**PROCESSES IN WOOD, PAPER PULP, FOOD, DRINK** 

(Neutral Sulphite Semi-Chemical Process)

09 01 xx

In addition to more conventional fuels such as wood/bark, coal, oil and natural gas, boilers at pulp and paper mills may combust non-condensable gases, small quantities of wastewater treatment sludge (from both virgin pulp and recycle operations), non-recyclable recovered paper, tire-derived fuel, old corrugated container materials etc. (NCASI 1993)

It is assumed that these non-conventional fuels that are combusted in boilers will be covered somewhere in SNAP group 03.

This section is under review by Scandinavian participants. Changes are anticipated as more information becomes available. These will be incorporated in a future edition of this manual.

Emission Inventory Guidebook

Waste water treatment

# Pulp and paper production has three major processing steps: pulping, bleaching, and paper

**ACTIVITIES INCLUDED** 

production. The type of pulping and the amount of bleaching used depend on the nature of the feedstock and the desired qualities of the end product. Neutral sulphite semi-chemical pulping (NSSC) is one of the chemical pulping processes that can be used. It involves partial delignification of hardwood feedstock using a buffered sodium sulphite solution, with completion of the pulping process by mechanical means. NSSC pulps are used in corrugating media and in certain writing and printing papers.

Not all neutral-sulphite pulping and related processes that could result in the emission of significant amounts of NMVOC, SOx, particulates, NOx and CO are included under SNAP code 040603. Other significant sources are listed in Table 1.

#### Other Relevant SNAP Codes for Paper Pulping - Neutral Sulphite Semi-Table 1:

Chemical Process					
Source	SNAP CODE				
Combustion in Boilers	03 01 xx				
Paper-mill industry (drying processes)	03 03 21				

**NOSE CODE:** 

**SOURCE ACTIVITY TITLE:** 

**NFR CODE:** 

2 D 1

1

pr040604

**SNAP CODE:** 



Paper Pulp

105.07.03

**AND OTHER INDUSTRIES** 

#### 2 CONTRIBUTIONS TO TOTAL EMISSIONS

Emissions inventoried from neutral sulphite semi-chemical pulp and paper processes are summarized in Table 2.

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO <sub>2</sub>	NO <sub>x</sub>	NMVOC	$\mathrm{CH}_4$	CO	CO <sub>2</sub>	$N_2O$	NH <sub>3</sub>
Paper Pulp (Neurtral Sulphite Semi-Chem. Proc.)	040604	0.1	-	-	-	-	-	-	-

 Table 2:
 Contribution to total emissions of the CORINAIR90 inventory (28 countries)

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)

- = no emissions are reported

This activity is not believed to be a significant source of  $PM_{2.5}$  (as of December 2006).

### **3 GENERAL**

#### 3.1 Description

In the NSSC process, a cooking liquor is used under high temperature and pressure to chemically dissolve the lignin that binds the cellulose fibres of the wood together. The main cooking agent is sodium sulphite, buffered with sodium bicarbonate to maintain a neutral solution. This prevents alkalinity and acidity from degrading the hemicelluloses in the pulp, but also retards delignification. Thus after blowing from the digester, the pulping is completed using mechanical disc refiners. The pulp is then cleaned and thickened and dried for sale as market pulp or further processed into paper products on-site. Spent liquor handling methods vary widely. Options include disposal, recovery of heat and/or chemicals or transfer of the spent liquor to conventional kraft recovery mills for cross recovery.

The Integrated Pollution Prevention and Control Reference Document on Best Available Techniques [IPPC, BREF] (European Commission, 2001) describe the process but not indicate specific emission factors for it. The IPPC BREF document declare that THE dominating sulphite pulping process in Europe is the magnesium sulphite pulping with some mills using sodium as base.

#### **3.2** Definitions

Blowing - evacuation of a vessel (the digester) under pressure.

#### 3.3 Techniques

The main process steps involved in neutral sulphite semi-chemical pulping are briefly described below. It should be noted that significant emission sources for this process are inventoried under separate SNAP codes (see section 1).

**Digestion** Digestion is carried out under high pressure and high temperature, in either batch mode or continuous digesters, in the presence of a buffered sodium sulphite cooking solution

(liquor). Delignification occurs by lignin sulphonation and hydrolysis. Buffering, usually by the addition of sodium carbonate to the cooking liquor, retards the delignification process. When about half the lignin is dissolved, delignification tends to slow down considerably. The pulp is blown to a blow pit at this point and dewatered. Pulping is completed using mechanical disc refiners. This method achieves yields as high as 60 to 80 percent, much higher than the 50 to 55 percent yields for other chemical processes.

The pulp may then be dried for sale as market pulp or further refined, cleaned and made into paper on-site. Most of the pulp used for the manufacture of printing products is bleached.

**Bleaching** Bleaching chemical pulps is generally complex and uses several chlorine-based chemicals. Strictly speaking, bleaching is part of the paper making process, as opposed to pulping, but has been included under this SNAP code for complete coverage of the pulp and paper industry as a whole.

<u>Chemical Recovery</u> In some NSSC processes, chemical recovery is not practiced. In other cases, NSSC spent liquor is delivered directly to a conventional kraft recovery system, a technique known as cross recovery. This is only feasible when a kraft mill is close by and where chemical losses in the kraft mill warrant cross recovery.

In some cases, however, chemical recovery is practiced on site. Fluidized-bed reactors are used to combust the spent liquors after preconcentration in multiple effect evaporators to 30-35% solids. The inorganic chemicals and sodium organic salts are chiefly oxidized to sodium sulphate and sodium carbonate pellets. This matter is removed from the reactor and can be sold to a kraft mill for use as its chemical make-up, if a suitable market exists.

#### Acid Preparation Plant

In an acid plant, sulphur is normally burned in a rotary or spray burner. The gas produced is then cooled by heat exchangers and a water spray and passed to an absorber tower.

#### 3.4 Emissions and Controls

Particulate emissions are a only potential problem when a fluidized bed reactor is used for chemical recovery. However, particulate controls are usually installed to improve chemical recovery rates, since the particulate is mainly sodium sulphate and sodium carbonate.

Absorbing towers, digester/blow tank systems and the recovery furnace are the main sources of  $SO_2$ . These sources are normally controlled with scrubbers.

The fluid bed reactor has been reported as a minor source of NOx and VOCs. Bleaching plants may also be minor sources of VOCs.

#### 4 SIMPLER METHODOLOGY

Due to a lack of emission factors, it is not possible to recommend a simple inventory methodology for neutral sulphite semi-chemical plants at this time.

### 5 DETAILED METHODOLOGY

The preferred methodology would involve the measurement of emissions from each plant to develop site-specific emission factors for all potentially significant sources. These emission factors could then be used to calculate emissions, as required, until such time as the process or emissions controls are significantly changed. At that point, new site-specific emission factors should be derived based on testing.

## 6 RELEVANT ACTIVITY STATISTICS

Emission factors for this sector would normally be based on tonnes of air dried pulp.

### 7 POINT SOURCE CRITERIA

A recent report (Stanley 1993) indicated that one semi-chemical mill emitted 24 Mg of NMVOC. Unfortunately, no production information was supplied for this facility. However, this would seem to indicate that NSSC facilities should be inventoried as point sources if plant specific data are available.

## 8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

There is a very limited data base available for NSSC. No particulate or  $SO_2$  emission factors were found. Available NOx and VOC emission factors (kg/tonne air dried pulp) are summarized in Table 3.

# Table 3:NOx and VOC Emission Factors for Neutral Sulphite Pulping (kg/tonne air<br/>dried pulp)

Source	NOx	VOC	Reference
Sulphur burners/absorbers	0.0*	0.0**	Stockton and Stelling n.d.
Digester/dump tank/blow pit	0.0*		Stockton and Stelling n.d.
Evaporator	0.0*		Stockton and Stelling n.d.
Fluid bed reactor	0.5***	0.1***	Stockton and Stelling n.d.
Bleach Plant		0.05+	NCASI 1993

\* No NOx because of low temperature.

\*\* No apparent source of VOCs.

\*\*\* Factor transferred from kraft mill processes.

This is on an as carbon basis. Range: 0.004 - 0.14 kgg/tonne air dried pulp. Based on tests of one to eleven vents at thirteen sources. The type of pulp is not specified. It was indicated that it was NMVOC. (NCASI 1993).

With the exception of the bleach plant emission factor, all factors would have a quality rating of E.

#### 9 SPECIES PROFILES

#### **10 UNCERTAINTY ESTIMATES**

#### 11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

An emission factor compilation should be done for this sector so that a simpler methodology can be recommended. This database must be detailed enough to accommodate the wide variety of processes that may be present at one of these facilities.

#### 12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Neutral sulphite semi-chemical processes are inventoried as point sources.

#### **13 TEMPORAL DISAGGREGATION CRITERIA**

Neutral sulphite semi-chemical pulping facilities normally run year-round. It may be assumed that emissions occur uniformly over diurnal and annual cycles, barring unusual operational disruptions.

Emission Inventory Guidebook

#### 14 ADDITIONAL COMMENTS

#### **15 SUPPLEMENTARY DOCUMENTS**

#### **16 VERIFICATION PROCEDURES**

#### **17 REFERENCES**

Environment Canada, 1983. AThe Basic Technology of the Pulp and Paper Industry and Its Environmental Protection Practices.@ Training Manual, EPS 6-EP-83-1. Environment Canada, Ottawa.

European Commission (2001), Integrated Pollution Prevention and Control (IPPC), Reference Document on Best Available Techniques (BREF) in the Pulp and Paper Industry, December 2001

National Council of the Paper Industry for Air and Stream Improvement Inc. (NCASI), 1993. AEmission Factors for NOx, SO<sub>2</sub>, and Volatile Organic Compounds for Boilers, Kraft Pulp Mills, and Bleach Plants.@ Technical Bulletin No. 646. February.

Pinkerton, J., 1993. AEmissions of SO<sub>2</sub> and NOx from Pulp and Paper Mills.@ Air & Waste, <u>43</u>: 1404-1407.

Stanley Industrial Consultants Ltd., 1991. ALiterature Survey of NOx/VOC@ Prepared for the Canadian Pulp and Paper Association, Montreal, Quebec.

Stanley Industrial Consultants Ltd., 1993. AEstimates of NOx and VOC Emissions for Canadian Pulp and Paper Mills.@ Prepared for the Canadian Pulp and Paper Association, Montreal, Quebec.

Stockton, M.B., and J.H.E. Stelling, n.d. ACriteria Pollutant Emission Factors for the NAPAP Emissions Inventory, National Acid Precipitation Assessment Program.@ Contract No. 68-02-3994, U.S. Environmental Protection Agency, Office of Research and Development. As cited in Stanley Industrial Consultants Ltd. 1991.

U.S. Environmental Protection Agency (U.S. EPA), 1991. AGeneral Information Document for the Pulp and Paper Industry.@ Draft. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

#### pr040604

U.S. Environmental Protection Agency, 1993. ANational Air Pollutant Emission Trends 1900-1992.@ EPA-454/R-93-032. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

#### **18 BIBLIOGRAPHY**

#### **19 RELEASE VERSION, DATE AND SOURCE**

Version: 1.7

Date: June 2005

- Source: Marc Deslauriers Environment Canada Canada
- Integrated with IPPC BREF information by: Carlo Trozzi Techne Consulting Italy

Updated with particulate matter details by: Mike Woodfield AEA Technology UK December 2006

#### 20 POINT OF ENQUIRY

Any comments on this chapter or enquiries should be directed to:

#### Carlo Trozzi

Techne Consulting Via G. Ricci Curbastro, 34 Roma, Italy

Tel: +39 065580993 Fax: +39 065581848 Email: carlo.trozzi@techne-consulting.com