the Reduction of TRSs at the Vent from the Foam Tank.**

Test	Dilution V/V	Time sec	TRS Reduction (mole %)			
			H <sub>2</sub> S	CH <sub>3</sub> SH	DMS	DMDS
#1	10:1	2.0	100.0	96.7	99.7	100.0
#2	5:1	2.0	100.0	97.7	99.8	100.0
#3	10:1	0.8	100.0	96.7	99.9	100.0

One can see, from these results, that the obtained TRS conversions are superior to 98%. Under the experimental conditions of the tests, the ratio of volumes mixed did not have a significant impact on the conversions, which can be explained by the important excess of chlorine dioxide, as was previously shown.

### Results of the Full-Scale Tests

The diluted NCG treatment system at the Thurso plant was commissioned at the fall of 2002, and the first sampling campaigns were performed over the weeks following the initial start-up.

Table 3 shows the TRS concentrations measured at the sources and at the outlet of the bleaching alkaline scrubber, when the bleaching process is in operation.

**Table 3- Reduction of the TRS at the Outlet of the Alkaline Scrubber by Oxidation with the Residual Oxidizer from the Bleaching Process.**

Test	[SRT] before ppmv	[SRT] after ppmv	Conversion % mol
#1	53.0	3.0	75
#2	-	2.7	79
#3	-	1.2	N/A

One can see that the TRS concentration decreases after mixing with the gases from the bleaching process. The decrease in

concentration is due to the dilution resulting from the low NCG flow (6 290 Nm<sup>3</sup>/h) mixed with the bleaching gases (31 500 Nm<sup>3</sup>/h), and to the reaction with the residual chlorine dioxide. In Table 3, the effect of the dilution was eliminated for the purpose of the calculations.

All measurements were taken while all TRS sources were vented to the atmosphere (test #1). In this situation, the TRS concentration is not zero, and results from the fact that the plant uses strong white liquor as a caustic make-up into the alkaline scrubber. Thus, the measured 1.2 ppmv TRSs at the outlet of the alkaline scrubber comes from the desorption of H<sub>2</sub>S from the white liquor. The conversions indicated in Table 3 take this residual concentration into account.

At the time this paper was submitted, the results of the TRS concentrations measured at the sources and at the outlet of the bleaching alkaline scrubber (with the backup system taking over when the bleaching process was not in operation) were not available.

However, the expected results should be at least equivalent to those shown above, since the added amounts of chlorine dioxide are controlled, and the residence time as well as the quality of the gas mixing are superior to those of the main system. These conclusions should be confirmed during the course of next spring.

## CONCLUSION

A diluted NCG treatment system based on the chemical oxidation of the TRSs was successfully implemented at the Nexfor Papier Fraser plant in Thurso, QC. The main treatment system, which consists in mixing the contaminated gases with the gases coming from the bleaching washers, offers a zero-cost alternative to the traditional approach of incineration. The capital investment is limited to piping connections, whereas important costs are involved when a boiler has to be modified for the incineration of the contaminated gases, or worse, when the plant is forced to purchase a dedicated incinerator.

The conditions in favor of the implementation of this new technology are the presence of a bleaching process on the

plant site, which is the case for several plants, and the presence of a bleaching alkaling scrubber, which makes possible the captation of the residual oxidizer vapors in the chemically treated gases.

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