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ORIGINAL ARTICLE

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Evaluation of chloroform formed in process of kraft pulp bleaching mill using chlorine dioxide

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Abstract Chloroform formation, balance, and discharge were estimated in a kraft pulp mill that used an elemental chlorine-free (ECF) bleaching line with chlorine dioxide as well as an effluent treatment process. This was achieved by collecting and analyzing discharge water and air samples that contained measurable levels of chloroform. Chloroform formation in ECF bleaching of hardwood oxygen-delignified kraft pulp (LOKP) was estimated to be 2.07–5.34 g/pulp air-dried ton (adt), and approximately 30% of the chloroform produced was discharged to bleaching effluents. Chloroform in the effluents was not decomposed by activated sludge, and more than 97% was emitted to the air by volatilization. It is suggested that chloroform formation in Japanese LOKP bleaching mills can be decreased to 16–42 t/year with a production of 8 million adt pulp by introducing ECF bleaching into all mills. This is a considerable fall from the chloroform discharge from ECF and chlorine bleaching mills in Japan that was estimated to be approximately 1000 t for the 1999 fiscal year.

Key words Kraft pulp · Bleaching · Chlorine dioxide · Chloroform · Activated sludge

Introduction

It is well known that chloroform ($CHCl_3$) is formed by pulp bleaching with chlorine (Cl_2) and hypochlorite (ClO^-),[1–10] and that $CHCl_3$ damages organs such as the heart, kidneys, and liver. It has been confirmed as carcinogenic and strongly toxic in animal experiments and is classified as 2B by the International Agency for Research on Cancer (IARC).[1]

It is known that 17 volatile organochlorine compounds (VOCCs) are formed during kraft pulp bleaching with chlorine dioxide (ClO_2), which is called elemental chlorine-free (ECF) bleaching.[11,12] Chloroform constitutes a major portion of them. The process modification of ECF bleaching is continuing to further reduce chloroform as well as other chlorinated compounds in the effluent.[13]

It is reported that anthropogenic emissions of chloroform in 1990 were estimated with a variety of methods specific to the source category, and that the largest source category was found to be pulp and paper manufacturing, responsible for an estimated 30 000 ± 8000 t/year as reactive chlorine in the form of $CHCl_3$ out of a total of 62 000 ± 25 000 t/year.[14]

For pulp bleaching, the regulation of chloroform discharge is enforced in each country. In the United States, the cluster rule took effect in 1998 and set the discharge limit of mill effluents at the daily average of 6.92 g of chloroform per ton of air-dried pulp (g/pulp adt) and the monthly average of 4.14 g/pulp adt. If a mill continues using conventional chlorine bleaching with Cl_2 and ClO^-, it cannot keep the discharge below the limit. Since that time, most of the pulp bleaching lines in the United States have been converted to ECF bleaching lines using ClO_2.

Japan revised the Air Pollution Control Law in 1996. The main purpose of the law is to reduce emissions of toxic pollutants such as carcinogenic substances to the air. The revised law specifies 234 kinds of toxic or carcinogenic compounds and 22 strongly injurious compounds including dioxins (polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, coplanar polychlorinated biphenyls) and chloroform. We reported previously on dioxins.[15]

The Japan Papermaking Association estimated the nationwide chloroform emission to the air for the fiscal year 1996 to be 1655 t on the basis of field studies, and initiated a reduction of the discharge. As a result, the estimated emis-

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Table 1. Chloroform formation from chlorine and elemental chlorine-free (ECF) bleaching lines for hardwood oxygen-delignified kraft pulp

	Line 1a (chlorine)		Line 2a (ECF)		Line 1b (ECF)		Line 2b (ECF)		Line 1c (ECF)	
Sequence	C-E/O-HD		D_0-E/P-dnD_1		D_0-E/P-D_1		D_0-E/P-dnD_1		D_0-E/P-D_1	
Pulp production (adt/day)	680		1090		710		1210		670	
Water										
Bleaching stage	C	E/O	D_0	E/P	D_0	E/P	D_0	E/P	D_0	E/P
Effluent flow (m^3/day)	7300	4300	4800	10 800	5900	4130	3170	12 000	5520	3790
Chloroform concentration (μg/l)	13 400	1830	28.0	14.0	241	41.6	90.1	66.0	148	64.0
Chloroform discharge (g/day)	97 700	7870	130	150	1420	172	286	791	815	241
Production-normalized chloroform formation (g/pulp adt)	144	11.4	0.119	0.139	2.00	0.24	0.24	0.65	1.22	0.36
Subtotal (g/pulp adt)	155		0.258		2.24		0.89		1.58	
Gas										
Volume of plume (m^3/h)	2160		10 900		3300		10 560		3840	
Chloroform concentration (mg/m^3)	216		7.50		28.0		15.5		12.5	
Chloroform discharge (g/day)	11 200		1970		2210		3930		1150	
Production-normalized chloroform formation (g/pulp adt)	16.5		1.81		3.10		3.25		1.72	
Total production-normalized chloroform formation (g/pulp adt)	172		2.07		5.34		4.14		3.30	

C, Chlorine stage; D_0, first chlorine dioxide stage; E/O, alkali-extraction stage reinforced with oxygen; E/P, alkali-extraction stage reinforced with hydrogen peroxide; HD, hypochlorite treatment followed by chlorine dioxide treatment; dn, chlorine dioxide treatment under neutralized conditions in a pretube; D_1, chlorine dioxide stage; adt, air-dried ton

sion was reduced to 1118 t, a reduction of 32%, for the fiscal year 1999. However, further reduction is required.

As mentioned earlier, chloroform discharge to water is regulated in the United States. In Japan, reduction of chloroform emissions to air is required. However, chloroform, once formed from one process, is discharged to both water and air. The reduction of chloroform discharge to water and air is important from an environmental standpoint and for the reduction of harmful effects to humans. To date, a comprehensive investigation of chloroform emissions to both water and air from kraft pulp bleaching mills has not been published.

Approximately 8 million adt of bleached pulp was produced in Japan, and more than 1000 t of chloroform was thought to be emitted to the air for the period of the fiscal year 1999, as estimated by the Japan Papermaking Association in July 2001. An ECF bleaching line with production of 1200 adt/day of hardwood oxygen-delignified kraff pulp (LOKP) commenced operation in 1998 at the Hokuetsu Paper Niigata Mill, and later several companies converted their mills to ECF bleaching. However, most mills continue to use conventional chlorine bleaching.

Therefore, it is important to clarify (1) the amount of chloroform formed in conventional chlorine bleaching and ECF bleaching, (2) the ratio of chloroform discharge to water and air for the bleaching processes, (3) the possibility of decomposition of chloroform in the effluent treatment process with activated sludge, and (4) the holistic behavior of chloroform on a mill scale.

To address these goals, we estimated the chloroform discharge in a mill equipped with a chlorine bleaching line, an ECF bleaching line, and an effluent treatment process. Sampling locations were selected on the basis that chloroform discharge to water and air could be defected in measurable quantities. In this study, we investigated chloroform formation and behavior in conventional chlorine bleaching of LOKP, in ECF bleaching, in effluent treatment, and finally in a holistic view of the mill operation.

Methods

Bleaching process description

The mill that was used in this study had two bleach lines for hardwood kraft pulp (LKP). At the beginning of the study, one of the two lines (line 1) was producing conventional chlorine bleached pulp. Each line had a two-stage oxygen delignification process for unbleached LKP. As shown in Table 1, line 1a was a conventional chlorine bleaching sequence (C-E/O-HD) using Cl_2 and ClO^-, and line 2(a,b,c) was an ECF bleaching sequence (D_0-E/P-dnD_1) using ClO_2. Notation used to describe the sequences is summarized as: C, chlorine stage; E/O, alkali-extraction stage reinforced with oxygen; HD, the stage of hypochlorite treatment followed by chlorine dioxide treatment; D_0, first chlorine dioxide stage; E/P, alkali-extraction stage reinforced with hydrogen peroxide; dn, a ClO_2 treatment under neutralized conditions in a pretube; D_1, chlorine dioxide stage.

Water sampling from bleaching processes

At line 1a, filtrates from the C and E/O stages were sampled. The filtrate from the HD stage was used for the counter-current washing of pulp. This means it was used for pulp washing in the first C stage. Therefore, the effluents from line 1a were the C filtrate, which contained the HD filtrate, and the E/O filtrate. In the same way, the D_0 filtrate and the E/P filtrate were sampled as the effluents from

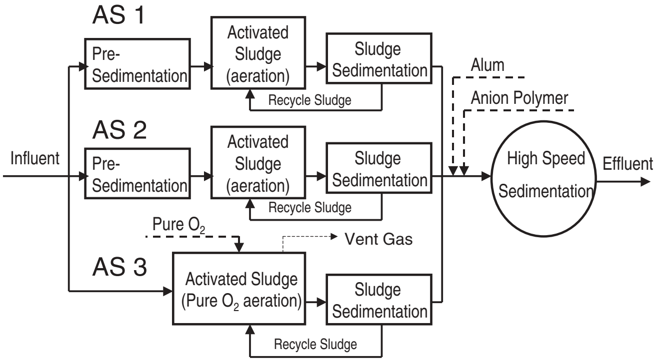


Fig. 1. Effluent treatment system at Niigata Mill of Hokuetsu Paper Mills

line 2 because the dnD$_1$ filtrate was used for washing in the D$_0$ stage. Each filtrate was poured into a brown-colored bottle until each bottle was full. The bottles were quickly capped and then taken to a laboratory for analysis.

Gas sampling from bleaching processes

Each washer in the bleaching stages of line 1a and line 2 consisted of an airtight pressure diffuser or press washer. Exhaust gas from each washer was drawn off with fans, combined, washed with a scrubber in each line, and discharged into the atmosphere.

Exhaust gas combined before the scrubber was sampled with a Teflon tube and a flex pump into a Teflon bag, which was kept away from sunlight prior to use, and was then taken to a laboratory for analysis. Volumes of exhaust gases were measured according to method JIS Z 8808.

Effluent treatment

In the mill used in this study, effluents from bleaching processes, papermaking equipment, and other facilities were combined in one place, and then treated. The system consisted of a first-stage treatment with activated sludge and sedimentation, as well as the second-stage treatment that is shown in Fig. 1. The first-stage system had three lines: AS1, AS2, and AS3. The AS1 and AS2 lines were standard types with presedimentation, activated sludge (aeration) treatment, and sludge sedimentation. The AS3 line had activated sludge treatment which was completely airtight with a small air vent and used pure oxygen aeration. This was followed by sludge sedimentation. Effluents from the three lines after sludge sedimentation were again combined and then treated in a high-speed sedimentation as the second-stage treatment.

Water and gas sampling from effluent treatment processes

Water samples were taken before and after the activated sludge treatments of the AS1, AS2, and AS3 lines, and also after the secondary treatment. Gas samples were taken from a vent on the activated sludge treatment of the AS3 line.

Water sample preparation for chloroform analysis

Water samples from the bleaching and effluent treatment processes were diluted between 1:3 and 1:20 with commercially available mineral water (Volvic or Evian). Ten milliliters of each diluted sample was put into a 22-ml sample vial for automatic headspace (HS) injection for gas chromatography-mass spectrometry (GC-MS) analysis ($n = 3$).

A standard solution provided by Tokyo Kasei containing 23 different VOCCs in drinking water, each present in concentration of 1 mg/ml (1000 ppm), was diluted, and standard solutions of chloroform at concentrations of 100 ppm and 10 ppm were prepared. Ten milliliters of the mineral water and 2 μl of each diluted standard solution were put into a 22-ml sample vial and subjected to GC-MS analysis to prepare a calibration line between 2 and 20 ppb for chloroform in water.

GC-MS analysis conditions for water samples

The analyses used a JEOL Automass II 50/HP-6890 GC-MS, coupled to a Tekmar 7050 HS autosampler with a cryo-focusing unit. The HS sampler conditions were: temperature 70°C, time 30 min, sample loop 1 ml, pressure 70 kPa, cryo-cooling N$_2$ (−150°C) for 6 min. The GC-MS conditions were: carrier gas (He) 1.2 ml/min; column DBVRX 60 m × 0.33 mm ID (film thickness 1.8 μm); column temperature 40°C for 5 min, elevation at 6°C/min, 220°C for 5 min; interface temperature 250°C; ion source temperature 200°C; electron impact ionization 70 eV.

Chloroform analysis of gas samples

From each Teflon sample bag, 0.01–1.0 ml of gas was taken and subjected to GC-MS analysis using a JEOL MS-GCmate II/HP-6890 GC-MS. For calibration, 0.1–2 ml of gas was taken with a gastight syringe from a standard gas (Matheson Aerotrace Mini-mat Gas, 1 ppm of chloroform) and subjected to GC-MS ($n = 3$).

The GC-MS conditions were: carrier gas (He) 1.0 ml/min; split ratio 10; column Aquatic 60 m × 0.25 mm ID (film thickness 1.0 μm); column temperature 40°C for 3 min, elevation at 10°C /min, 200°C for 5 min; interface temperature 200°C, ion source temperature 200°C, electron impact ionization 70 eV.

Results and discussion

Behavior of chloroform in beaching processes

Table 1 shows the amounts of chloroform found in effluent and exhaust gas samples from the chlorine bleaching and ECF bleaching processes. In the chlorine bleaching process (line 1a), the levels of chloroform in the effluents and exhaust gas were estimated to be 155 g/pulp adt and 16.5 g/pulp adt, respectively, to give a total of 172 g/pulp adt. The kappa number of the LOKP being produced was about 8–9, with about half based on hexenuronic acid and half on residual lignin.

It has been reported that chloroform formation was estimated to be 430 g/pulp t in laboratory C-E-H-D bleaching of LKP with a kappa number of 14.4.[4] Approximately 10 points of this kappa number should correspond to residual lignin. Furthermore, chloroform was formed by the hypochlorite treatment of lignin model compounds in 12% yield based on product weight.[4] If chloroform formation is proportional to residual lignin content of pulps, the amount produced from line 1a is assumed to be about 40% of that obtained by laboratory bleaching. The amount of chloroform discharge measured in this survey (172 g/pulp adt) was in accordance with this assumption.

Therefore, we demonstrated that the sampling and analysis methods used in this study revealed the total amount of chloroform formed in the bleaching process, and the methods are of similar accuracy to those used in laboratory experiments.

Sharp reduction of chloroform formation in ECF bleaching

From the results for lines 1a and 2, it was shown that chloroform discharge from ECF bleaching for the effluents and the exhaust gas were reduced by 99.8% and 89%, respectively, when compared with conventional chlorine bleaching. There was an overall reduction in chloroform discharge of 98.8%.

In addition, although 90% of chloroform was discharged to the water at line 1a, only a minor part of the chloroform produced in ECF bleaching in line 2 was discharged to the water. The distribution of chloroform discharge between the water and gas is extremely variable depending on chloroform amounts and bleaching methods used.

Line 1a was later converted into an ECF bleaching process (D_0-E/P-D_1). After conversion, the amount of chloroform discharge was measured, and two of the results are shown in lines 1b and 1c of Table 1. The discharge was reduced to the same level as that of line 2. However, the ratios of chloroform discharge between water and gas were 0.72 for line 1b and 0.92 for line 1c. These values are noticeably different from that of line 2 (0.14), and we are currently attempting to identify the causes of this difference.

Behavior of chloroform in effluent treatment processes

Volatile organic compounds such as chloroform are removed in the effluent treatment process using activated sludge.[12] However, these compounds are assumed to be mostly removed by volatilization, and it is not clear whether compounds such as chloroform can be decomposed by activated sludge. As shown in Table 2, chloroform concentrations in the effluents from activated sludge were 10% of those of the influents for the AS1 and AS2. Contrary to these results, that for AS3 was not decreased in the completely airtight system. Chloroform concentrations may also be increased by the activated sludge treatment of organic chlorinated compounds in the effluent.

Chloroform concentrations in vent gas samples from AS3 are also shown in Table 2. The AS3a and AS3b,c designations represent the treatments under chlorine bleaching (line 1a) and ECF bleaching after the conversion of line 1, respectively. The results show that the chloroform volatilization through a small vent was 4% of the total amount. We demonstrated that chloroform was not decomposed by the activated sludge treatment of ECF bleaching mill effluents.

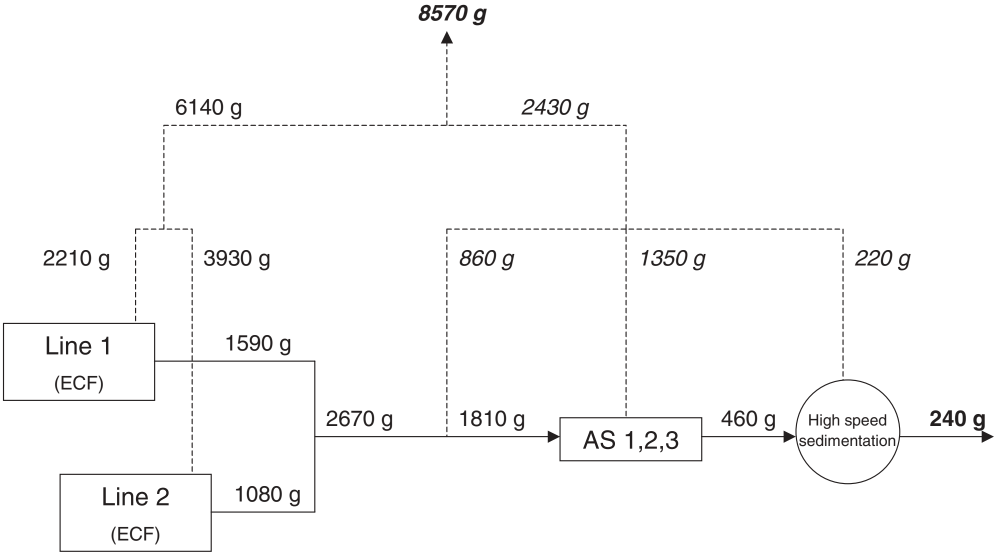
Volatilization of chloroform

In the mill, bleaching effluents flow in open drains from the bleaching process to the effluent treatment process. A daily

Table 2. Chloroform discharge from effluent treatment with activated sludge and high-speed sedimentation

	AS1a	AS2a	AS3a	AS1b	AS2b	AS3b	AS3c
Bleaching sequence	Line 1a (chlorine)	Line 1a (chlorine)	Line 1a (chlorine)	Line 1b (ECF)	Line 1b (ECF)	Line 1b (ECF)	Line 1c (ECF)
Influent							
Flow (m^3/day)	47 700	47 700	7200	44 900	44 900	10 760	7860
Chloroform concentration (μg/l)	259	259	302	18.0	18.0	18.0	21.2
Chloroform amount (g/day): x	12 400	12 400	2170	808	808	194	167
Effluent							
Chloroform concentration (μg/l)	23.0	21.0	373	2.9	2.8	18.2	15.5
Chloroform discharge (g/day): y	1 100	1 000	2690	130	126	196	122
y/x	0.089	0.089	1.24	0.16	0.16	1.01	0.73
Vent gas							
Volume (m^3/h)	–	–	24	–	–	34	34
Chloroform concentration (mg/m^3)	–	–	31	–	–	15	9.6
Chloroform discharge (g/day): z	–	–	18	–	–	12	7.8
z/x	–	–	0.008	–	–	0.062	0.047
Mill effluent							
Chloroform concentration (μg/l)		35			2.4		–
Chloroform discharge (g/day)		3590			240		–

Fig. 2. Daily balance of chloroform in a mill producing approximately 1900 air-dried tons of hardwood elemental chlorine-free bleached kraft pulp. Numbers in *italics* are assumed



balance sheet for chloroform in the mill is shown in Fig. 2. Assumed data in Fig. 2 are expressed with italics.

As shown in Fig. 2, chloroform formation in line 1b (ECF bleaching) and line 2 (ECF bleaching) was 8810 g in total. Approximately 30% (2670 g) of chloroform was discharged to water in the bleaching lines, and it decreased to 1810 g at the entrance to the activated sludge treatment. The difference should be the result of volatilization from the open drains. The amount discharged in water was decreased further to 460 g after the activated sludge treatment. The difference of 1350 g should also be a result of volatilization, and not caused by decomposition. In a similar way, approximately 50% of the chloroform in water appears to be volatilized at the high-speed sedimentation step because only 240 g of chloroform was determined in the final effluent that was discharged from the mill into a river. Overall, 97% of chloroform should be discharged to the air.

The fact that such quantities of chloroform were volatilized from open drains in a mill suggests that effects on employees in a mill should be great, and that reduction of chloroform discharges is very important for the global environment and the health of employees.

It is reported that 0.6–7.7 g of VOCCs per ton of ECF bleached pulp is formed, and that most of the VOCCs are removed during effluent treatment with activated sludge.[12] In Finland, it was estimated that 2–30 t of VOCCs would be removed annually from treatment plants in kraft pulp mills using ECF bleaching, most likely by volatilization.[12]

In this study, we demonstrated that the chloroform formation in the ECF bleaching of LOKP was 2.07–5.34 g/pulp adt, and that in Japanese LOKP bleaching mills, it can be decreased to 16–42 t/year for the production of 8 million tons of pulp by ECF bleaching.

Conclusions

Chloroform formation in ECF bleaching of LOKP was found to be 2.07–5.34 g/pulp adt, approximately 30% of which was discharged to bleaching effluents. Chloroform in the effluents was found not to be decomposed by activated sludge, and more than 97% of the chloroform was discharged to the air by volatilization.

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