研 究 報 文

ECF 漂白への転換による環境負荷低減効果（第2報）

—排水中のクロロホルムとクロロフェノール類の減少—

株式会社日本紙パルプ研究所*¹ 岩 田 ひ ろ*²Reduction of Pollutants from Bleached Kraft Pulp Mills by the Process
Conversion to Elemental Chlorine Free Bleaching (Part II)

—Reduction of Chloroform and Chlorinated Phenolic Compounds in Pulp Mill Effluents—

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Abstract

Chlorinated organic compounds are produced by the chlorine bleaching of pulp. Many of them are persistent and accumulative and toxic. To reduce chlorinated organic compounds, the pulp and paper manufacturing companies in Japan have advanced the ECF conversion of the bleaching process since 1996.

At Japan Pulp and Paper Research Institute, Inc. the environmental impact of the pulp mill effluent was investigated according to the progress of the ECF conversion of Oji Paper Co., Ltd. and Nippon paper Industries Co., Ltd. Reduction of chloroform and chlorinated phenolic compounds were reported here.

Chloroform production in the bleaching process was decreased by 95% or more, and the main purpose to convert ECF in the bleaching process was sufficiently achieved. The concentration of chloroform in the effluent also decreased drastically, and it came to fall below 0.06 mg/L of the water quality standard for drinking water.

Hazardous highly chlorine substituted chlorinated phenolic compounds produced by the chlorine bleaching were reduced by almost 100% with the ECF conversion. In addition, the production of chlorinated phenolic compounds has been clearly kept a level by the regulation of chlorinated phenolic compounds of the bleaching filtrate, which is demanded by the cluster rule in the United States.

Keywords : chlorinated organic compounds, chloroform, chlorinated phenolic compounds, ECF

分類 : K₇ 二酸化塩素漂白, X₄ 排水

1. はじめに

パルプの塩素漂白により有機塩素化合物が発生する。それらの多くは難分解性、蓄積性という性質があり、さらに毒性を示すために環境への放出が問題視されてきた。この

有機塩素化合物の削減を目的として、日本の製紙会社は1996年から漂白工程のECF転換を進めてきた。

日本紙パルプ研究所では王子製紙、日本製紙のECF転換の進行に合わせ、排水による環境負荷削減状況を調査してきた。ここでは、前報¹⁾に引続きその過程で明らかになったクロロホルムとクロロフェノール類の削減状況を報告する。

クロロホルムはパルプの漂白工程で塩素、あるいは次亜塩素酸ナトリウムが主にリグニンと反応し発生する^{2,3,4,5)}。

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多段漂白においては次亜塩素酸ナトリウム段（H 段）がクロロホルムの最大の発生源であるが、塩素段で生成した前駆物質がアルカリ段へ持ち込まれ反応液の pH が高くなり加水分解が起こることでもクロロホルムは生成する^{3,4,5)}。クロロホルムは水への溶解度、沸点ともに低いために、その大半は大気中に放出されると考えられる。

クロロホルムの大気と水質への排出バランスを調べたものとしては例えば日本製紙連合会が作成したマニュアルがある。これは 2001 年（平成 13 年）に始まった「特定化学物質の環境への排出量の把握等及び管理の改善の促進に関する法律」（PRTR 法）の第一種指定化学物質であるクロロホルムが非意図的生成物であることから、届出のために排出ポイント、排出量把握の考え方を示したものである。そこには各工場独自に排出バランスを作成していない場合のモデル的な排出バランスが記載されており、それによると漂白段で発生したクロロホルムは大気と排水に半々に分配され、工場内でさらに大気への移動があり、排水処理で一部が除去され最終的に 75% が大気に 7.5% が排水に排出されることとしている。

1996 年の大気汚染防止法の一部改正に伴い、クロロホルムは有害大気汚染物質の中でも「特に健康リスクが高く優先的な排出抑制の取り組みが必要な物質」に指定された。日本製紙連合会は 1997 年から二度にわたり優先取り組み物質であるクロロホルム、ベンゼン、ホルムアルデヒドの 3 物質について自主管理計画を定め削減に取り組み、自主管理目標を達成している。しかし、2001 年に PRTR 法が実施され、対象物質であるクロロホルムの環境への排出が把握されるようになった。それによれば、全国で排出されるクロロホルムの半分はパルプ・紙・紙加工品製造業からの排出であった。

クロロホルムの排出削減には、漂白に塩素、次亜塩素酸ナトリウムを使わない漂白法への転換が最も有効である。米国では紙パルプ排水の規制法であるクラスタールールで、クロロホルムの規制値を漂白工程水でパルプ 1 t 当たり 4.14 g (g/t) 以下（月間平均）としている。これは発生段階での規制であり、排水処理で対応するのではなく発生を抑制しなければ達成できないレベルで事実上、塩素、次亜塩素酸ナトリウムの使用を制限するものである。

クロロホルムの排出削減は ECF 転換の主要な目的であり、その削減状況の調査には大気、水を合わせた総排出量の変化を押さえることが望ましい⁶⁾。しかし、工場それぞれに大気放出、水への放出を分析するのは困難なので、今回の調査では排水中のクロロホルムのみ分析することにした。漂白工程水、総合排水中のクロロホルムを分析することで水系へのクロロホルムの発生と排出を評価した。

クロロフェノール類も漂白過程で塩素とリグニンが反応して生成される。塩素を二酸化塩素で置換すると、塩素数 3 以上の高塩素置換体は二酸化塩素置換率の増加とともに減少し、二酸化塩素 100% ではほとんど生成しなくなる。一方、塩素数 2 以下の低塩素置換体は、置換率が小さいと一旦増加するがその後は置換率が上がると減少する。結果として有害性が指摘される高塩素置換体クロロフェノール

類は ECF 漂白では生成されず、塩素置換数が少ないものが僅かに残るといわれている^{7,8,9,10,11,12)}。

米国のクラスタールールでは有害物質は出来る限り生成を抑えるという観点から、塩素数 3 以上の有害なクロロフェノール類 12 種類を発生源である漂白排水で定量下限（クラスタールールでは 345 TCC, 346 TCC, TECG, PCP は 5 µg/L, それ以外は 2.5 µg/L と規定されている。）以下にすることを求め、事実上 ECF 化を義務づけている。

今回の調査では、上の 12 種類に加えて漂白排水中に多く見られる 5 種類の 1, 2 塩素置換体も測定対象とし、発生源である漂白工程水と工場からの排出を表す総合排水中のクロロフェノール類を測定し、ECF 転換による削減状況を分析した。

2. 実 験

2.1 調 査 工 場

2000 年から 2006 年にかけて ECF 転換した王子製紙、日本製紙グループの 14 工場、21 系列（広葉樹系：転換前は 12 系列、転換後は 13 系列、針葉樹系：8 系列）について、転換前後に調査を行った。各工場の総合排水と漂白工程（塩素または二酸化塩素段とアルカリ段）の工程水を別々に採取し、当研究所に輸送して分析した。

2.2 クロロホルムの測定

クロロホルムの測定は JIS K 0125「用水・排水中の揮発性有機化合物試験方法」に準じて、ヘッドスペース-ガスクロマトグラフ-質量分析法で行った。

1) サンプルの採取

- ・250 ml 耐圧瓶にヘッドスペースを残さず静かに注ぎ入れて密栓し、水で冷却して当所まで輸送した。

2) 試 薬 類

- ・標準試料には市販の VOC 23 物質分析用混合試料を用いた。
- ・内部標準には市販のフロロベンゼン溶液を用いた。
- ・検量線用標準試料はトリハロメタン測定用メタノールを用いて標準試料を適宜希釈して調製した。
- ・塩析用の塩化ナトリウムは水質分析用のものを用いた。
- ・市販のミネラルウォーターをブランク水として用いた。
- ・水、塩化ナトリウム、メタノールとも分析対象物の測定に支障がないことをあらかじめ確認した。

3) 前 処 理

- ・塩析用の塩化ナトリウム 3.6 g を入れたヘッドスペース用サンプル容器に試料水 12 ml を入れ、内部標準溶液、メタノールを加え密栓し、塩化ナトリウムを溶解させた。

4) ヘッドスペースサンプラー条件

- ・Agilent 製 HP-7694 ヘッドスペースサンプラーを用いた。

加熱温度：60℃，加熱時間：20 分，試料ループ：1 ml

5) GC-MS 測定

- ・Agilent 製 5890 GC-5972 MSD あるいは、Agilent 製 6890 GC-5975 MSD を用いた。

- ・使用カラム：AQUATIC (内径 0.25 mm, 膜厚 1.0 μm , 長さ 60 m)
- ・カラムオープン温度：40 $^{\circ}\text{C}$ (7 分) $\sim$ 8 $^{\circ}\text{C}/\text{分}$ $\sim$ 200 $^{\circ}\text{C}$ (3 分)
- ・注入口圧力：45 psi (1 分) $\sim$ 99 psi/分 $\sim$ 15 psi   コンスタントフロー
- ・注入口温度：150 $^{\circ}\text{C}$
- ・EI モード・イオン化電圧：70 eV

2.3 クロロフェノール類の測定

日本紙パルプ研究所では 1980 年以前からパルプ漂白排水中の有機塩素化合物について研究していた。クロロフェノール類の測定に関しても抽出法、誘導体化法の検討を重ね、エチルエーテルで排水から抽出後、エチル化して GC-ECD あるいは GC-MS で測定していた。1980 年代後半に、簡便で感度良く分析できるアセチル誘導体化法が海外でよく行われるようになり、当所でもこの方法で分析するようになった。

EPA が紙パルプ工場排水の規制物質選定のために調査対象とした 28 種のクロロフェノール類¹³⁾から、実際に規制物質となった 12 種類と紙パルプ工場排水に多量に存在する 5 種類の合計 17 種類を分析した。分析は NCASI Method CP-86.01 に準じたアセチル誘導体化-ガスクロマトグラフ-質量分析法にて測定した。

1) 誘導体化

- ・試料水 25 ml に炭酸カリウム溶液 (150 g を水 250 ml に溶解させたもの) 0.65 ml を加え、pH を 11.6 $\pm$ 0.1 になるように 5 % 水酸化ナトリウムで調整した。
- ・無水酢酸 0.5 ml を加え 30 秒攪拌した後 5 分間放置後、2.5 ml の内部標準試料 (2, 2 ジフロロビフェニル) を加えたヘキサンで激しく攪拌、抽出した。
- ・ヘキサン層を硫酸ナトリウムで脱水し GC-MS 分析した。

2) GC-MS 条件

- ・使用カラム：HP-5 ms (内径 0.25 mm, 膜厚 0.25 μm , 長さ 30 m)
- ・カラムオープン温度：40 $^{\circ}\text{C}$ (1 分) $\sim$ 15 $^{\circ}\text{C}/\text{分}$ $\sim$ 120 $^{\circ}\text{C}$ (0 分) $\sim$ 5 $^{\circ}\text{C}/\text{分}$ $\sim$ 250 $^{\circ}\text{C}$
- ・注入口圧力：15 psi スプリットレス
- ・注入口温度：210 $^{\circ}\text{C}$
- ・MS：EI モード、イオン化電圧 70 eV

3. 結果と考察

3.1 漂白工程水におけるクロロホルム

図 1 には ECF 転換前の各漂白段工程水中のクロロホルム発生量を広葉樹、針葉樹系別にパルプ原単位で示した。広葉樹系で発生量が多い場合には C 段より E 段排水での発生が多い傾向が見られるが、広葉樹系で発生量の少ない場合、針葉樹系の数系列など逆の場合も少なくなかった。多段漂白では、後段排水を順次前段の洗浄水として向流で用いる。したがって、前段の排水にはそこでの発生に加えて、向流洗浄のために後段での発生分が持ち込まれることになる。ECF 転換前は多くの工場で三段目に次亜塩素ナ

Fig.1 Chloroform production in the chlorine bleach filtrates

トリウム段があり、そこでの発生は大きいと考えられるがその発生分も前段に持ち込まれることになる。つまり、ここで示した C 段、E 段でのクロロホルム発生量は単純に当該段での発生量ではなく、工場毎に異なる操業条件、水廻しに加え、漂白装置によって異なる発生したクロロホルムの大気と排水への分配割合などが複合された結果である。そのために C,E 段の発生が一定の傾向にならなかったと思われる。

広葉樹、針葉樹別の発生量は、平均して広葉樹系で 46 g/t、針葉樹系で 43 g/t とほとんど違いは認められなかった。しかし、工場間のバラツキは広葉樹系の方が大きかった。通常、針葉樹系の方が漂白段に入る銅価が高いため薬品添加量が多くなり、発生する有機塩素化合物も多いと考えられる。しかし、クロロホルムの場合は最初に述べたように、今回測定したのは排水への放出のみであり、より多いと考えられる大気への放出が測定されていないので、違いが明確に現れなかったと考えられる。広葉樹系でクロロホルム発生量の低い工場は、ECF 転換前にも C 段が一部二酸化塩素置換されていたのでそのためと考えられる。この工場の 2 g/t という値は、ECF 転換前でもクラスターールの規制値 (4.14 g/t: 月間平均) を下回っていた。

図 2 には ECF 転換後の各漂白段排水中のクロロホルム発生量を針葉樹、広葉樹系別にパルプ原単位で示した。図 1 と同じように ECF 転換後も D, E 段のクロロホルム発生量に一定の傾向は見られなかった。針葉樹、広葉樹別の発生量は広葉樹系で平均 0.50 g/t、針葉樹系で 0.55 g/t と差はなかった。また ECF 転換後の削減率は、ECF 転換前の発生量が低かった 2 系列を除けば、95% 以上であった。広葉樹系で一段目にオゾンで漂白を行っている工場は、漂白排水中にクロロホルムは検出されなくなった。ECF 転換後のクロロホルム発生量は最大の工場でも 2.12 g/t であり、クラスターールの定める規制値を下回った。

3.2 総合排水におけるクロロホルム

総合排水で排出されるクロロホルムは発生段階での

Fig.2 Chloroform production in the ECF bleach filtrates

ECF 転換による 95% 以上の発生削減にともない、図 3 に示すように ECF 転換により 74~99% 削減された。

クロロホルムに関する国内規制としては水道水質基準と要監視項目となっている環境基準がある。規制値はどちらも 0.06 mg/L 以下である。総合排水の排出濃度をみると、図 4 のようであり、ECF 転換後はいずれの工場も 0.02 mg

/L 以下であり、水道水質基準値の 0.06 mg/L を大きく下回っていた。

当研究所では 1996 年から、紙パルプ工場総排水が環境に及ぼす影響について年一回の調査を継続して行っており、クロロホルムについても排出濃度の分析を行ってきた。今回の調査対象の工場のうち過去のデータのある 12 工場について一日当たりの排出量合計の年別推移を図 5 に示す。多少の増減はあるが、1997 年にはおよそ 350 kg/日あった排出量は ECF 転換の進行に伴い、2006 年には 13 kg/日にまで 95% 以上減少していた。これは水域への排出であるが大気への排出も同様に減少していると考えられる。PRTR で集計されるパルプ・紙・紙加工品製造業からの排出は、2001 年の PRTR 開始当初、大気、水域合わせておよそ 1,000 t で全業種中最大であったが、2006 年には 300 t にまで減少している。また、排出割合も当初、全国の排出のほぼ 50% を占めていたが、2006 年には 35% 程度にまで減少し、最大の排出業種ではなくなった。

3.3 漂白工程水におけるクロロフェノール類

図 6 と図 7 に 17 種類の測定対象のクロロフェノール類を示す。図 6 はクラスターールの規制対象である 3 塩素化以上のクロロフェノール類 (12 種類) で、図 7 は 1, 2

Fig. 3 Comparison of chloroform discharge in whole mill effluents

Fig. 4 Comparison of chloroform concentration in whole mill effluents

Fig. 5 Changes of chloroform discharge in 12 BKP mills

Fig. 7 Analyzed mono and di chlorinated phenolic compounds

Fig. 6 Chlorinated phenolic compounds regulated by the cluster rule of USEPA

塩素化体で、紙パルプ排水中に多量に検出されるクロロフェノール類 (5 種類) である。

実際の工場排水での ECF 転換によるクロロフェノール類の削減効果の調査に先立ち、二酸化塩素置換率によってクロロフェノール類の発生がどのように変化するかを見た。当所でラボ蒸解したパルプについて二酸化塩素の置換率を 0, 25, 50, 100% の 4 段階に変えて O-C/D-E のシーケンスで漂白し、モデル排水を調製した。漂白条件は表 1 の通りである。

二酸化塩素置換率の変化によるクロロフェノール類発生の状況を図 8 に示す。

針葉樹パルプの方が広葉樹パルプと比べてカッパー価が高かったためにクロロフェノール類の発生量は全体に多く

Table 1 Bleaching conditions of the model experiments

Sequence	Kappa no.	Beech	Yezo spruce
		19	29
O	Oxygen pressure	0.4 MPa	
	Temp. and time	100℃, 40 min	
	Pulp consistency	10%	
	Kappa no.	11	16
C/D	Active chlorine	Kappa no.×0.18	
	Temp. and time	40℃, 60 min	
	Pulp consistency	3.5%	
E	Oxygen pressure	0.2 MPa	
	Temp. and time	60℃, 60 min	
	Pulp consistency	10%	

なっている。針葉樹では漂白初段で発生するクロロフェノール類の大部分はカテコール類であり、二酸化塩素置換率が 25% では置換率 0% の時よりも増加した。その後は置換率が上がると発生は減少し、二酸化塩素 100% ではクロロフェノール類の発生は認められなくなった。アルカリ段ではグアイアコール類、アルデヒド類の発生が多く置換率の上昇に伴い発生は減少し、100% ではその他のクロロフェノール類が僅かに見られるだけになった。広葉樹でも発生量は少ないが変化の傾向は針葉樹と同様であった。

本調査における漂白で発生するクロロフェノール類の ECF 転換前後の変化を図 9 に示す。

転換前のクロロフェノール類の発生は図 9 の上段と中段に示すように、(1)C 段ではクロロカテコール類が主に発生しており、(2)クロログアイアコール類は E 段での発生が主であり、(3)E 段ではその他のクロロフェノール類の発生

Fig. 8 Change of chlorinated phenolic compounds in the bleach filtrates by chlorine dioxide substitution of laboratory experiments

も多く、(4)全体ではE段の方がC段より発生が多い、というモデル実験と同様の状況であった。ECF 転換後には下段に示すように半数の工場でクラスター規制対象の3塩素化以上のクロロフェノール類は検出されなくなった。本調査ではクロロフェノール類の測定をEPAのクラスター規制のNDレベル(2.5 µg/L)以下まで行ったので、ECF 転換後でも3塩素化クロロフェノール類が検出された工場がある。しかし、いずれもEPAの規定する検出限界以下であった。ECF 転換後に発生するクロロフェノール類は6-クロロバニリンが主であった。二酸化塩素漂白でも微量持ち込まれる塩素や二酸化塩素から生成する次亜塩素酸により、有機塩素化合物が発生することは避けられないが、漂白初段がオゾンあるいはZ/Dである工場の広葉樹系では、測定対象のクロロフェノール類は低塩素化クロロフェノール類も含めてまったく検出されなくなった。

図10には広葉樹系、針葉樹系別にECF 転換前後の漂白工程でのクロロフェノール類の発生量を示した。図には発生量を3塩素化以上のクロロフェノール類とそれ以外の低塩素化クロロフェノール類に分けて原単位で示した。図

10左の転換前では広葉樹系は平均7.64 g/t(3塩素化以上のクロロフェノール類は3.20 g/t)、針葉樹系は平均13.43 g/t(3塩素化以上のクロロフェノール類は6.25 g/t)であり、針葉樹系の方が発生量が多かった。漂白段入りのカップー価、薬品添加量からみて、針葉樹系の方が多くなるのは妥当な結果と思われる。

図10右には漂白工程でのECF 転換後のクロロフェノール類発生量を広葉樹系、針葉樹系別に原単位で示した。平均すると広葉樹系では0.08 g/t、針葉樹系では0.40 g/tであった。ECF 転換による削減率は3塩素化以上のクロロフェノール類についてはほぼ100%であり、全体で見ても90%以上であった。

3.4 総合排水におけるクロロフェノール類

図11にECF 転換前の漂白段におけるクロロフェノール類の発生量と総合排水における排出量の比較を示す。1工場を除いて排出量は発生量から平均75%削減されており、排水処理によってクロロフェノール類が削減されたと考えられる。ECF 転換後も同様に微量発生したクロロフェノール類はおよそ70%削減されて排出されていた。

図12に示すように総合排水へのクロロフェノール類の

Fig. 9 Comparison of chlorinated phenolic compounds by family in the bleach filtrates

Fig. 10 Production of chlorinated phenolic compounds in the bleach filtrates

排出量は ECF 転換による発生量の大幅な削減に伴い激減した。しかし、3 工場で漂白工程の分析では認められなかった 3 塩素体のクロロフェノール類が微量検出された。他の工程からの持ち込みが原因と思われるが詳細は不明である。

る。

4. ま と め

漂白工程でのクロロホルム発生は広葉樹系で平均 46 g/t

Fig. 11 Comparison of production and discharge for chlorinated phenolic compounds in the chlorine bleach filtrates

Fig. 12 Discharge of chlorinated phenolic compounds from ECF bleaching mills

から 0.50 g/t に、針葉樹系で平均 43 g/t から 0.55 g/t へ 95% 以上減少し、漂白工程の ECF 転換の主要な目的であったクロロホルムの発生抑制は十分達成された。

総排水での排出濃度も発生量の削減をうけ激減し、水道水質基準の 0.06 mg/L を下回るようになった。

塩素漂白により発生する有害性の指摘される 3 塩素化以上のクロロフェノール類も、ECF 転換によって発生はほぼ 100% 削減され、EPA のクラスタールールが求める漂白排水のクロロフェノール類の規制をクリアするレベルとなった。

References

- 1) Takagi H. and Nakagawa M. : Japan Tappi J. in press
- 2) Hrutford B.F. and Negri A.R. : TAPPI J. 73(6) 219-225 (1990)
- 3) Dallons V.J., Hoy D.R., Messmer R.A. and Crawford R. J. : Tappi J. 73(6) 91-95 (1990)
- 4) Crawford R.J., Dallons V.J., Jain A.K. and Jett S.W. : Tappi J. 74(4) 159-163 (1991)
- 5) NCASI technical bulletin No. 585 (1990)
- 6) Nakamata K., Motoe Y. and Ohi H. : Japan Tappi J. 62 (7) 874-879 (2008)
- 7) Alliance for Environmental Technology, Summary Report, "A Review and Assessment of the Ecological Risks Associated with the Use of Chlorine Dioxide for the Bleaching of Pulp", October 18 (1993)
- 8) Haglund I., Stromberg L. and Hultman B. : TAPPI Environmental Conf., Proceedings. Boston 1993, p 245-251
- 9) Spengel D.B., Anderson D.F., Smith M. and Bodien D. G. : Int. Pulp Bleaching Conf., Papers. Vancouver 1994, 133-144
- 10) Axegard P. : Tappi J. 69(10) 54-59 (1986)
- 11) Pryke D.C., Winter P., Bouree G.R., Mickowski C. : Pulp and Paper CANADA 95(6) T 230-T 236 (1994)
- 12) Smith T.J., Wearne R.H. and Wallis A.F.A. : Holzfor-schung 49(3) 279-284 (1995)
- 13) NCASI special report 92-12 (1992)

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1. Introduction

When pulp is bleached with chlorine, chlorinated organic compounds are produced, which are persistent and accumulative. As they are toxic in their nature to some extent, their discharge to environment has been concerned to be problematic. In order to reduce these chlorinated organic compounds, paper companies in Japan has been promoting to convert their bleaching processes to ECF.

Japan Pulp and Paper Research Institute, following ECF conversions in mills that belonged to Oji paper Co. and Nippon Paper Industries Co., studied how the conversion to ECF reduced environmental load discharged from mills. Following the previous paper¹⁾, we are going to report on reductions of chloroform and chlorinated phenolic compounds by the conversion.

Chloroform is produced during bleaching of pulp, when chlorine or sodium hypochlorite react with lignin^{2,3,4,5)}. Though a sodium hypochlorite stage (H-stage) in multi-stage bleaching is the largest producer, precursors produced in a chlorine stage are also converted to chloroform in a following alkaline stage by hydrolysis due to increased pH in the stage^{3,4,5)}. As chloroform is little soluble in water and has a low boiling temperature, most of chloroform produced is likely to be purged into air.

Regarding the balance of discharges of chloroform to air and water, Japan Paper Association published a manual. The manual was prepared to counter the law entitled "Act on confirmation, etc. of release amounts of specific chemical substances in the environment and promotion of improvements to the management thereof", PRTR law in abbreviation, which started in 2001 and nominated chloroform that belonged to Class I of specified chemicals. The manual gave information on sites of sampling in mills and determination of chloroform as an unintentional product. It showed a model distribution balance between air and water to help mills which could not measure the balances of their own. According to the model, chloroform produced in bleaching was distributed to air and water by half and half. Some chloroform in water was transferred to air in its due course in a mill. Then, some was removed by effluent treatment. Finally, 75% of chloroform was discharged to

air and 7.5% remained in effluent.

In 1996, air pollution control law was modified in some parts, and specified chloroform as one of air pollutants which were liable to affect human health and should be dealt with high priority for reducing their discharges. Japan Paper Association, being enforced by the law, set up a voluntary guide line in 1997 for reducing the discharges of three chemicals, chloroform, benzene and formaldehyde, which were listed in the substances requiring priority action. The guide line was revised once, and paper companies accomplished the voluntary guideline by due times. Then, PRTR law got in act in 2001, and the discharge of chloroform to environment was monitored. It turned out that a half of chloroform discharged in the whole country was by pulp, paper and paper products industries.

To reduce chloroform discharge, the conversion to bleaching processes that do not use chlorine and sodium hypochlorite is most effective. For instance, the U.S., by its cluster rule that regulated effluents from pulp and paper mills, enforced that chloroform production in filtrates at bleaching plant should be below 4.14 g per ton of bleached pulp (as an average of a month). It was a regulation aiming at the point of production, and should not be satisfied by effluent treatment. Its level of allowable chloroform production substantially asked not to use chlorine and sodium hypochlorite in bleaching.

The conversion to ECF was mainly for chloroform reduction and it was preferable to monitor its total discharge, to air and water, to make survey on the reduction⁶⁾. It was, however, difficult to measure the discharge to air as well as the discharge to water in every mill, and only the discharge to effluent was analyzed in this paper. By analyzing chloroform in bleach filtrates and chloroform in effluents, chloroform production and discharged to water was calculated.

Chlorinated phenolic compounds were also produced by reaction between chlorine and lignin. By increasing the ratio of replacement of chlorine dioxide to chlorine, highly chlorinated compounds which had more than three chlorine atoms per molecule got reduced. No such compounds were produced by 100% chlorine dioxide. Regarding low chlorinated compounds, which had less than two chlorine

atoms per molecule, they increased along with larger replacement ratios of chlorine dioxide in the range of small replacement. Then, with further increase of the replacement, the compounds got reduced. As results, highly chlorinated phenolic compounds that were hazardous were not produced by ECF bleaching and compounds which were substituted with less number of chlorine resided in small amount^{7, 8, 9, 10, 11, 12}.

The cluster rule of the U.S., aiming to depress the production of hazardous compounds as little as possible, restricted the presences of 12 chlorinated phenolic compounds in bleach filtrates below their detection limits (5 $\mu\text{g/L}$ for 3, 4, 5 TCC, 3, 4, 6 TCC, TCCG and PCP, and 2.5 $\mu\text{g/L}$ for the rest of the compounds). This restriction practically forced bleaching to be ECF.

In our survey, 5 other chlorinated compounds which had one or two chlorine atoms per molecule and were frequently founded in bleach filtrates, in addition to those 12 compounds, were taken as subjects. Those chlorinated phenolic compounds in bleach filtrates as well as in effluents were measured, and the effects by ECF conversion were investigated.

2. Experiment

2.1 Mills under survey

14 mills, which belonged to two companies, Oji Paper Co. and Nippon Paper Industries Co., and converted their bleaching lines to ECF during the years from 2000 to 2006, were surveyed. In total, 21 bleaching lines were surveyed (12 lines for hardwood which became 13 lines after the conversions, and 8 lines for softwood). The effects were studied by analyzing the compounds before and after the conversions. Samples were taken, at every mill, from its final mill effluents and bleach filtrates (chlorine or chlorine dioxide stages and alkaline stages) respectively and were transported to our research institute.

2.2 Determination of chloroform

Chloroform was determined according to JIS K 0125 entitled "Testing methods for volatile organic compounds in industrial water and waste water", using headspace-gas chromatographic mass spectroscopy.

1) Sampling

- Every sample was poured into a pressure-resistant bottle of 250 ml, without leaving any head space, sealed and transported under cooled with ice.

2) Reagents

- Standard specimen for determining VOC 23 mixtures, which was available in market, was used as a reference solution.
- Fluorobenzene solution in market was used as an internal standard.
- Methanol for determining trihalomethane was used to

dilute the standard specimen to desired concentrations for preparing a calibration curve.

- Sodium chloride used for salting-out was one for water analysis.
- Commercial mineral water was used as blank water.
- Water, sodium chloride and methanol were proved, beforehand, not to affect the determination of chloroform.

3) Pretreatment

- 12 ml of sample water was poured into a sample vessel for headspace which already had 3.6 g of sodium chloride in it. Then, internal standard solution and methanol were poured into the vessel, which was then sealed. Sodium chloride was then dissolved.

4) Conditions for headspace sampler

- Headspace sampler HP-7694 by Agilent was used
Heated temperature : 60°C Heating time : 20 minutes Sample loop : 1 ml

5) GC-MS

- Equipment was 5890 GC-5972 MSD by Agilent or 6890 GC-5975 MSD by Agilent
- Column : AQUATIC (inside diameter : 0.25 mm, film thickness : 1.0 μm , length : 60 m)
- Column oven temperature : 40°C (7 minutes) $\sim$ 8°C /minute $\sim$ 200°C (3 minutes)
- Injection pressure : 45 psi (1 minute) $\sim$ 99 psi/minute $\sim$ 15 psi constant flow
- Injection temperature : 150°C
- EI mode ionization voltage : 70 eV

2.3 Determination of chlorinated phenolic compounds

We, Japan Pulp and Paper Research Institute, started investigation on chlorinated organic compounds in effluent from pulp bleaching in years before 1980, and studied on the method of extracting chlorinated phenolic compounds and making derivatives of them. Our method was extracting them from effluent with ethyl ether, and then ethylating and analyzing them by GC-ECD or GC-MS. In the late 1980 s, a method converting them to acetyl derivatives, which was simple and very sensitive, got commonly used overseas and we started to use that method also in our lab.

EPA surveyed and studied on 28 chlorinated phenolic compounds in effluents from pulp and paper mills¹³⁾. We, however, analyzed 17 chlorinated phenolic compounds as our subjects, 12 out of which were subjects of the regulation by EPA and 5 out of which were frequently found in pulp and paper mill effluents. The method was based on NCASI Method CP-86.01. After acetylating, they were determined by GC-MS.

1) Converting to derivatives

- 0.65 ml of potassium carbonate solution (150 g dis-

solved in 250 ml water) was added to 25 ml of sample. Its pH was adjusted to 11.6 ± 0.1 by 5 % sodium hydroxide solution.

- 0.5 ml of anhydrous acetic acid was added to the solution. It was shaken for 30 seconds and left still for 5 minutes. It was extracted with 2.5 ml hexane that contained internal standard solution (2,2'-difluorobiphenyl) with vigorous shaking.
- The hexane layer was dehydrated with sodium sulfate and was analyzed by GC-MS.

2) Conditions for GC-MS

- Column : HP-5 ms (inside diameter : 0.25 mm, film thickness : 0.25 μ m, length : 30 m)
- Column oven temperature : 40°C (1 minute)-15°C/minute-120°C (0 minute)-5°C/minute-250°C
- Injection pressure : 15 psi splitless
- Injection temperature : 210°C
- MS : EI mode, ionization voltage 70 eV

3. Result and discussion

3.1 Chloroform in bleach filtrates

Fig.1 summarizes chloroform produced per ton of bleached pulp at each bleach filtrates of bleaching lines, grouped by their wood sources, hardwood and softwood, surveyed before ECF conversion. In cases of hardwood lines where a lot of chloroform was produced, filtrates in E-stages contained more chloroform than those in C-stages. However, the opposite trend was also observed in hardwood lines where chloroform was less produced and also in several softwood lines. In multi-stage bleaching, filtrate from one stage behind was used as washing water for a stage ahead in a countercurrent way. Therefore, filtrate of a certain stage contains chloroform produced in that stage as well as chloroform carried over in washing water from a stage behind. Before ECF conversions, most mills used sodium hypochlorite in their third stages, which would produced a lot of chloroform. This chloroform was carried over to stages ahead in a countercurrent way. Therefore, values of chloroform at C-stage and E-stage did not mean the actual amounts produced at those stages, and were affected by many other factors in combined such as operating conditions, water circulations and distribution between air and water which were very specific to each mill.

The average of chloroform produced in hardwood lines was 46 g/t and that in softwood lines was 43 g/t, and there was not much difference between them. However, hardwood lines had more variance than softwood lines. It was believed that softwood pulp coming to bleaching was higher in Kappa number, therefore needed more dosages of bleaching chemicals and would produce more chlorinated organic compounds. In our survey, we measured chloroform only discharged to water, and that to air which

would be larger in volume was not measured. That might be a reason of little difference between the wood sources. Some hardwood lines gave small chloroform productions. In these lines, chlorine was already replaced to chlorine dioxide to some extent in their C-stages before their ECF conversions. One mill showed 2 g/t which was less than the regulation by the cluster rule (4.14 g/t as a monthly average).

Fig.2 summarizes chloroform produced per ton of bleached pulp at each bleach filtrates of bleaching lines, grouped by wood sources, hardwood and softwood, surveyed after the ECF conversion. Like in Fig. 1, there was not observed any definite trend among chloroform production in D-and E-stages. The average of chloroform produced in hardwood lines was 0.50 g/t and that in softwood lines was 0.55 g/t, and there was not much difference between them. The reduction ratios by the conversion were more than 95%, excepting 2 mills which were already in very low levels before the conversions. No chloroform was detected in a mill which used ozone in the first stage of its hardwood line. The largest chloroform production after the conversion was 2.12 g/t and was less than the regulation by the cluster rule.

3.2 Chloroform in mill effluent

As the ECF conversion reduced chloroform production at bleaching by more than 95%, chloroform in mill effluent was also reduced by 74-99% as in Fig. 3.

Regarding regulations on chloroform in Japan, there are one for drinking water quality standards and one for environmental quality standard monitoring substances. The regulation value is 0.06 mg/l for both cases. As in Fig. 4, all chloroform concentrations of mill effluents were less than 0.02 mg/l, and were far less than the regulation for drinking water quality standards which is 0.06 mg/l.

We had been monitoring the influence of pulp and paper mill effluents on environment once a year since 1996, and chloroform discharge had been one of measurements. As 12 mills that were also listed in this survey had data in the past time, their chloroform discharges (kg/day) were summed up on yearly basis, and depicted in Fig. 5. Though there was some variance, the chloroform discharge was reduced by more than 95% from 350 kg/d in 1997 to 13 kg/d in 2006. This was discharge to water, and we think that its discharge to air would be also reduced in a similar manner. When PRTR started in 2001, the discharge to air and water combined from pulp, paper and paper products industries was about 1000 tons and it was the largest of all industries. It went down to 300 tons in 2006. The share in the national discharge was 50% in the beginning. It was 35% in 2006 and the industry was not the largest polluter.

3.3 Chlorinated phenolic compounds in bleach filtrates

We determined 17 chlorinated phenolic compounds of which structures were depicted in Fig. 6 and Fig. 7. 12 chlorinated phenolic compounds in Fig. 6 are subjects of the cluster rule and have more than three chlorine atoms per molecule. Fig. 7 shows 5 chlorinated phenolic compounds which have one or two chlorine atoms per molecule and were detected in a large amount in pulp and paper mill effluents. Before surveying the effect of the ECF conversion, we studied in lab how the replacement ratio of chlorine dioxide to chlorine affected the production of chlorinated phenolic compounds. Pulp cooked in our lab was bleached in O-C/D-E sequence with four replacement ratios of chlorine dioxide, 0, 25, 50 and 100%, and model effluents were prepared. The bleaching conditions were in Table 1. The result was in Fig. 8.

As softwood pulp had higher Kappa number than hardwood pulp, it produced more chlorinated phenolic compounds. With softwood pulp, most of chlorinated phenolic compounds produced in the first stage were catechols. Their production increased until the replacement ratio with chlorine dioxide reached to 25% from 0% replacement. Then, its production got smaller, and no production was observed at 100% replacement. In alkaline filtrates, guaiachols and aldehydes were produced in a large amount. Their production got down along with increased replacement ratios, and only small amount of other phenolic compounds were detected at 100% replacement. Hardwood pulp also behaved in the same way, though its production was very small.

Changes in the production of chlorinated phenolic compounds by the ECF conversion were surveyed and depicted in Fig. 9. The production of chlorinated phenolic compounds before the conversion was in the upper and the middle graphs of Fig. 9. The results were summarized as follows.

- (1) Chlorocatechols were mostly produced in C-stages.
- (2) Chloroguaiachols were mostly produced in E-stages.
- (3) E-stages also produced other chlorinated phenolic compounds
- (4) E-stages produced more amounts of chlorinated compounds than C-stages in total

The results were similar to those in our lab test. After the ECF conversion, as in the lower graph of Fig. 9, chlorinated phenolic compounds, which had more than three chlorine atoms per molecule and were subjects of the regulation by the cluster rule, were not detected at a half number of mills. As, in our survey, chlorinated phenolic compounds were analyzed with higher sensitivity than one required by the cluster rule, of which ND level was

2.5 $\mu\text{g/L}$, trichlorinated phenolic compounds were detected in some mill effluents. The values, however, were below ND level of the cluster rule. It was mostly 6-chlorovaniline that was detected after the conversion. Some chlorine was carried over to chlorine dioxide stage and hypochlorite was also produced from chlorine dioxide in the stage, chlorinated organic compounds were inescapably produced. In mills where ozone or Z/D were used in the first stages, chlorinated phenolic compound, including those of low substitution, were not detected at all.

Fig. 10 summarizes chlorinated phenolic compounds produced in bleaching before and after the ECF conversion, grouped by wood sources, hardwood and softwood. Chlorinated phenolic compounds were expressed as unit production (g/ton of bleached pulp), and were categorized by the degree of chlorination, ones chlorinated with more than three chlorine atoms and ones with less chlorine substitution. The left hand side was for before the conversion, and the average of hardwood lines was 7.64 g/t of which highly chlorinated was 3.20 g/t. The average of softwood lines was 13.43 g/t, and that of highly chlorinated was 6.25 g/t. It was reasonable that softwood lines produced more volumes due to their higher incoming Kappa numbers and higher chemical dosages.

Chlorinated phenolic compounds produced in bleaching after the ECF conversion, expressed as unit production (g/ton of bleached pulp) and grouped by wood sources, were shown in the right hand side of Fig. 10. The average of hardwood lines was 0.08 g/t and that of softwood lines was 0.40 g/t. The reduction ratio for highly chlorinated phenolic compounds (more than three chlorines per molecule) was almost 100% and that including all kinds of chlorinated phenolic compounds was over 90%.

3.4 Chlorinated phenolic compounds in mill effluents

Fig. 11 summarizes chlorinated phenolic compounds produced in bleaching and those measured in mill effluents before the conversion. The average of cut rates by effluent treatments was 75%, except one mill, and effluent treatment systems worked well for their removal. After the conversion, chlorinated phenolic compounds, though they were very small, were removed by 70% just as cases before the conversion.

Fig. 12 shows that chlorinated phenolic compounds in mill effluents were greatly reduced because of their little productions after the conversion. Small amount of chlorinated phenolic compounds with more than three chlorines per molecule were detected in three mills, though they were not measured in bleach filtrates. Carry over from other processes would be responsible, but details were unknown yet.

4. Conclusion

By the ECF conversion, the average of chloroform produced in bleaching in hardwood lines was reduced from 46 g/t to 0.50 g/t. That in softwood lines was reduced from 43 g/t to 0.55 g/t. Their reduction ratios were more than 95%, and the ECF conversion well accomplished its purpose of restricting chloroform production.

Their concentrations in mill effluents were greatly lowered due to reduced productions, and were below the regulation for drinking water quality standards that was 0.06 mg/l.

Chlorinated phenolic compounds with more than three chlorine substitutions, which were produced in bleaching and were regarded to be hazardous, were reduced by almost 100% by the conversion. Their level satisfied the regulation for chlorinated phenolic compounds in bleach filtrates by the cluster rule by EPA.

References

- 1) Takagi H. and Nakagawa M. : Japan Tappi J. in press
- 2) Hrutfiord B.F. and Negri A.R. : TAPPI J. **73**(6) 219–225 (1990)
- 3) Dallons V.J., Hoy D.R., Messmer R.A. and Crawford R. J. : Tappi J. **73**(6) 91–95 (1990)
- 4) Crawford R.J., Dallons V.J., Jain A.K. and Jett S.W. : Tappi J. **74**(4) 159–163 (1991)
- 5) NCASI technical bulletin No. 585 (1990)
- 6) Nakamata K., Motoe Y. and Ohi H. : Japan Tappi J. **62**(7) 874–879 (2008)
- 7) Alliance for Environmental Technology, Summary Report, “A Review and Assessment of the Ecological Risks Associated with the Use of Chlorine Dioxide for the Bleaching of Pulp”, October 18 (1993)
- 8) Haglund I., Stromberg L. and Hultman B. : TAPPI Environmental Conf., Proceedings. Boston 1993, p 245–251
- 9) Spengel D.B., Anderson D.F., Smith M. and Bodien D. G. : Int. Pulp Bleaching Conf., Papers. Vancouver 1994, 133–144
- 10) Axegard P. : Tappi J. **69**(10) 54–59 (1986)
- 11) Pryke D.C., Winter P., Bouree G.R., Mickowski C. : Pulp and Paper CANADA **95**(6) T 230–T 236 (1994)
- 12) Smith T.J., Wearne R.H. and Wallis A.F.A. : Holzfor-schung **49**(3) 279–284 (1995)
- 13) NCASI special report 92–12 (1992)