

**SNAP CODE:** **040603**

**SOURCE ACTIVITY TITLE:** **PROCESSES IN WOOD, PAPER PULP, FOOD, DRINK  
AND OTHER INDUSTRIES  
*Paper Pulp (Acid Sulphite Process)***

**NOSE CODE:** **105.07.02**

**NFR CODE:** **2 D 1**

**1 ACTIVITIES INCLUDED**

Pulp and paper production has three major processing steps: pulping, bleaching, and paper 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. Sulphite pulping is one of the chemical pulping processes that can be used. It involves chemically pulping the wood using SO<sub>2</sub> adsorbed in a base solution. Sulphite pulping produces a weaker paper than some other types of pulping, but the pulp is less coloured, making it more suitable for printing, often with little bleaching.

Not all sulphite pulping and related processes that could result in the emission of significant amounts of NMVOC, SO<sub>x</sub>, particulates, NO<sub>x</sub> and CO are included under SNAP Code 040603. Other significant sources are summarized in Table 1

**Table 1: Other Relevant SNAP Codes for Paper Pulping - Acid Sulphite Process**

Source	SNAP CODE
Combustion in boilers	03 01 xx
Paper-mill industry (drying processes)	03 03 21
Waste Water Treatment	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 red liquor (see section 3 below), small quantities of wastewater treatment sludge (from both virgin pulp and recycle operations), nonrecyclable 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.

## 2 CONTRIBUTIONS TO TOTAL EMISSIONS

Table 2 summarises emissions reported from acid sulphite pulp and paper processes.

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

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO <sub>2</sub>	NO <sub>x</sub>	NMVOC	CH <sub>4</sub>	CO	CO <sub>2</sub>	N <sub>2</sub> O	NH <sub>3</sub>
Paper Pulp (Acid Sulphite Process)	040603	0.2	0	0.1	-	-	-	-	-

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

- = no emissions are reported

**Table 2b: Emissions from Paper Pulping - Acid Sulphite Process**

Country	Particulate		SO <sub>x</sub>		NO <sub>x</sub>		CO		NMVOC	
	Emissions (Mg)	% <sup>1</sup>	Emissions (Mg)	% <sup>1</sup>	Emissions (Mg)	% <sup>1</sup>	Emissions (Mg)	% <sup>1</sup>	Emissions (Mg)	% <sup>1</sup>
Canada (1985)	2163	0.1	32591	0.9	130	<0.0				
United States (1985)			22000							

<sup>1</sup> % of total anthropogenic emissions.

## 3 GENERAL

### 3.1 Description

In the acid sulphite process, a caustic solution (cooking liquor) is used under high temperature and pressure to chemically dissolve the lignin that binds the cellulose fibres of the wood together. The caustic solution is SO<sub>2</sub> adsorbed in a base solution. The bases commonly used are calcium, magnesium, ammonia or sodium. After digestion, the wood pulp is washed and dried for sale as market pulp, or further treated by refining, cleaning and addition of other pulps and chemicals, and made into paper on-site. Depending on the intended use of the product, the pulp may or may not be bleached. Heat and/or chemical recovery may also be done, depending on the cooking liquor used. An acid plant will normally be necessary to supply the mill sulphite requirement.

### 3.2 Definitions

### 3.3 Techniques

The main process steps involved in acid sulphite pulping are briefly described below. It should be noted that some of the main sources for acid sulphite pulping are inventoried under other SNAP codes (see section 1 above). (Environment Canada 1983, U.S. EPA 1985 and U.S. EPA 1991)

**Digestion** Digestion is carried out under high pressure and high temperature, in either batch mode or continuous digesters, in the presence of a sulphurous acid/bisulphite cooking liquid (see acid plant below). The delignification is accomplished by sulphonation and hydrolysis reactions which form soluble ligno-sulphates. When this is completed, the contents of the digester are either discharged at high pressure into a blow pit or pumped into a dump tank at lower pressure. A blow pit is a tank with a finely perforated bottom to allow liquids to drain out while retaining the pulp. A blow tank is commonly an atmospheric cyclone. The spent sulphite liquor (sometimes called red liquor) is drained, and discharged or treated and incinerated or sent to a plant for recovery of heat and/or chemicals.

**Washing** The pulp is then washed with fresh water to further remove dissolved chemicals. This water is usually routed to recovery operations.

**Bleaching** The pulp is produced as a slurry after removal of spent cooking chemicals and dissolved wood organics. Bleaching chemical pulps is generally complex. 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.

**Chemical Recovery** More than a dozen types of recovery systems, using widely different processes, are in operation around the world. The variety of systems for heat and/or chemical recovery is largely due to the variety of cooking bases used.

In calcium base systems, chemical recovery is not practical, and the spent liquor is usually discharged or incinerated. In ammonium base operations, heat can be recovered by combusting the spent liquor, but the ammonium base and sulphur are lost. In sodium or magnesium base operations, the heat, sulphur and base may all be recovered.

The first step in all recovery systems is the concentration of red liquors in a multiple effect evaporator, and possibly a direct contact evaporator, to anywhere from 35 to 60 percent solids, depending upon the type of combustion unit to be used. The liquor is then sprayed into a furnace and burned, producing steam to operate the processes or other power requirements.

When only heat recovery is practiced, the recovery process might actually be considered conventional combustion and inventoried under snap code 03 as mentioned in section 1.

When magnesium base liquor is burned, the combustion products are a carbon-free MgO ash and SO<sub>2</sub>. The gases pass through a series of multiple cyclones where the ash is collected and flushed with water to a retention tank. The MgO slurry is then converted to Mg(OH)<sub>2</sub> in the

slaking system and used for absorption of the SO<sub>2</sub> in a series of venturi scrubbers. The overall chemical recovery of sulphur and Mg(OH)<sub>2</sub> is around 80%.

When sodium base liquor is burned, the inorganic compounds are recovered as a molten smelt containing sodium sulphide and sodium carbonate. This smelt may be further processed and used to adsorb SO<sub>2</sub> from the flue gas and sulphur, or sold to a kraft mill as raw material for producing green liquor. It is not suitable for reuse in sulphite cooking.

**Acid 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 then absorbed in a variety of different scrubbers containing either limestone or a solution of the base chemical. In the past, limestone was used exclusively in the gas absorption tower, serving both as a packing and a chemical source of calcium. More recently, soluble bases such as magnesium, sodium and ammonium are used for environmental reasons as well as improved pulp strength. Before the raw acid is used in pulping it is fortified with relief SO<sub>2</sub> from the digester. The fortification takes place in the low and high pressure accumulators, which are pressurized to increase the solubility of SO<sub>2</sub> in the liquor.

### 3.4 Emissions

SO<sub>2</sub> is usually considered the major pollutant from acid sulphite processes. The digester and blow pit (or blow tank) system is a major source of SO<sub>2</sub>. It is present in the intermittent digester relief gases, as well as in the gases released when the digester is discharged into the blow pit or blow tank. SO<sub>2</sub> is also released from the recovery system, the various pulp washing, screening and cleaning operations, as well as from evaporators and acid fortification towers. (Environment Canada 1983 and U.S. EPA 1985).

Particulate may be released from the absorption system handling the recovery furnace exhaust. Ammonium base systems generate less particulate than do magnesium or sodium base systems. (U.S. EPA 1985)

The recovery furnace is a source of VOCs (Stockton and Stelling n.d.) Bleaching operations may also be minor sources of VOCs. (NCASI 1993)

### 3.5 Controls

Many mills have separate blow tanks, or pits, and emission stacks for each digester. Water showers may be installed in the blow tank vents to control the blowing SO<sub>2</sub> emissions, or a scrubber may be used. The latter may achieve an efficiency of as high as 99 percent. (Environment Canada 1983).

Magnesium, sodium and ammonium base recovery systems all use absorption systems to recover SO<sub>2</sub> from sources such as the recovery furnaces, acid fortification towers and multiple effect evaporators. Generally these recover better than 95 percent of the sulphur for reuse, by scrubbing with the base chemical slurry or solution. (Environment Canada 1983, U.S. EPA 1985)

#### 4 SIMPLER METHODOLOGY

Acid sulphite pulping facilities are inventoried as point sources using total production statistics for each plant in combination with the most appropriate emission factors. Default emission factors are provided in section 8.1.

#### 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 this time, new site-specific emission factors should be derived based on testing.

Reference emission factors for comparison with users own data are provided in Section 8.2.

#### 6 RELEVANT ACTIVITY STATISTICS

Most emission factors are based on the production of air dried tonnes of unbleached pulp.

#### 7 POINT SOURCE CRITERIA

A recent report (Stanley 1993) indicated that six sulphite mills in Canada emitted a total of 456 Mg of NO<sub>x</sub> and 1597 Mg of NMVOC in 1990. Unfortunately, neither a breakdown of this information nor production information was supplied. However, this would seem to indicate that sulphite pulping processes should be inventoried as point sources if plant specific data are available.

### 8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

#### 8.1 Simpler Methodology

A summary of default emission factors for use with the simpler methodology for estimating emissions is provided in Table 8.1.

**Table 8.1 Default emission factors from Paper Pulp (Acid Sulphite Process)**

Pollutant	Emission factor	Units
Particulate matter Total suspended particulate	2	kg/tonne (unbleached dried pulp)
PM10	0.8	kg/tonne (unbleached dried pulp)
PM2.5	0.5	kg/tonne (unbleached dried pulp)
Dioxins and furans	0.07	µg/tonne feed

**8.2 Detailed Methodology**

Long term particulate and SO<sub>2</sub> average emission factors for sulphite pulping are summarized Table 8.2a (U.S. EPA 1985).

**Table 8.2a Particulate and SO<sub>2</sub> Emission Factors for Sulphite Pulping (U.S. EPA 1985)**

Source	Base	Control	Emission Factor (kg/Mg air dried unbleached pulp)		
			Particulate	SO <sub>2</sub>	Rating
Digester/blow <sup>a</sup> pit or dump tank	All	None	neg	5 to 35	C
	MgO	Process Change <sup>b</sup>	neg	1 to 3	C
	MgO	Scrubber	neg	0.5	B
	MgO	Process change/scrubber	neg	0.1	B
	MgO	All exhaust to recovery	neg	0	A
	NH <sub>3</sub>	Process Change	neg	12.5	D
	NH <sub>3</sub>	Process Change/scrubber	neg	0.4	B
	Na	Process Change/scrubber	neg	1	C
	Ca	Unknown	neg	33.5	C
Recovery system <sup>c</sup>	MgO	Multicyclone/venturi	1	4.5	A
	NH <sub>3</sub>	Ammonia absorption/mist eliminator	0.35	3.5	B
Acid Plant <sup>d</sup>	Na	Sodium Carbonate Scrubber	2	1	C
	NH <sub>3</sub>	Scrubber	neg	0.2	C
	Na	Unknown <sup>e</sup>	neg	0.1	D
	Ca	Jenson Scrubber	neg	4	C
Other <sup>f</sup>	All	None	neg	6	D

Notes

- a. Factors represent emissions after cook is completed and when digester contents are discharged into blow pit or dump tank. Some relief gases are vented from digester during cook cycle, but these are usually transferred to pressure accumulators and SO<sub>2</sub> therein reabsorbed for use in cooking liquor. In some mills, actual emissions will be intermittent and for short periods.
- b. May include such measures as raising cooking liquor pH (thereby lowering free SO<sub>2</sub>), relieving digester pressure before contents discharge, and pumping out digester contents instead of blowing out.
- c. Recovery system at most mills is closed and includes recovery furnace, direct contact evaporator, multiple effect evaporator, acid fortification tower, and SO<sub>2</sub> absorption scrubbers. Generally only one emission point for entire system. Factors include high SO<sub>2</sub> emissions during periodic purging of recovery systems.
- d. Necessary in mills with insufficient or no recovery systems.
- e. Control is practiced, but type of system is unknown.

f. Includes miscellaneous pulping operations such as knotters, washers, screens, etc.

These emission factors are cited as being from: Background Document: Acid Sulfite Pulping. EPA-450/3-77-005.U.S. EPA January 1977.

A recent publication from the Canadian Pulp and Paper Association (Stanley 1991) summarized available NOx and VOC emission factors from Stockton and Stelling n.d.: as provided in Table 8.2b.

**Table 8.2b NOx and VOC Emission Factors for Sulphite Pulping (Stockton and Stelling n.d.)**

Source	Base	Control	Emission Factor (kg/tonne air dried pulp)		
			NOx	VOC	Rating
Acid Plant	NH <sub>3</sub>		0.0 <sup>a</sup>	0.0 <sup>b</sup>	
	Na		0.0 <sup>a</sup>	0.0 <sup>b</sup>	
	Ca		0.0 <sup>a</sup>	0.0 <sup>b</sup>	
Digester/blow <sup>a</sup> pit or dump tank	Ca		0.0 <sup>a</sup>	neg <sup>c</sup>	
	All others		0.0 <sup>a</sup>	neg <sup>c</sup>	
	NH <sub>3</sub>	Process Change, scrubber	0.0 <sup>a</sup>	neg <sup>c</sup>	
	MgO	Process Change, scrubber	0.0 <sup>a</sup>	neg <sup>c</sup>	
	MgO	Recovery System	0.0 <sup>a</sup>	neg <sup>c</sup>	
	Na	Process Change, scrubber	0.0 <sup>a</sup>	neg <sup>c</sup>	
Other Misc. Sources			0.0 <sup>a</sup>	neg	
Recovery System	NH <sub>3</sub>		0.0 <sup>a</sup>	1.8 <sup>d</sup>	
	MgO		0.0 <sup>a</sup>	1.8 <sup>d</sup>	
	Na		0.0 <sup>a</sup>	1.8 <sup>d</sup>	

Notes

- a. No test data available. NOx emissions expected to be zero due to low temperatures of operation.
- b. Based on VOC emissions for sulphuric acid plant.
- c. Based on data from U.S. state files specifically for the ammonia digester/blow pit/dump tank but should be similar for other digester/blow pit/dump tanks.
- d. Based on NCASI (National Council of the Paper Industry for Air and Stream Improvement Inc., U.S. referenced in Stockton and Stelling n.d.) data. Data were specific to the MgO process but levels should be similar to those at any acid plant. These data are an approximation in the absence of better information.

An emission factor of 0.05 (range 0.004 - 0.14) kg VOC (as C)/tonne air dried pulp is reported by the NCASI (1993) for pulp bleaching. This is based on tests of one to eleven vents at thirteen sources. The type of pulp is not specified.

Although ratings for these NOx and VOC emission factors are not given, a D or E rating would seem appropriate.

## **9 SPECIES PROFILES**

## **10 UNCERTAINTY ESTIMATES**

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

The simpler methodology relies on emission factors that may not be representative of the process. The detailed methodology is costly and labour intensive, and may still not result in accurate estimates of emissions. However, continuous measurements are thought to be too costly in view of the total contribution to emissions from this sector.

## **12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES**

National emissions estimate can be disaggregated on the basis of plant capacity, employment or population statistics.

## **13 TEMPORAL DISAGGREGATION CRITERIA**

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

## **14 ADDITIONAL COMMENTS**

## **15 SUPPLEMENTARY DOCUMENTS**

## **16 VERIFICATION PROCEDURES**

## **17 REFERENCES**

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## 18 BIBLIOGRAPHY

### 19 RELEASE VERSION, DATE AND SOURCE

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## 20 POINT OF ENQUIRY

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