



Study report for

**Review of ECF and TCF
bleaching processes and
specific issues raised in the
WWF report on Arauco
Valdivia**



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softwood kraft pulp mill, Germany*

Prepared at the request of

Resource Planning and Development
Commission

TASMANIA

Please note:

This report is a contribution to the information concerning ECF and TCF bleaching processes and related issues. The Commission does not endorse the content, comment or conclusions expressed in the study report.



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Appendix C	Article 5 and Annex C of the Stockholm Convention
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REPORT SCOPE AND THIRD PARTY DISCLAIMER

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- Review of ECF and TCF bleaching processes and specific issues raised in the WWF report on Arauco Valdivia.

This report is a contribution to the information concerning ECF and TCF bleaching processes and related issues. The Commission does not endorse the content, comment or conclusions expressed in the study report.

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EXECUTIVE SUMMARY

INTRODUCTION

The WWF (www.panda.org) (formerly known as the World Wildlife Fund and World Wide Fund for Nature) has recently published a report which describes the impact CELCO's BKP mill may have had on the Carlos Anwandter Nature Sanctuary and suggests possible mitigating actions to redress the situation [WWF, 2005].

The WWF report makes several references to ECF and TCF bleaching processes and their impact on the environment.

The Commission engaged Beca AMEC to carry out a review of ECF and TCF bleaching processes and specific issues raised in the WWF report on Arauco Valdivia.

The Beca AMEC report is a review of ECF and TCF bleaching processes and specific issues raised in the WWF report on Arauco Valdivia and is based on the scientific evidence available to its authors as of May 2006.

CONCLUSIONS

The conclusions made in this report are summarised in the following tables, which correspond to the main sections of the report and include the sub-sections or appendices for ease of reference for the interested readers who want to have more details.

SECTION 2 – “REVIEW OF ECF AND TCF BLEACHING PROCESSES”

Section 2.4 – “ECF bleaching”

No	Conclusion	Sub-section
1	Chlorine dioxide can potentially generate molecular chlorine Cl ₂ in ECF bleaching but this chlorine is converted to hypochlorous acid at the typical conditions of pH and temperature of a D stage.	2.4.2
2	<p>Hypochlorous acid generates small amounts of substituted chlorinated organic compounds (measured as AOX in bleach plant and OX in ECF bleached pulp), however:</p> <ul style="list-style-type: none"> • Compounds identical or similar to those produced in ECF bleaching are formed as a result of natural processes. These naturally produced compounds range from simple alkanes, such as chloromethane, to numerous complex halogenated alcohols, ketones, carboxylic acids, carboxylic amides, aldehydes, epoxides and alkenes and chlorophenolic isomers such as 2,4,6-trichlorophenol and its methylated analogue 2,4,6-trichloroanisole. • Chlorinated compounds formed during ECF bleaching are biologically degradable in the environment. Pulp mill AOX will ultimately be mineralised through photochemical and biological processes and during mineralisation the chlorinated organic material will be released as chloride and carbon dioxide (CO₂). 	2.4.3
3	Hypochlorous acid also generates PCDD and PCDF from their precursors CDD and CDF but the probability of their formation is so low that they are undetectable with present sampling and analytical techniques (i.e. at low pg/L or ppq level).	2.4.4
4	PCDD and PCDF are emitted as a consequence of combusting a wide variety of materials including fossil fuels, wood, and municipal solid wastes and are, therefore, widely distributed in the environment. The ubiquitous presence of these compounds could explain their detection in bleached pulp and filtrate samples from ECF and TCF mills through contamination of either the raw materials or product samples, or both.	2.4.4
5	ECF bleaching is at present (Q2 2006) the dominant bleaching method worldwide (75% of total bleached kraft pulp production) and has been adopted in most new installations.	2.4.5
6	A rapid decrease in the concentration of PCDD/ PCDF has been measured at several pulp mill locations in North America and Europe either in sediments or biota after the introduction of either ECF or TCF bleaching.	2.4.6
7	PCDD and PCDF emissions in ECF and TCF effluents are about the same.	2.4.6
8	If ECF bleaching is used, the emissions of 2,3,7,8-TCDD and 2,3,7,8-TCDF to water are lower than the limit of quantitation (US EPA Method 1613 ¹).	2.4.4

¹ US EPA Method 1613 for Analysis of Dioxins and Furans in Wastewater, which has a minimum level of 10 pg/L for 2,3,7,8-TCDD and 2,3,7,8-TCDF.

Sections 2.5 and 2.6 – “TCF bleaching” and “Current status of BKP mills employing TCF bleaching”

No	Conclusion	Sub-section
9	If TCF bleaching is used, the emissions of 2,3,7,8-TCDD and 2,3,7,8-TCDF to water are lower than the limit of quantitation (US EPA Method 1613 ¹⁾ .	2.5.3
10	TCF bleaching developed in the early 1990s and reached a market share of around 5% of the total bleached kraft pulp production. Since then, this market share has gradually declined to around 4%. The TCF market is at present stagnant or decreasing, no premium is paid for TCF pulps and the expectation for less problematic recycle of effluents has not been realised. Thus, mills in Germany and the Nordic countries have either abandoned or reduced TCF production in favour of ECF production.	2.5.4 and 2.6

Section 2.7 – “Effluent characteristics and treatability”

No	Conclusion	Sub-section
11	The treatability of ECF and TCF bleaching effluents in a biological treatment plant is for all practical purposes about the same. Because of this, the treated effluent characteristics depend more on the pulpwood, mill geographical location and pulping process than on the selected bleaching process.	2.7.1
12	The COD removal efficiency in effluents from BKP mills using hardwood is commonly above 80% but is in the range 60- 70% for kraft mills using softwood.	2.7.1
13	Treatment efficiency in ECF mills varies between 85-98% BOD removal, 60-80% COD removal and 40-65% AOX removal. Phosphorus is reduced by 40-85% and nitrogen by 20-50% (calculated on net incoming amounts before addition of nutrients). Overall TSS removal for the primary and secondary stages is around 85-90%.	2.7.2.2
14	Tertiary treatment with inorganic chemicals is not regarded as AMT unless the recipient is very sensitive because of its very high sludge production. If polymer is used instead of inorganic salts or lime, the sludge generated can be burned in the recovery (Tembec Skookumchuk BKP mill in Cranbrook, BC, Canada).	2.7.2.2
15	Chlorate ion formed in ECF bleaching may be toxic to large brown algae, such as kelps, which are common in many parts of the Australian marine environment, because of a competitive uptake with nitrate. Chlorate formation can be reduced by adopting ZD or DZ stages in ECF bleaching.	2.7.2.4
16	Emissions to the atmosphere from the chemical recovery area of BKP mills are for all practical purposes identical whether ECF or TCF bleaching is employed. Two additional emissions sources to the atmosphere in ECF kraft mills are the ClO ₂ plant environmental scrubber and the bleach plant scrubber, which may occasionally emit minor amounts of either inorganic or organic chlorinated compounds, or both. Collection and scrubbing with alkaline scrubbing solutions of residual chlorinated compounds from the bleaching chemical preparation plant and the bleach plant is standard practice in ECF kraft mills and this technique is considered AMT.	2.7.2.6

No	Conclusion	Sub-section
17	The amounts, composition, handling etc. of the solid wastes from BKP mills employing either ECF or TCF bleaching are comparable.	2.7.2.7
18	Possible methods of disposal for biosludge are: <ul style="list-style-type: none"> • Addition to weak black liquor, evaporation and burning in the recovery boiler. • Stabilisation by a drying and composting process, then utilisation as a soil conditioner. • Utilisation as cover material on old landfills due to its low water permeability . • Dewatering, mixing with either fibre sludge or bark, or both and burning in the power boiler. 	2.7.2.7
19	Approximately 50-70% of the dioxins/furans in BKP mill are transferred from the water phase onto the biological sludge	2.7.2.8
20	Traces of dioxin were detected in late 2005 in tank deposits in the chlorine dioxide plant of 3 Swedish BKP mills. The process used in all cases is Cellchem's Hydrogen Peroxide Atmospheric (HP-A [®]) process (http://www.cellchem.com/docs/products-services/chlorine_dioxide.htm) To the best knowledge of the authors of this report, no dioxins have been emitted to the environment from this source.	2.7.2.9
21	The legal detection limit (minimum level) for 2,3,7,8 TCDD and 2,3,7,8 TCDF in the USA is 10 pg/L and is measured in the bleach plant effluent. Virtually all the analyses report values less than this level, however, there is insufficient data available to calculate the margin by which bleach plant discharges are below the legal detection limit. It is estimated that treated effluents discharged from American mills may contain less than about 2-3 pg/L of 2,3,7,8 TCDD.	2.7.2.10
22	Virtually all Canadian mills are at present authorised by Environment Canada to reduce sampling, analysis and reporting of dioxin and furan discharges to once annually, and virtually all analyses are undetectable at the regulatory levels of 15 pg/L for 2,3,7,8 TCDD and 50 pg/L for 2,3,7,8 TCDF. Environment Canada verifies that mills report discharges as required, but does not maintain a database of actual values, since all are considered "non-measurable".	2.7.2.10
23	Discharges of PCDD/ PCDF in Canada and the USA are dramatically below the levels of the early 1990s, but there is insufficient data available to quantify the current discharge levels.	2.7.2.10
24	TCF and ECF mills have the same non-process elements (NPE) entering with their pulpwood and water. This includes an array of heavy metals, chloride and potassium ions. These combine with organic and inorganic material in the mill systems and form scales and deposits in tubes and on equipment leading to operational upsets and a need to shut down to carry out cleaning cycles. These problems are equally difficult to handle in BKP mills employing either ECF or TCF bleaching, hence, bleaching effluent recycle to chemical recovery must include some treatment and purge of NPE. Chloride and potassium ions are soluble and enter the liquor circuits in both ECF and TCF mills and the lower concentration in the TCF mills has not proved to be an advantage.	2.7.3.1
25	The overall conclusion from the review of recent studies of environmental impact of bleached kraft mill effluents confirms that neither ECF nor TCF bleaching gives clear environmental advantages. It is noted that EDS have also been shown to occur in the effluent from a BKP mill employing TCF bleaching.	2.7.3.3

No	Conclusion	Sub-section
26	<p>Chelant charge in TCF bleaching is normally about 2 kg/ADt. There is concern about the ability of chelants to remobilise toxic heavy metals out of sediments and their biodegradability.</p> <ul style="list-style-type: none"> The chelant DTPA is not degraded in biological treatment but up to 30% of the DTPA charged may be adsorbed onto the biological sludge and up to 50% may be chemically precipitated with metal salts. The chelant EDTA is resistant to aerobic biodegradation in an activated sludge plant operated under "normal" conditions (about 10% reduction at pH 7 and short sludge age). EDTA does not adsorb onto sludge so it passes through the treatment plant without significant removal. EDTA is however biodegradable under special conditions. If the pH is higher than 8 and the sludge age (retention time of the biosludge in the biological treatment) is long enough (>20 days), the reduction will be about 75% as an annual average. 	2.7.3.4

Section 2.8 – “Environmental impact of ECF and TCF bleaching”

No	Conclusion	Sub-section
27	There is no systematic difference in effect intensity or effect pattern between the whole mill effluents from mills employing ECF or TCF bleaching.	2.8.1
28	There is no indication of a difference between ECF and TCF bleaching in terms of acute and chronic toxic effects on aquatic eco-systems. The remaining environmental effects of modern mills (e.g. sub-lethal toxicity to aquatic organisms) cannot be predicted from the bleaching sequence alone. Future evaluations of these environmental effects should focus also on other unit operations within the mill (e.g. wood handling, cooking, washing, screening, spill and foul condensate handling).	2.8.1
29	ECF pulps have better paper-making properties than TCF pulps. TCF bleaching offers no advantage over ECF bleaching in terms of reducing or eliminating an effluent discharge.	2.8.1
30	Biological toxicity tests carried out at the Mercer International Rosenthal BKP mill in Blankenstein, Germany, while producing both ECF and TCF pulps, indicate no difference in ECF and TCF effluent quality.	2.8.1
31	A secondary effluent treatment is a prerequisite for both ECF and TCF wastewaters to minimise long term toxic impacts on aquatic ecosystems.	2.8.1
32	Organic halogen (OX) content of pulp is a suitable parameter for assessing the aquatic eco-friendliness of ECF pulp production.	2.8.1
33	There is growing evidence that endocrine disrupting substances (EDS) are either derived from wood or are chemical or bio-degradation by-products of naturally occurring chemicals, and not organochlorine compounds. Consequently, the impacts are likely to be the same whether the mills use ECF or TCF bleaching sequences.	2.8.2

Section 2.9 – “Process closure of the bleach plant”

No	Conclusion	Sub-section
34	Both ECF and TCF bleaching offer paths to process closure. Based on current knowledge, the degree of closure in TCF mills can be only partial whereas ECF mills are more likely to offer full bleaching closure. As of Q2 2006 there are no papergrade BKP mills that operate fully closed on a continuous basis, more specifically there are no bleach plants in papergrade bleached kraft mills that operate fully closed on a continuous basis. The principal impediment to closure in a BKP mill is the recycle of bleach plant effluents, which typically comprise about half of the total effluent volume. For ECF mills the prime concern has been the build-up of chloride in the chemical recovery cycle, with secondary concerns with pulp quality and mill operability. For TCF mills the prime concern has been pulp quality (strength and brightness) with secondary concerns in operability, and potassium and chloride build-up in the recovery system. Both ECF and TCF bleaching closure can cause operating difficulties with increased chemical consumptions, poorer pulp quality and provide challenges in minimising deposition and scaling on equipment.	2.9.3

Section 2.10 – “Bleaching chemical preparation”

No	Conclusion	Sub-section
35	The methanol process (ERCO R8/ R10 and Cellchem SVP-Lite/ SVP-SCW) is the dominant modern method for generation of chlorine dioxide with low chlorine content. There are a few installations using H ₂ O ₂ as the reducing agent (ERCO R11 and Cellchem SVP-HP). The advantage of this method is that the risks associated with methanol handling as an additional hazardous chemical are eliminated whereas H ₂ O ₂ is also used as a bleaching chemical. In all other respects the process conditions and the unit operations are similar to those used in the generation of ClO ₂ using methanol. Due to the relatively short operating time of the existing installations and the consequent lack of consistent track record for low Cl ₂ contamination of the ClO ₂ solution, the low-chlorine integrated chlorine dioxide plant (IDP) is at present considered to be an emerging technology.	2.10.1 and 2.10.1.1

Section 2.11 – “Pulp quality and marketability”

No	Conclusion	Sub-section
36	The analysis of properties of ECF and TCF bleached market pulps produced in different regions of the world has shown that these pulps display different properties. Possible reasons for this observation include climate, harvest age and maturity, wood species, processing conditions including the bleaching sequence, and customer requirements. Consequently, this analysis is influenced by many more factors than ECF and TCF bleaching processes alone and it is not possible to generalise about which bleaching process is superior with	2.11

No	Conclusion	Sub-section
	respect to pulp properties.	
37	<p>Property comparisons made between ECF and TCF bleached pulps produced at the same mill using the same pulpwood are more representative than those of pulps from different regions. The following results are reported:</p> <p>Hardwood ECF and TCF bleached pulps produced at Kymmene Pietarsaari, Finland:</p> <ul style="list-style-type: none"> • Can be equal in brightness (89% ISO) and strength provided the refining energy for the TCF bleached pulp is sufficiently high <p>Softwood ECF and TCF bleached pulps produced at Mercer International Rosenthal, Germany:</p> <ul style="list-style-type: none"> • ECF bleached pulp reaches a certain tensile strength at a higher freeness than TCF bleached pulp. • ECF bleached pulp has higher tear strength and loses it less rapidly with refining than TCF bleached pulp. • ECF bleached pulp has higher brightness than TCF bleached pulp. • TCF bleached pulp needs more refining energy to reach a certain strength level. 	2.11.3
38	<p>The level of delignification in cooking, the cooking process and oxygen delignification determine the final pulp yield.</p> <p>The yield loss in bleaching is in the range 1-3% (on wood) and is most likely independent on whether an ECF or TCF sequence is employed. There is a tendency for increased yield loss if either alkaline peroxide or ozone bleaching are carried out. This is particularly noticeable in the bleaching of hardwood pulps.</p> <p>Because TCF bleached pulps tend to have lower oxygen-delignified pulp kappa number, they have a lower overall bleached yield than ECF bleached pulps.</p>	2.11.4.2
39	<p>According to present knowledge it is difficult to achieve full brightness (+90% ISO) with alkaline peroxide based TCF sequences, e.g. Q(OP)Q(PO), on softwood pulps. If acid stages are included in the bleach sequence, e.g. Paa, and in particular Z, a full brightness can be reached but then it is difficult to get high pulp strength.</p>	2.11.4.3
40	<p>Brightness reversion for ECF and TCF bleached pulps is a complex issue which has not been completely elucidated so far.</p>	2.11.4.4
41	<p>The following is a summary of the strength characteristics of eucalypt and pine BKP at comparable operation of the mill:</p> <ul style="list-style-type: none"> • Eucalypt kraft pulp: TCF pulp strength properties² are 90-100% of those for ECF pulp. • Pine kraft pulp: TCF pulp strength properties are 85-95% of those for ECF pulp. 	2.11.4.5
42	<p>ECF bleached pulp dominates the world bleached chemical pulp market. Data shows a widening gap between ECF and TCF bleached pulp production. ECF bleaching continues to grow whereas TCF, at approximately 5% of the world market at present (Q2 2006), is declining. There are mills originally built with the intention of producing TCF bleached pulp that have converted or plan to convert to ECF bleaching with the capability of producing TCF bleached pulp as required.</p>	2.11.4.5

² Eucalypt pulp strength properties are arguably not the most important parameters, whereas light scattering coefficient, opacity and parameters promoting formation are more important.

No	Conclusion	Sub-section
43	TCF bleaching has continued to develop, for example Södra no longer uses ozone to produce TCF softwood pulps, and Kymmene has similarly discontinued the use of ozone. Södra and Kymmene indicated strength concerns with ozone during mill visits carried out in 2005 and advised they are developing better alternative bleaching techniques. All major companies that pioneered kraft TCF bleaching in their fibre lines have recently purchased, built or plan to build new ECF capacity. This includes Metsä-Botnia, Kymmene and ENCE.	2.11.4.5
44	The risks identified in a risk inventory of TCF and ECF bleaching are all in the low risk area in the risk matrix where additional risk mitigating measures normally can be regarded to have low priority. All risk scenarios are either "less likely" or "unlikely" or "very unlikely" to occur, i.e. the probability for their occurrence is once in 10 years to once in over 1000 years. Even though there are two more risk scenarios identified for ECF bleaching and the probability level for some ECF scenarios is slightly higher than for TCF, the overall risk levels for the two processes may be considered comparable.	2.12.5
45	A review of the Driscoll report prepared for the Commission in 2005 and a discussion of the extremely low potential for exposure to organochlorines in ECF mills leads to the tentative conclusion that the risk level for any health effects from working in ECF and TCF mills is comparable.	2.12.6

SECTION 3 – "CONVENTIONS RELEVANT TO THE DEBATE ON ECF AND TCF BLEACHING"

Section 3.1 – "United Nations Environment Programme - Chemicals"

No	Conclusion	Sub-section
46	As the ECF and TCF bleaching processes are considered BAT in [IPPC BREF, 2001] and acceptable for use in pulp bleaching in [UNEP, 2006], they should also be acceptable for pulp bleaching according to: <ul style="list-style-type: none"> • BAT and BEP as defined in Article 5 and qualified in Annex C of the Stockholm Convention. • General prevention measures relating to BAT and BEP as defined in Annex C of the Stockholm Convention. In Annex C to the Convention process changes such as moving to closed systems are recommended. This may however lead to build up of non-process elements such as chloride in the systems which could increase any formation of TCDD and TCDF in the recovery boiler.	3.1.4

SECTION 4 – “GUIDELINES AND REGULATIONS RELEVANT TO THE DEBATE ON ECF AND TCF BLEACHING”

Section 4.5 – “World Bank Group”

No	Conclusion	Sub-section
48	<p>The WBG and its private sector arm International Finance Corporation (IFC) adopt the guidelines contained in [PPAH, 1999] as benchmarks to decide whether to approve investments.</p> <p>Because the PPAH was published in 1999 and probably researched and written from 1995 and onwards statements like “the trend is to avoid the use of any kind of chlorine chemicals and employ “totally chlorine free” (TCF) bleaching” are not quite relevant in 2006 when TCF bleaching accounts for less than 5% of the global production capacity of bleached chemical pulp and there has in fact been a reduction in total TCF capacity over the last few years.</p> <p>Another statement in the PPAH “TCF processes allow the bleaching effluents to be fed to the recovery boiler for steam generation, thereby reducing the amount of pollutants discharged” was a high expectation of the 1990s, however, the recycling of bleach effluents from TCF processes has proven equally difficult to manage as from ECF processes.</p> <p>Zero -effluent discharge from kraft pulping is at present (Q2 2006) not a feasible option and the possible recycle and incineration of bleach effluents (from ECF and TCF bleaching alike) is limited.</p> <p>The PPAH states that “ECF processes are acceptable, and, from an environmental perspective, TCF processes are preferred”. Except for the statements discussed above there is no further evidence given to support this preference in the text.</p>	4.5.3

SECTION 5 – “SPECIFIC ISSUES RAISED IN THE WWF REPORT ON ARAUCO VALDIVIA”

Section 5.1 – “Hazard profile of chlorine dioxide”

No	Conclusion	Sub-section
49	Comment in answer to Recommendation 58 of [WWF, 2005]: The risk and health assessment of ECF and TCF bleaching (reported in section 2.12) concludes that the overall risk levels for the two processes may be considered comparable. Similarly, the risk level for any health effects from working in ECF and TCF mills is comparable.	5.1

Section 5.2 – “Increased concentration of dioxins in the Baltic Sea near ECF mills during 1979-2000”

No	Conclusion	Sub-section
50	Comment in answer to Recommendation 60 of [WWF, 2005]: The WWF has misinterpreted the study by [Olsson, 2005a]. It is possible that dioxin levels have increased in fatty fish from the Bothnian Sea during the period 1979-2000, although the number of measurements has been insufficient from a statistical point of view. However, this increase has not been observed in fish from ECF pulp mill primary recipients but in herring (<i>Clupea harengus</i>) collected at one station in the southern part of the Bothnian Sea [Olsson, 2003]. One hypothesis among others (e.g. oligotrophication and thereby less biological dilution) to explain this increase in dioxin levels raised by [Olsson, 2003] was an ongoing pollution in the catchment area of the Bothnian Sea. Consequently, a study was initiated to measure dioxin levels in stationary fish (perch and eelpout) from pulp mill recipients. The results from this study have so far [Olsson, 2005a] shown low levels of dioxins although somewhat higher in the recipients compared to the reference areas. The only recipient where it is possible to compare with historical data shows a decrease of dioxins in perch by a factor 20 during the last 15 years. These results are thus in conflict with those for pelagic herring and indicate a dramatic reduction in dioxin discharges from the pulp mill compared to the situation in the 1980s.	5.2

Section 5.3 – “Catalytic oxygen bleaching”

No	Conclusion	Sub-section
51	<p>Comment in answer to Recommendation 62 of [WWF, 2005]: The news article (in Swedish) referenced in the WWF report [Lehtimaa, 2005] explains that catalytic oxygen bleaching (COB) is being investigated at Helsinki Technical University (www.tkk.fi) as a means to increasing oxygen delignification selectivity. This would allow the kappa number of oxygen delignified kraft pulp to be lower without the serious drawback of strength loss due to carbohydrate attack. Lehtimaa also says that “The problem with current technology for bleaching with totally chlorine free chemicals (TCF) is that it is primarily suitable for relatively lightly bleached pulp or in cases where lower run-off volumes are desirable for environmental or market reasons” and concludes by saying “Catalytic oxygen gas bleaching would thus provide the advantages of TCF technology while being even more cost-effective than ECF, which is still defined as the best available technology for bleaching”.</p> <p>Another comment made in the news article is: “No one has so far presented an economically feasible alternative for catalytic bleaching on an industrial scale”.</p> <p>Hence, catalytic oxygen bleaching is considered to be an emerging technology.</p>	5.3

Section 5.4 – “Multibio system at SCA Östrand”

No	Conclusion	Sub-section
52	<p>Comment in answer to Recommendations 69 and 70 of [WWF, 2005]: Biological effluent treatment is considered to be AMT for BKP mills. With modern technology it is possible to achieve both high reduction of biodegradable organic matter and low discharge of nutrients. The biological treatment system can be designed in different ways and the selection of treatment system should be based on a techno-economical evaluation considering the site specific conditions. It is not true that a special type of biological system (e.g. the Multibio process) should be generally superior in comparison to others with respect to removal of COD and other environmental parameters.</p>	5.4

Section 5.5 – “Tertiary treatment”

No	Conclusion	Sub-section
53	<p>Comment in answer to Recommendation 71 of [WWF, 2005]:</p> <p>While it is agreed that a tertiary treatment stage cannot generally be considered AMT because it requires high chemical dosages and produces large amounts of sludge, in some cases (not only the mills mentioned in Recommendations 70 and 71) it has been considered necessary, due to special local requirements, to include that type of treatment to achieve a lower discharge than can be obtained by only secondary treatment.</p> <p>It is not possible to design or redesign a secondary treatment system for as high removal efficiency as is achieved with the combined secondary and tertiary treatment. Some type of substances (e.g. high molar mass organic compounds) that are removed in a tertiary treatment cannot be removed by biological methods.</p>	5.5

1 INTRODUCTION

1.1 WWF REPORT ON ARAUCO VALDIVIA

The WWF (www.panda.org) (formerly known as the World Wildlife Fund and World Wide Fund for Nature) has recently published a report which describes the impact the Celulosa Arauco y Constitución (CELCO) BKP mill near Valdivia, Chile may have had on the Carlos Anwandter Nature Sanctuary and suggests possible mitigating actions to redress the situation [WWF, 2005].

The WWF report makes several references to ECF and TCF bleaching processes and their impact on the environment.

This study report reviews ECF and TCF bleaching processes and specific issues raised in the WWF report on Arauco Valdivia.

1.2 TERMINOLOGY

The following terminology describing minimum environmental impact technologies and management practices will be used in this report [Beca AMEC, 2004]:

1.2.1 Accepted modern technology

AMT is defined in the *State Policy on Water Quality Management 1997 and Environment Protection Policy (Air Quality) 2004* as a "technology which has a demonstrated capacity to achieve the desired emission concentration in a cost-effective manner, takes account of cost-effective engineering and scientific developments and pursues opportunities for waste minimisation."

The AMT included in this report are technologies that have a demonstrated track record of being technically effective and economically viable on an industrial scale for minimising the discharge of pollutants from BKP mills to the environment. These technologies are an integral part of worldwide supra-national, national and sub-national environmental guidance.

1.2.2 Best available techniques

The European Commission's [IPPC BREF, 2001] defines best available techniques (BAT) as "...the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent, and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole".

- "Best" means most effective in achieving a high general level of protection of the environment as a whole.
- "Available" refers to those techniques developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member States in question, as long as they are reasonably accessible to the operator.
- "Techniques" include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned.

1.2.3 Best practice environmental management

BPEM is defined in the *Environmental Management and Pollution Control Act 1994* as "the management of an activity to achieve an ongoing minimisation of the activity's environmental harm through cost-effective measures assessed against the current international and national standards applicable to the activity".

BPEM includes practices like:

- High standards of maintenance.
- Environmental management systems carried out to an international standard and independently audited.
- Process control monitoring and optimisation.
- Training, education and motivation of personnel.

1.2.4 Reference tables

The reader should refer to the tables "Units and conversion factors", "Abbreviations and acronyms" and "Glossary of terms" included at the end of this report whenever an unfamiliar term is found.

2 REVIEW OF ECF AND TCF BLEACHING PROCESSES

2.1 GENERAL

2.1.1 Pulping and oxygen delignification

Kraft pulp is made by dissolving most, but not all, of the lignin originally present in wood. Much of the hemicellulose is removed at the same time, but the cellulose, responsible for the pulp's strength, remains. The remaining lignin, called "residual lignin", is responsible for the dark brown colour of unbleached kraft pulp.

The residual oxidisable material (largely hexenuronic acids³ (HexA), lignin and lignin-carbohydrate residues) in kraft pulp is measured by the kappa number test.

A number of modified cooking (MC) techniques were developed in the last two decades to modify the conditions in kraft digesters with the aim to lower the kappa number while minimising strength and yield losses. These techniques are considered AMT [Beca AMEC, 2004].

After cooking, the fibres still contain some lignin which must be removed to ensure low-environmental-impact bleaching. To preserve pulp strength, the lignin must be removed selectively, i.e. with minimum damage to cellulose and yield loss. Oxygen delignification has become the dominant technology to achieve these aims and is also considered AMT [Beca AMEC, 2004].

³ HexA derive from *xylan*, which is the dominant component of hardwood hemicellulose. Xylan has a lower concentration in softwood hemicellulose, hence, the generation of HexA in kraft pulping of radiata pine (a softwood) is lower.

2.1.1.1 Unbleached kappa number and viscosity limits

Despite the widespread adoption of these AMT, there is a lower limit for kappa number below which strength and yield losses become unacceptable.

Figure 2.1 shows indicative kappa number limits for cooking and oxygen delignification from the perspective of polysaccharide degradation or pulp strength (as measured by pulp viscosity).

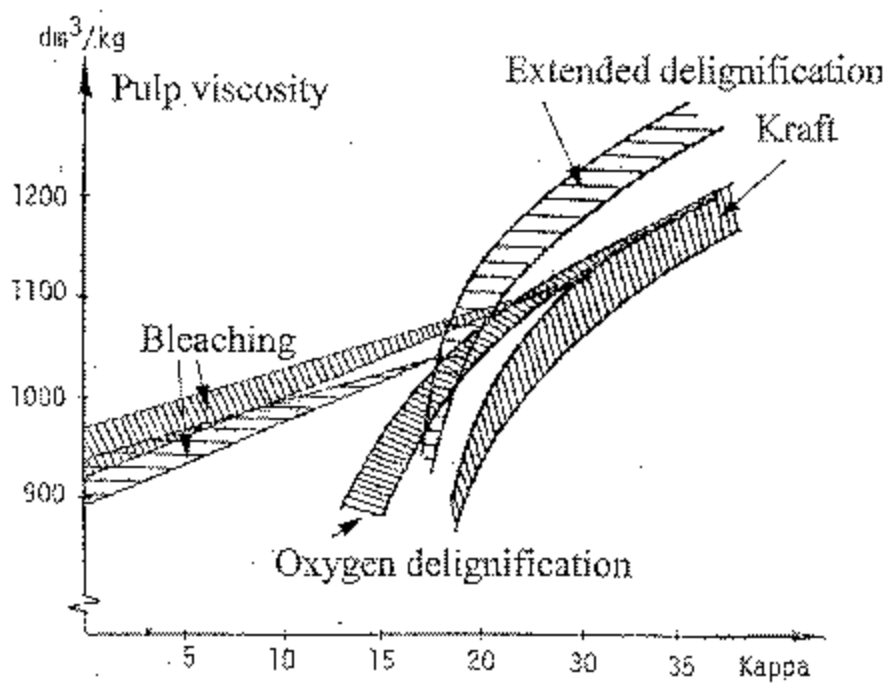


Figure 2.1 Kraft pulp viscosity v kappa number

Source: [Nguyen, 1997].

A lower limit for pulp viscosity is generally considered to be around 900 dm³/kg. Hence, further kappa number reduction needs to be carried out by using a "milder" and more selective process. This process is described in the following section.

2.1.2 Bleaching

2.1.2.1 Working definition of bleaching

Chemical pulp bleaching aims to remove coloured residual lignin from the pulp and increase its brightness, brightness stability and cleanliness⁴ while preserving the strength (cellulose integrity) and carbohydrate yield (cellulose and hemicellulose) of the unbleached fibre, with due regard for potential effects on the environment [McDonough, 1997].

2.1.2.2 Brightness levels for kraft market pulp

Table 2.1 shows typical kraft market pulp brightness levels in oxygen delignified pulp and final product.

Table 2.1 Kraft market pulp brightness

Pulp stage	Hardwoods	Softwoods
Oxygen delignified	~ 45% ISO	~ 40% ISO
Fully bleached	~ 90% ISO	~ 90% ISO

Sources: ÅF-Process, Beca AMEC.

There are many other pulp properties important in selling pulp, and these include optical and formation properties (such as opacity) for hardwoods, and tensile strength and stiffness for softwoods. Individual fibre properties such as coarseness (mass to length ratio), kink and curl (how bent the individual fibres are) are also important for some manufacturers. Some pulp manufacturers tailor pulps for individual clients and grades.

2.1.2.3 The bleach plant

A bleach plant consists of a sequence of separate bleaching stages where different chemicals are added. Each bleaching stage includes the following equipment:

- A device for mixing chemicals, steam and pulp.
- A bleaching reactor (upflow or downflow tower) designed with a suitable residence time for completion of chemical reactions.
- Washing equipment for separation of residual chemicals, lignin and other dissolved compounds from the pulp (e.g. wash presses or diffusion washers).

The bleaching stages are designated by using symbolic shorthand according to the bleaching chemical applied, as shown in Table 2.2 on the following page.

⁴ I.e. decolourise dirt and shives that contaminate the stock.

Table 2.2 includes (in *italics*) those stages that are no longer used in modern kraft pulp bleach plants⁵ and the oxygen delignification stage upstream of the bleach plant (see also Tables 2.7 and 2.8 following).

Table 2.2 Bleaching stage designation

Stage name	Description	pH
A	Acid stage to remove either transition metal ions or HexA, or both. Hot acid stages specifically designed to remove HexA formed in kraft pulping of hardwoods are designated A_{hot} , $(AD)_{hot}$ and D_{HT} . The acid is usually sulfuric acid (H_2SO_4)	Acid
C	<i>Chlorination stage using either chlorine (Cl_2) gas or a solution of Cl_2 in water</i>	<i>Acid</i>
D	Chlorine dioxide stage using a solution of chlorine dioxide (ClO_2) in chilled water	Acid
(DN)	Chlorine dioxide stage with subsequent neutralisation	Acid/ Neutral
E	Extraction stage using sodium hydroxide (NaOH)	Alkaline
(EO)	Extraction stage using NaOH with subsequent addition of gaseous oxygen (O_2) as a reinforcing agent	Alkaline
(EOP)	Extraction stage using NaOH with subsequent addition of O_2 and hydrogen peroxide (H_2O_2) as reinforcing agents	Alkaline
(EP)	Extraction stage using NaOH with subsequent addition of H_2O_2 as a reinforcing agent	Alkaline
H	<i>Hypochlorite stage using sodium hypochlorite ($NaClO$)</i>	<i>Alkaline</i>
O	Pressurised oxygen delignification	Alkaline
(OP)	Pressurised peroxide stage using H_2O_2 with O_2 (low peroxide charge)	Alkaline
P Paa	Atmospheric peroxide stage using H_2O_2 Peracetic acid (CH_3COOOH) stage	Alkaline Slightly acid
(PO)	Pressurised peroxide stage using H_2O_2 with O_2 (high peroxide charge)	Alkaline
Pxa	Stage with a mixture of peracids	Slightly acid
Q	Acid stage where a chelating agent, EDTA or DTPA, has been used for removal of transition metal ions. More efficient than an A stage for this purpose. The acid is usually H_2SO_4	Acid
X	Enzyme treatment stage	Usually slightly acid
Z	Ozone stage using gaseous ozone (O_3)	Acid

Sources: ÅF-Process/ Beca AMEC.

⁵ Chlorine and NaClO are not longer used in modern kraft pulp bleach plants because Cl_2 has been found to contribute to the formation of dioxins and furans (see following sections 2.2 and 2.3) and NaClO generates chloroform and degrades pulp strength.

Despite a few applications of hot acid stages in the Brazilian and South African BEKP mills, adoption of acid hydrolysis as a standalone stage (A_{hot} , $(AD)_{\text{hot}}$ and D_{HT}) for the selective removal of HexA has not been widespread [Eiras, 2003] and is debatable as an environmental measure. Hence, these stages are at present considered to be an emerging technology⁶.

Different types of enzymes were used to a limited extent by several mills in Europe, North America and South America during the mid-late 1990s, however, long term use of enzymes proved to be unprofitable. The main goal for the use of enzymes was to reduce the ClO_2 or, if applicable, the Cl_2 charge. Some mills used enzymes because their ClO_2 capacity was limited, that is, enzymes were used for debottlenecking. North American experience has shown that enzyme bleaching is more effective in mills without oxygen delignification. The use of enzymes is today less prevalent than in the past due to concerns over higher than expected yield losses. Hence, this treatment is at present also considered to be an emerging technology.

2.1.2.4 Bleaching chemical characteristics

Bleaching chemicals are oxidising agents that:

- Break up the lignin molecule by attack on the aromatic rings [Lachenal, 1999].
- Introduce solubilising groups (phenolic hydroxyl and carboxylic acid groups) into the fragments.
- Disrupt lignin-carbohydrate bonds, allowing fragments to dissolve.
- Remove coloured compounds (chromophores).
- May (Cl_2 , ClO_2 , Paa and O_3) or may not (O_2 and H_2O_2) react with HexA.

Table 2.3 on the following page presents a summary of bleaching chemical characteristics (bleaching chemicals no longer used in modern bleach plants *italicised*).

⁶ Emerging technologies are defined as either:

- Technologies under development which may, if proven technically and economically attractive, also result in the reduction of emissions or energy and resource savings; or
- Technologies that have been used for some time and are technically proven but whose economies vary depending on local cost conditions and are, therefore, used in some countries but not in others.

Table 2.3 Summary of bleaching chemical characteristics

Formula	Equiv mass ¹	Reactivity ²	Selectivity ⁴	Dirt removal	Environmental implications ⁵
<i>Cl₂</i>	35.5	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>
<i>ClO₂</i>	13.5	<i>M/H</i> ³	<i>H</i>	<i>H</i>	<i>M</i>
<i>H₂O₂</i>	17	<i>L</i>	<i>H</i>	<i>L</i>	<i>L</i>
<i>NaClO</i>	37.2	<i>M</i>	<i>M</i>	<i>H</i>	<i>H</i>
<i>O₂</i>	8	<i>L</i>	<i>M</i>	<i>M</i>	<i>L</i>
<i>O₃</i>	8	<i>H</i>	<i>M</i>	<i>L</i>	<i>L</i>

Notes:

1. Equivalent mass is the mass required to do a specified amount of oxidation, hence, the reciprocal of oxidising power.
2. Reactivity is a measure of the degree to which the oxidising power is used in kappa number reduction and not wasted in unproductive reactions.
3. High reactivity at higher temperature.
4. Selectivity is a measure of the degree to which the reaction is primarily with lignin as opposed to the other main fibre components (cellulose and hemicellulose).
5. Different bleaching chemicals engender different levels of concern for the environment. Whether the concern is justified may be irrelevant.
6. H = high; L = low; M = medium.

Source: [McDonough, 1997].

The most common and widely used bleaching chemicals in modern bleach plants are *ClO₂*, *O₂* and *H₂O₂*. Ozone is also used, but not as much as *ClO₂*, *O₂* and *H₂O₂*. Peracetic acid is also used in some mills, but is less common than *O₃*. Sodium hydroxide or acid (usually *H₂SO₄*) need to be added to create the right conditions (pH) in the stages. Furthermore, NaOH extracts the oxidised structures formed by the other bleaching chemicals (hence, the name "extraction stage").

Ozone is a very reactive bleaching agent while *ClO₂*, *O₂* and *H₂O₂* are less reactive. Several bleaching chemicals are used in a bleaching sequence because their reaction mechanisms are different. Acid and alkaline stages are typically used alternatively in the bleaching sequence.

A number of mills have stopped using their ozone stages, particularly on softwood. This is due to concern on the impact of ozone on pulp strength.

Hydrogen peroxide bleaching (P) is relatively slow and requires long reaction times. Large reactor volumes or increased pulp consistency are, therefore, required. Higher reaction temperatures are possible if the pressure is increased, as in (OP) or (PO) stages, resulting in a reduced reaction time or improved bleaching outcome. Removal or immobilisation of transition metal ions (mainly Mn, Fe and Cu) is necessary to avoid degradation of *H₂O₂*. This is accomplished by using either metal chelating agents (i.e. EDTA or DTPA), or acid stages (A) or acid washing. Compared to *O₂* and *O₃*, *H₂O₂* has the advantage of being able to brighten the residual lignin when used at optimal conditions. However, the bleaching of pulp with a high charge of *H₂O₂* increases the content of residual lignin in the pulp. The lignin is brightened but causes brightness reversion (reduced brightness stability) after bleaching. The reversion may occur during transportation of pulp, at the paper manufacturing site or in the final paper product.

Effective use of P stages is not possible in all mills. Control of Mn and Fe levels is necessary. These metal ions originate in wood, and most of them carry through to the bleach plant. Levels in bleaching can vary by more than 100 times between mills. Low levels are in the < 1 to 5 ppm range, moderate levels in the 5-30 ppm range and high levels above 50 ppm. Mills applying high H₂O₂ charge generally find that H₂O₂ is not effective in bleaching. The effectiveness of P stages in TCF and ECF-light bleaching sequences is generally low for woods with high levels of Mn.

Chlorine dioxide and O₃ have to be produced on site due to their instability. Hydrogen peroxide, O₂, NaOH, Paa and H₂SO₄ can be purchased and delivered to the mill.

2.1.2.5 Modern bleaching methods

The two principal modern bleaching methods are described in Table 2.4. They are usually designated by the chemicals they do not use.

Table 2.4 Modern bleaching methods

Bleaching method	Description
ECF or elemental ⁷ chlorine free bleaching	If molecular chlorine and sodium hypochlorite (NaClO) are excluded, the term applied for the bleaching sequence is chlorine dioxide bleaching (CDB) or elemental chlorine-free (ECF) bleaching
TCF or totally chlorine free bleaching	If the sequence only uses oxygen-based chemicals, such as oxygen, ozone, alkaline or acidic peroxide, the terms oxygen chemical bleaching (OCB) or totally chlorine-free (TCF) bleaching can be used

Sources: Beca AMEC, [UNEP, 2006].

⁷ I.e. molecular.

2.2 SIGNIFICANT MILESTONES IN BLEACHING

Significant developments in the history of bleaching are shown in chronological order in the following table:

Table 2.5 Significant developments in the history of bleaching

Year	Description
Late 1960s	Low chlorine dioxide substitution for chlorine (5-30%) in (CD) bleaching stages to improve pulp strength
1970	First oxygen delignification plant
Late 1970s to early 1980s	Higher chlorine dioxide substitution for chlorine (30-90%) in (DC) bleaching stages is adopted to various extents in different mills and countries primarily to decrease the use of Cl ₂ and thereby to considerably reduce the formation of chlorinated organic compounds
1978	Great Lakes Paper Company in Thunder Bay, ON, Canada adopts a concept for bleached kraft mill process closure called the Rapson-Reeve Process, from the names of its developers. A major factor in taking that decision was the lack of sufficient space to install wastewater treatment facilities at the site. The mill operated in a partially closed manner for several years before the concept was abandoned in 1988 and a secondary treatment plant was installed. This pioneering effort clearly established the technical challenges that must be overcome to eliminate bleached kraft mill discharges [Stratton, 2003a], [Stratton, 2003b]
1985	<ul style="list-style-type: none"> • First reinforced extraction bleaching stage, (EO), (EP) and (EOP), is started up primarily to decrease the use of Cl₂ • Chlorine bleaching is found to contribute to the formation of the toxic and environmentally persistent compounds 2,3,7,8-tetra chloro dibenzo-<i>p</i>-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetra chloro dibenzofuran (2,3,7,8-TCDF)
1990	<ul style="list-style-type: none"> • ECF bleach plants begin operating in existing mills • First BKP mill employing TCF bleaching (Smurfit Munksjö Aspa Bruk, Sweden)
1993	First purposely built BKP mill employing ECF bleaching and other AMT starts up at Alberta-Pacific, Boyle, AB, Canada
1995	<ul style="list-style-type: none"> • First BKP mill to successfully recycle the first acidic bleaching stage at Blue Ridge Paper Products Canton, NC, USA. Operating continuously since 1995 • Full identification and verification of the occurrence of hexenuronoxylan during alkaline pulping

Source: Beca AMEC, AMEC.

These developments had a considerable impact on the reduction of emissions, particularly to the aquatic environment.

2.3 THE SIGNIFICANCE OF DIOXINS IN THE DEVELOPMENT OF MODERN BLEACHING PROCESSES

2.3.1 General

The term “dioxins”⁸ refers to 75 congeners of polychlorinated dibenzo-*p*-dioxins (PCDD) and 135 congeners of polychlorinated dibenzofurans (PCDF) [UNEP Chemicals, 2005].

The structures of both compound classes are shown in Figure 2.2; they are tricyclic, aromatic compounds formed by two benzene rings connected by two oxygen atoms in PCDD and by one oxygen atom and one carbon-carbon bond in PCDF and whose hydrogen atoms may be replaced by up to eight chlorine atoms [UNEP, 2006].

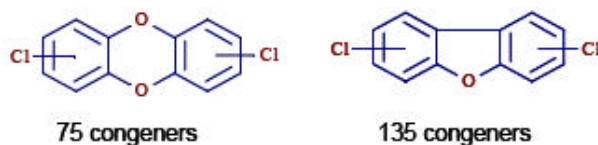


Figure 2.2 Structure of PCDD and PCDF

Source: [UNEP Chemicals, 2005].

Among these 210 compounds, 7 PCDD congeners and 10 PCDF congeners can have chlorine atoms at least in the lateral (i.e. 2, 3, 7, and 8) positions of the aromatic ring of the parent molecule.

These seventeen 2,3,7,8-substituted congeners are highly toxic, persistent (lasting for years or even decades before degrading into less dangerous forms), highly volatile and accumulate in fatty tissue, hence, they are called persistent organic pollutants (POP).

Because PCDD/PCDF are by-products of industrial processes they are also sometimes called unintentionally produced POP (UPOP).

These POP are included in Part I of Annex C – “Unintentional production” of Article 5 – “Measures to reduce or eliminate releases from unintentional production” of the Stockholm Convention (see Section 3 for a summary on this Convention).

⁸ In this report, where the term “dioxin” or “dioxins and furans” is used alone, it should be interpreted as including all polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans, unless specifically stated otherwise.

Emission sources of PCDD/PCDF from BKP mills are the:

- Recovery boiler.
- Power boiler.
- Liquid effluent.
- Sludge, which may be applied on land, incinerated or landfilled.
- Pulp.

2.3.2 Dioxin and furan precursors

The finding in 1985 that Cl₂ bleaching contributes to the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF, and the resulting broader concern about potential impacts of chlorinated organic compounds in general, drove many mills to greatly reduce Cl₂ use in the bleach plant and ultimately to eliminate its use entirely [Stratton, 2003a], [Stratton, 2003b].

The specific chlorinated organic compounds 2,3,7,8-TCDD and 2,3,7,8-TCDF are generated by electrophilic aromatic substitution (chlorination) of the unchlorinated precursors dibenzo-p-dioxin (DBD) and dibenzofuran (DBF).

The unchlorinated dioxin precursors are prevalent in certain mineral oils, which are part of some defoamer formulations used in the pulp and paper industry and are the major source of precursors [UNEP, 2006] but have been also found in municipal water supply, precipitated kraft lignin and unbleached pulp thoroughly extracted with methanol and steam [NCASI, 2002]. Several jurisdictions ban the use of defoamers containing dioxin and furan precursors.

Wood itself may act as the source of dioxin precursors:

- Compression wood in particular contains higher concentrations of precursors than normal wood. The compression of wood also entails higher levels of coumaryl-type lignin, which may be a source of DBD- and DBF-like precursors [UNEP, 2006].
- Sawmill chips contaminated with polychlorinated phenols can result in the formation of PCDD in the digester.

The chlorination of non-aromatic structures, such as HexA, does not lead to the formation of polychlorinated aromatic degradation products [UNEP, 2006].

2.3.3 Toxicity equivalency factors

Many regulatory agencies have developed so-called Toxicity Equivalency Factors (TEF) for the risk assessment of complex mixtures of PCDD/PCDF.

The TEF are based on acute toxicity values from *in vivo* and *in vitro* studies. This approach is based on the evidence that there is a common, receptor-mediated mechanism of action for these compounds. However, the TEF approach has its limitations due to a number of simplifications.

Although the scientific basis cannot be considered as solid, the TEF approach has been developed as an administrative tool and allows conversion of quantitative analytical data for individual PCDD/PCDF

congeners into a single Toxic Equivalent (TEQ) and express cumulative toxicity of complex PCDD/PCDF mixtures as one single TEQ value.

It should be noted that TEF are interim values and administrative tools for order of magnitude estimates. They are based on present state of knowledge and may be revised as new data become available [UNEP/ PCDD & PCDF, 2005].

Today there are two schemes applied:

- The older scheme was established by a NATO/CCMS Working Group on Dioxins and Related Compounds as International Toxicity Equivalency Factors (I-TEF) [NATO/CCMS, 1988], [Kutz, 1990].
- The most recent scheme was established by a WHO/IPCS working group, who re-evaluated the I-TEF and established a new scheme.

The two schemes are found in the following table, which lists the TEF for human and mammalian risk assessment.

Table 2.6 Comparison of the two most commonly used TEF schemes

Congener	I-TEF	WHO-TEF
PCDD		
2,3,7,8-Cl ₄ DD	1	1
1,2,3,7,8-Cl ₅ DD	0.5	1
1,2,3,4,7,8-Cl ₆ DD	0.1	0.1
1,2,3,6,7,8-Cl ₆ DD	0.1	0.1
1,2,3,7,8,9-Cl ₆ DD	0.1	0.1
1,2,3,4,6,7,8-Cl ₇ DD	0.01	0.01
Cl ₈ DD	0.001	0.0001
PCDF		
2,3,7,8-Cl ₄ DF	0.1	0.1
1,2,3,7,8-Cl ₅ DF	0.05	0.05
2,3,4,7,8-Cl ₅ DF	0.5	0.5
1,2,3,4,7,8-Cl ₆ DF	0.1	0.1
1,2,3,6,7,8-Cl ₆ DF	0.1	0.1
1,2,3,7,8,9-Cl ₆ DF	0.1	0.1
2,3,4,6,7,8-Cl ₆ DF	0.1	0.1
1,2,3,4,6,7,8-Cl ₇ DF	0.01	0.01
1,2,3,4,7,8,9-Cl ₇ DF	0.01	0.01
Cl ₈ DF	0.001	0.0001

Source: [UNEP/ PCDD & PCDF, 2005].

Notes:

1. For all non-2,3,7,8-substituted congeners, no TEF has been assigned.
2. Numbers in bold represent TEF which have been changed by WHO from the I-TEF.

2.4 ECF BLEACHING

2.4.1 Sequences

Examples of typical modern ECF bleaching sequences are: D(EOP)D, D(EOP)DD, D(EOP)DP, D(EOP)D(PO), Q(PO)DD, Q(PO)(DQ)(PO) or Z(EOP)DD.

Sequences including only D and E stages are called “straight ECF” whereas those including D in combination with P and (PO) are called “ECF light” and “ECF super light”⁹ [Bergnor-Gidnert, 2006].

Generally, to reach a certain brightness target, hardwood requires fewer chemicals than softwood, which usually means that the number of bleaching stages can be shorter. Over the years, the use of ClO₂ has substantially decreased in bleaching and has been replaced by oxygen based chemicals. ECF light and ECF super light sequences can be applied for both hardwood and softwood, depending on the brightness target [UNEP, 2006].

2.4.2 Comment regarding Article 5, Annex C of the Stockholm Convention

Annex C – “Unintentional production (of POP)” of Article 5 – “Measures to reduce or eliminate releases from unintentional production (of POP)” of the Stockholm Convention (see Section 3 for a summary on this Convention and Appendix C for the full text of Article 5 and Annex C) states in Part V: “General guidance on best available techniques and best environmental practices” that “priority should be given to the consideration of approaches to prevent the formation and release of the chemicals listed in Part I (POP). Useful measures could include....avoiding elemental chlorine or chemicals generating elemental chlorine for bleaching”.

Although the Stockholm Convention provides only general guidance to the Parties, it is important to clarify whether ClO₂ can be considered a chemical generating molecular Cl₂ in ECF bleaching, thus contributing to the formation of POP.

The following discussion is a summary of the detailed technical discussion included in Appendix B – “Chemistry of chlorine dioxide bleaching”.

Several chemical reactions occur in a D stage whose reactants or products are chlorous acid (HClO₂), chlorite ion (ClO₂⁻), hypochlorous acid (HClO), hydrochloric acid (HCl), chlorate ion (ClO₃⁻), water (H₂O), ClO₂ and Cl₂.

⁹ These sequences are also sometimes called “low-impact ECF”, “low-AOX ECF” (e.g. Aracruz Barra do Riacho, Brazil) and “low-OX ECF” (e.g. Line C at Votorantim Celulose e Papel Jacarei, Brazil).

When Cl₂ dissolves in water, it undergoes a reversible hydrolysis, in which both HClO and HCl are formed:



This equilibrium is pH and temperature dependent.

Modern D stages typically operate at a pH range of 3 to 4 and a temperature range of 60 to 80°C. At these conditions, reaction (1) “goes to completion”, that is, it proceeds only to the right (forward direction) and the dominant species are HClO and dissociated HCl.

Consequently, any Cl₂ that may be formed from ClO₂ when it reacts with pulp or may be present in the ClO₂ solution¹⁰ in a D stage is converted to HClO.

Therefore, chlorine dioxide can potentially generate molecular chlorine in ECF bleaching but this chlorine is converted to hypochlorous acid at the typical conditions of pH and temperature of a D stage.

2.4.3 Chlorinated organic compounds

Hypochlorous acid generates small amounts of substituted chlorinated organic compounds and chloroform when reacting with lignin. These are measured as AOX in bleach plant effluents (0.2- 1.0 kg/ADt) and OX in ECF bleached pulp (30- 120 g/ADt).

Compounds identical or similar to those produced in ECF pulp bleaching are formed as a result of natural processes. These naturally produced compounds range from simple alkanes, such as chloromethane, to numerous complex halogenated alcohols, ketones, carboxylic acids, carboxylic amides, aldehydes, epoxides and alkenes [Gribble, 1994] and chlorophenolic isomers such as 2,4,6-trichlorophenol and its methylated analogue 2,4,6-trichloroanisole [Grimvall, 1994].

Chlorinated compounds formed during ECF bleaching are biologically degradable in the environment. Pulp mill AOX will ultimately be mineralised through photochemical and biological processes and during mineralisation the chlorinated organic material will be released as chloride and carbon dioxide (CO₂) [Archibald, 1997].

¹⁰ Depending on the generation method used, up to 0.22 kg Cl₂/kg ClO₂ may be present in the chlorine dioxide solution, corresponding to a substitution of 91.6%.

2.4.4 Dioxins and furans

Electrophilic substitution reactions that form PCDD and PCDF from their precursors require positively-charged chlorine species such as chloronium ion, Cl^+ [Berry, 1989].

Both Cl_2 and HClO can function as electrophiles, although HClO does so to a much lesser degree than Cl_2 [NCASI, 2002].

The initial reacting electrophile is Cl^+ , formed from Cl_2 by cleavage of the Cl-Cl bond and from HClO by cleavage of the O-Cl bond in its conjugate acid [Dence, 1996], as shown in reaction (2).



Chlorination of lignin and PCDD and PCDF precursors follows the mechanistic principles of electrophilic aromatic substitution, and thus proceeds in a stepwise manner. The initial chlorine substitution on an aromatic structure may occur readily, but the introduction of the second and subsequent chlorine atoms is more difficult because the aromatic ring is deactivated by an order of magnitude with each successive chlorine substitution [Ni, 1995]. Thus, formation of highly chlorinated PCDD and PCDF by electrophilic substitution is not thermodynamically favoured [NCASI, 2002].

Because of the above, the probability of formation of PCDD and PCDF in ECF bleaching is extremely low, as demonstrated by the following excerpts from UNEP documents:

“Increasing the ClO_2 substitution decreases the formation of chlorinated aromatic substances and eliminates the formation of PCDD/PCDF” [UNEP PCDD & PCDF, 2005].

“When the ClO_2 substitution level is higher than 85%¹¹ in Cl_2 bleaching, or if ECF bleaching¹² is used, emissions of 2,3,7,8-TCDD and 2,3,7,8-TCDF to water are lower than the limit of quantitation (US EPA Method 1613¹³)” [UNEP, 2006].

In spite of this, highly chlorinated congeners do sometimes appear in bleached pulps and filtrates. The presence of significant amounts of hexa- and hepta-chlorinated CDD at some Canadian west coast mills was attributed to the use of sawmill chips made from polychlorinated phenol-treated wood as a furnish in kraft pulping [Luthe, 1993]. In these mills, the PCDD were formed in the pulping process, not in the bleach plant. Another study showed that highly chlorinated dioxins, especially octachlorodibenzo-p-dioxin (OCDD), are found in common, everyday materials and in all of the 19 unbleached pulp samples that were tested [Berry, 1993]. Filter media from house furnaces and car air intakes had the highest levels, suggesting that these compounds are widely dispersed in inhabited areas. Testing of

¹¹ This corresponds to a ratio of 0.395 kg Cl_2 /kg ClO_2 .

¹² In this case the ClO_2 substitution level depends on the “purity” of the ClO_2 solution. The methanol- and peroxide-based ClO_2 processes (AMT) can produce a ClO_2 solution containing 0.02 kg Cl_2 /kg ClO_2 , equivalent to 99.2% substitution. It is claimed that the low- Cl_2 integrated dioxide process (an emerging technology) is able to produce a ClO_2 solution of the same purity.

¹³ US EPA Method 1613 for Analysis of Dioxins and Furans in Wastewater, which has a minimum level of 10 pg/L for 2,3,7,8-TCDD and 2,3,7,8-TCDF.

soils in the State of Washington revealed the presence of dioxins even in remote wilderness areas (WDOE 1998). It is known that PCDD and PCDF are emitted as a consequence of combusting a wide variety of materials including fossil fuels, wood, and municipal solid wastes [Thomas, 1994], so their broad distribution in the environment is not surprising. The ubiquitous presence of these compounds could explain their detection in bleached pulp and filtrate samples through contamination of the raw materials and/or product samples [NCASI, 2002].

2.4.5 Market position

ECF bleaching is at present (Q2 2006) the dominant bleaching method worldwide (75% of total bleached kraft pulp production) and has been adopted in most new installations.

2.4.6 PCDD/ PCDF in aquatic biota near kraft mills employing ECF bleaching

Indirect evidence for the elimination of PCDD/ PCDF in kraft mill effluents after introduction of ECF bleaching may be found in the PCDD/ PCDF content in tissues of biota (e.g. fish and crab) and in sediments. Since the concentrations of PCDD/ PCDF are generally very low and practically undetectable¹⁴ in effluent water, accumulation in biota and sediments may be the only indication that these substances are released from pulp mills, albeit in small amounts. A rapid decrease in the concentration of PCDD/ PCDF has been measured at several pulp mill locations either in sediments or biota after the introduction of either ECF or TCF bleaching. However, the ecological half-life of these substances in lakes, rivers and coastal areas may typically be 1-3 years which means that measurable amounts of PCDD/ PCDF will be present in biota several years after elimination in pulp mill effluents. A few examples of such measurements are presented below.

[Abbott, 1996] analysed 2,3,7,8-TCDD concentrations in fish tissues from 39 sites in riverine environments impacted by treated pulp and paper industry effluent in different parts of the USA. The results provided strong evidence of a trend of decreasing TCDD concentrations in fish tissue, with 84% of the examined sites showing a decrease.

[Hagen, 1997] reported that process changes made by 10 pulp mills in British Columbia (BC), Canada discharging to marine waters reduced their dioxin and furan loadings by over 97% between 1989 and 1994. In the same review, data from a monitoring program conducted at sites adjacent to pulp mill outfalls documented the following average declines in PCDD/ PCDF (measured as I-TEQ) between 1990 and 1995: sediment (61%), dungeness crab hepatopancreas (80%), dungeness crab muscle (85%), oyster (93%), prawn (92%) and shrimp (87%).

[Macdonald, 1998] used sediment data collected from Kamloops Lake, BC, Canada, to establish the emission history for PCDD/ PCDF and PCB. The sediments were layered and could be dated using radioactive lead as a tracer. In this way the sediment core was used as a historical record of PCDD/ PCDF and PCB emissions from different sources. Sediment layering

¹⁴ With present sampling and analytical techniques (i.e. at low pg/L or ppq level).

implied that there was no benthic fauna present, making the contaminants effectively unavailable to the biosphere. A bleached kraft pulp mill was constructed in 1965 about 8 km above Kamloops Lake and the production was gradually increased during the following years. ECF production started in 1988 and in 1993 the mill was 100% ECF. The analysis showed that the PCDD/ PCDF associated with Cl_2 bleaching started to increase above background levels in the mid-1960s, peaked in the mid-1980s and then dropped drastically around 1990 to approximately the same concentrations that were recorded before 1960. Trends in other groups of PCDD/ PCDF were also found but they could not be correlated to changes in the mill indicating that these compounds originated from other sources.

Data from crab hepatopancreas (inner organ) outside one Swedish kraft mill have been collected on 4 occasions between 1986 and 2000. Data were also collected at an offshore reference station. The mill gradually eliminated the use of Cl_2 between 1989 and 1994 and at present employs TCF bleaching. The PCDF and PCDD in crab hepatopancreas decreased rapidly after 1989 to near background levels. The measured TEQ concentration in crab hepatopancreas collected in the recipient is shown in Figure 2.3 on the following page. In 1989 the TEQ-value for dioxins and furans in crab hepatopancreas was 73.4 pg/g and in 1993 the same parameter had decreased to 24.8 pg/g in crabs collected near the discharge point. In 2000 the TEQ-value was 19.0 pg/g near the discharge point. In the reference station the TEQ-value was 18.2 pg/g in 1993. No measurement at the reference station was made in 2000, however, there were almost equal concentrations near the discharge point in 1993 and 2000, and the rate of decrease was comparable to decrease rates reported in sites where ECF bleaching was introduced. These data indicate that PCDD and PCDF emissions in TCF and ECF effluents are about the same.

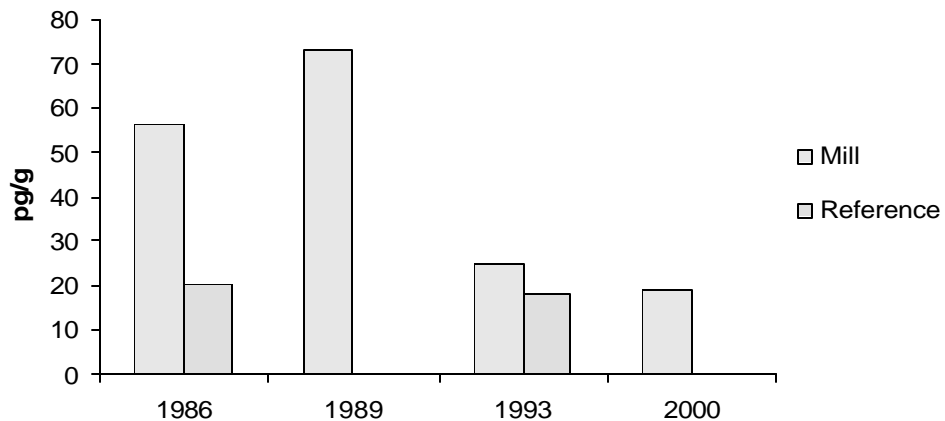


Figure 2.3 The measured TEQ concentration in crab hepatopancreas outside a Swedish bleached kraft mill 1986-2000

Source: ÅF-Process (personal communication from Jan Malmström, Södra Cell).

[Olsson, 2005a] measured dioxin concentration in fish muscle from perch (*Perca fluviatilis*) and viviparous blenny (*Zoarces viviparous*) collected outside 5 ECF bleached Swedish pulp mills. A few km outside one of the mills the TEQ concentration was 0.8 pg/g fresh weight. Compared to the concentration measured 5 km outside the mill in the mid-1980s (21 pg/g)

[SEPA, 1989], the concentration was around 20 times lower. Chlorine bleaching was discontinued in 1992. Assuming that no dioxin entered the system after 1992, this implies an ecological half-life around 2.5 years. A similar value is obtained for the half-life in crab hepatopancreas outside the TCF mill mentioned above.

The ecological half-life obviously varies depending on the ecosystem structure and the hydrological regime. For instance, in mountain whitefish in Wapiti River, BC, Canada the ecological half-life of dioxin was around 8 months (calculated from [Pryke, 1995]).

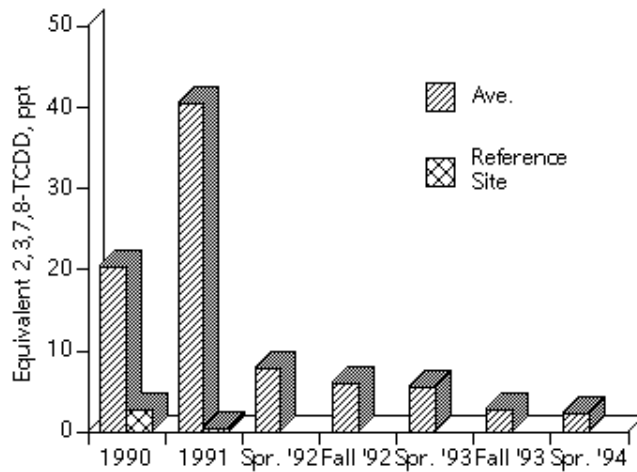


Figure 2.4 Wapiti River mountain whitefish dioxin (TEQ), 1990-1994

Source: [Pryke, 1995].

In the study by [Olsson, 2005a] reference TEQ concentrations of dioxins in fish muscle were between 0.26 and 0.36 pg/g fresh weight. Concentrations in fish muscle collected close to the mills were between 0.3 and 0.9 pg/g fresh weight, or between 1.2 and 2.5 times the reference concentrations.

The authors discuss several possible reasons for the elevated concentrations near some of the mills. According to the authors, the most likely sources for the measured PCDD/ PCDF include the raw material used in the pulping, the bleaching process and contaminated sediments outside the mills. The authors do not discuss the possibility that the findings are consistent with a decreasing trend, although the values fit well into the decreasing pattern observed in other sites (above).

[Pryke, 2006] reported measurements in mill effluent, fish (white sucker and small mouth bass), mussels and semi-permeable membrane devices at 5 bleached kraft mills in Maine, USA employing ECF bleaching. In essence, PCDD/ PCDF were not detected in effluent after the introduction of ECF. In most cases there were no statistically significant differences in PCDD/ PCDF concentrations upstream and downstream of the mills in fish tissue, mussel tissue and in lipid-filled semi-permeable membrane sampling devices. Single measurements with statistically significant different concentrations upstream and downstream of one of the mills do however exist for white suckers and small mouth bass. Results for fish tissue in 2004 are shown in Figure 2.5.

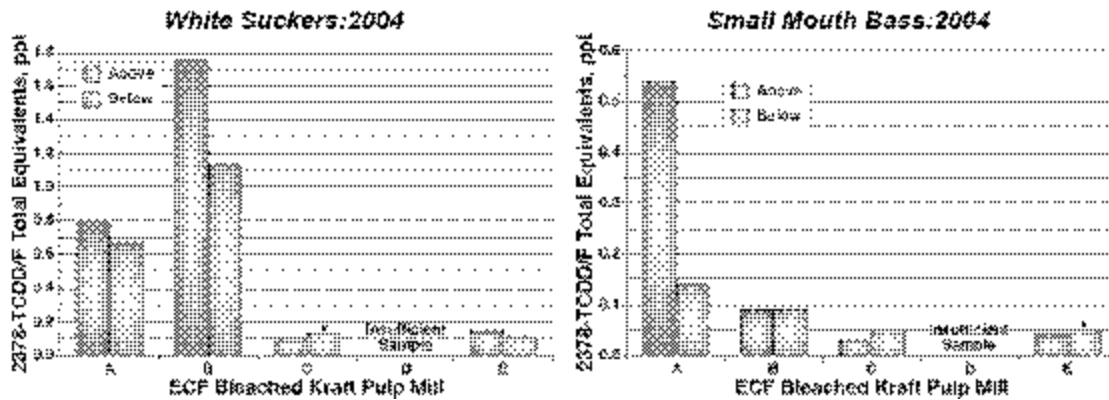


Figure 2.5 Average fish tissue concentrations upstream and downstream of Maine's BKP mills: 2,3,7,8 TCDD/F expressed as TEQ

Source: [Pryke, 2006].

Note: Wet weight basis, non detect (ND) assigned value of $1/2$ detection limit (DL). Statistically significant at $p < 0.05$.

2.5 TCF BLEACHING

2.5.1 Sequences

Examples on modern TCF bleaching sequences are: Q(OP)(ZQ)(PO), Q(OP)(PaaQ)(PO), QZPEP, (OP)ZQ(PO) or Q(OP)Q(PO).

Sequences including only peroxide stages are called “straight peroxide TCF” or “alkaline TCF” [Bergnor-Gidnert, 2006].

Peroxide-based sequences include one or more chelation (Q) stages to control and remove transition metal ions, which decompose hydrogen peroxide.

In ozone stages, transition metal ions can promote carbohydrate degradation, which lowers pulp strength. Since ozone stages are operated at low pH (2-3), metal ion control is typically achieved by acidification and washing to dissolve and purge the metal ions. The pH range 2-3 is also optimum for efficient delignification and pulp strength preservation in O₃ bleaching.

2.5.2 Chlorinated organic compounds

In TCF bleaching the formation of AOX and OX is usually undetectable with present sampling and analytical techniques (i.e. at low pg/L or ppq level).

However, low levels of AOX and OX may be present in undetectable or at very low measurable levels in effluents from kraft pulp mills with TCF bleaching because of the combined action of chloride entering with either wood, or chemicals, or water and the oxidation potential of O₃ or Paa. [Süss, 2000] has shown that these bleaching chemicals have sufficient redox potential to oxidise Cl⁻ ion to Cl₂.

TCF bleaching with peracids in the presence of traces of chloride ions generates halogenated by-products which are detected as an OX residual in the pulps which is similar to that of low-OX ECF bleaching (see Table 2.8 below). However, the reaction of O₃ with lignin is much faster than that with chloride ions and the amounts of Cl₂ generated remain very low [Süss, 2000].

2.5.3 Dioxins and furans

If TCF bleaching is used, emissions of 2,3,7,8-TCDD and 2,3,7,8-TCDF to water are lower than the limit of quantitation (US EPA Method 1613¹⁵) [UNEP, 2006].

PCDD and PCDF may be present in effluents from TCF bleach plants for the same reasons mentioned at the end of Section 2.4.4 – “Dioxins and furans”, taken from [NCASI, 2002].

2.5.4 Market position

The [UNEP, 2006] Draft Guidelines include TCF bleaching of kraft pulp as an “alternative”, however they state “The TCF-process developed rapidly in the 1990s but has gradually lost its attraction because of its weaknesses in fibre characteristics, lower pulp yield and higher energy consumption. The ECF process has taken over as the leading bleaching method. Some TCF processes have started to lose their share in the market and TCF mills are converted to ECF pulp production. The operating costs of TCF pulping are usually higher than those of ECF pulping due to the higher chemical costs in order to reach the same level of pulp brightness”.

¹⁵ US EPA Method 1613 for Analysis of Dioxins and Furans in Wastewater, which has a minimum level of 10 pg/L for 2,3,7,8-TCDD and 2,3,7,8-TCDF.

The trends of total chemical pulp production in the world are shown in Figure 2.6. At present (Q2 2006) TCF kraft and sulfite pulps account for less than 5% of production and are primarily produced in Northern and Central Europe [UNEP, 2006]. The percentage for kraft pulp only is 4%.

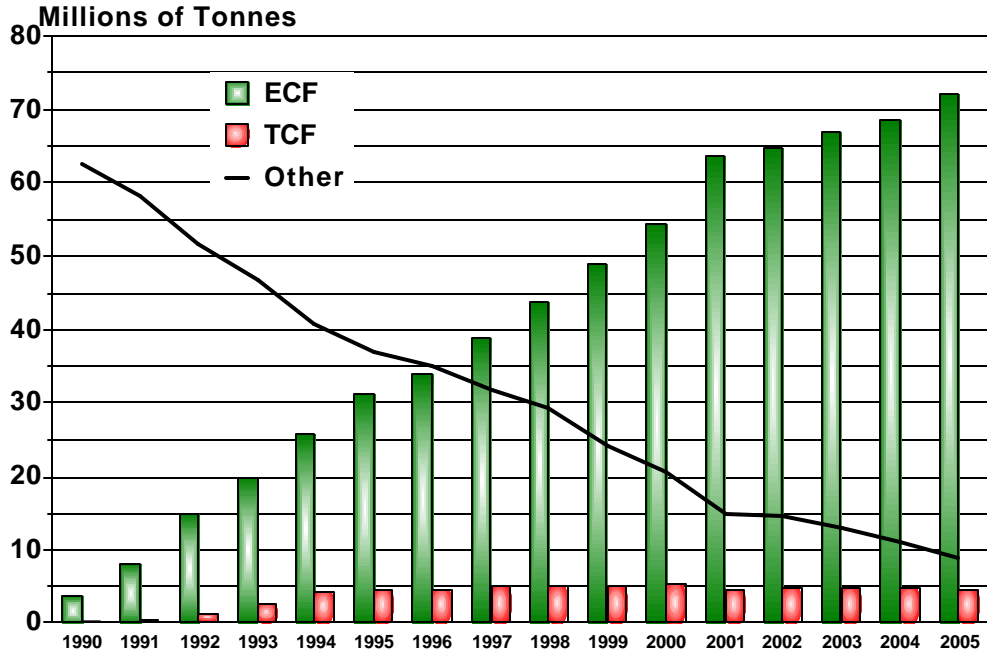


Figure 2.6 Trends in the bleached chemical pulp production in the world, excluding China and India

Sources: American Forest & Paper Association, [UNEP, 2006].

2.6 CURRENT STATUS OF BKP MILLS EMPLOYING TCF BLEACHING

TCF bleaching was first employed for sulfite pulps, which are much easier to bleach than kraft pulps. When in the early 1990s the Scandinavian kraft mills started employing TCF bleaching, the main driver was the possibility to take advantage of the developing market for chlorine-free bleached pulp and paper primarily in Germany but also Sweden, the Netherlands, Switzerland and Austria. Initially TCF pulps were also paid a premium compared to conventionally bleached kraft pulp. An additional driver was the expectation that it would be feasible to recycle bleach plant effluents to the chemical recovery system for incineration thereby reducing the effluent load.

TCF pulps are produced in a few BKP mills in Brazil, Europe and USA.

The following table lists the BKP mills that are employing TCF bleaching.

Table 2.7 BKP mills employing TCF bleaching

Mill	Wood type	Sequence or bleaching agents used
ENCE Pontevedra, Spain	HW	OOQPQP
Klabin Bacell Camacari, Brazil	HW	OOA _{hot} ZP/ Fully integrated
Klabin Telêmaco Borba, Brazil	HW	OOQ(PO)(EO)P/ Fully integrated
Korsnäs Frövi, Sweden	HW	Fully integrated
Metsä -Botnia Rauma , Finland	SW	O(ZQ)(PO)(ZQ)(PO/PO)
SCA Munksund, Sweden	HW	Fully integrated
SCA Östrand, Sweden	SW	OOQ(OP)(ZQ)(PO)
Evergreen Pulp Samoa, CA, USA	SW	OOQPQ(PO)
Smurfit Piteå, Sweden	HW	Fully integrated
Södra Cell Värö, Sweden	SW	O, P, Q
Södra Cell Mönsterås, Sweden	HW, SW	O, Z, P, Q

Sources: ÅF-Process/ Beca AMEC.

The “fully integrated” mills in Brazil and Sweden bleach only part of the production. Furthermore they may not bleach to full brightness since the entire amount of bleached pulp is directly used in the linerboard/board product.

A few BKP mills have the capability to produce both ECF pulps and TCF pulps. Table 2.8 lists the BKP mills that are employing both ECF and TCF bleaching.

Table 2.8 BKP mills employing both ECF and TCF bleaching

Mill	Wood type	Sequence or bleaching agents used
Smurfit Munksjö Aspa Bruk, Sweden	SW	OQ(PO)
		OQ(PO)DD
Kemijärvi, Finland	SW	n/a
Kymmene Pietarsaari, Finland, Line 1	HW	OA(Z/D)(OP/P)Z/DP OA(Z/Q)(OP)(Z/Q)P
Mercer Rosenthal, Germany	SW	OQOPQZ(PO)P
Mercer Stendal, Germany	SW	O(OP)DD(PO)
Metsä Botnia Kaskinen, Finland	HW	n/a
Södra Cell Mörrum, Sweden	SW, HW	O, P, Q, D
Stora Enso Skoghall, Sweden	SW	O(PO)DQ(PO)
Votorantim Celulose e Papel Jacareí, Brazil, Line B	HW	(O/O)A _{hot} ZD(PO) ^{1/} O(OP)Z(PO)
Notes:		
1. VCP also employs Votorantim Chlorine Free (VCF) bleaching. This is a low-OX ECF with small charge of ClO ₂ under controlled conditions (ECF pulp OX = 80-120 g/ADt - VCF pulp OX = 30 g/ADt).		

Sources: ÅF-Process/ Beca AMEC.

The estimated production of BKP in major producing countries is given in Table 2.9. The present total production of TCF bleached kraft pulp is about 3.25 million tonnes of which about 1 million tonnes is in integrated or captive production. Production of TCF in Scandinavia has historically been higher and the present trend is a further slow decrease in capacity.

Table 2.9 Estimated annual ECF and TCF bleached kraft pulp capacity in major producing countries
(million ADt/a)

Country	ECF	TCF	% TCF
Argentina	0.35	0	0
Brazil	8.2	0.3	3.5%
Canada	11	0	0
Chile	3.4	0	0
Finland	7.1	0.65	8.4%
Germany	0.85	0	0
New Zealand	0.47	0	0
Norway	0.4	0	0
Portugal	1.5	0	0
South Africa	0.45	0	0
Spain	0.55	0.3	55.5%
Sweden	5.5	2.0	26.7%
USA	28.6	0	0
Total	68.37	3.25	4.75%

Source: ÅF-Process/ AMEC/ Beca AMEC.

In Germany the Mercer kraft mills Rosenthal (300 000 ADt/a) and Stendal (550 000 ADt/a) have the possibility to produce TCF pulp. Stendal is reportedly not producing TCF pulp and Rosenthal possibly only minor quantities.

Assuming that all sulfite pulps produced in Sweden, Germany, Austria, Switzerland and Portugal are bleached with a TCF sequence, primarily using hydrogen peroxide, this would amount to an additional about 1.75 million tonnes in 2004. Therefore, the total production of chemical TCF bleached pulps in Europe in 2004 was about 4.5 million tonnes. Total TCF pulp production capacity was, however, about 5.5 million tonnes.

The current worldwide production of bleached chemical pulp is about 90 million tonnes of which BKP pulp is estimated at 87 million tonnes. The current best assessment for global production of TCF pulp is about 5 million tonnes or a market share of about 5% and a market share of about 4% for BKP. The production of bleached TCF pulps reached a maximum around 1995 and has been slowly decreasing since then.

The TCF market is at present stagnant or decreasing, no premium is paid for TCF pulps and the expectation for less problematic recycle of effluents has not been realised. Thus, mills in Germany and the Nordic countries have either abandoned or reduced TCF production in favour of ECF production.

2.7 EFFLUENT CHARACTERISTICS AND TREATABILITY

2.7.1 General comments on effluent treatability

The organic materials in ECF and TCF bleaching effluents have a slightly different composition:

- ECF bleaching effluent contains resin acids¹⁶, aliphatic acids, unsaturated hydrocarbons and phenols.
- TCF bleaching effluent contains aliphatic acids, resin acids and unsaturated hydrocarbons.

The treatability of these effluents in a biological treatment plant is for all practical purposes about the same.

Because of this, other parameters such as pulpwood, place of growth of the pulpwood, effluents from the unbleached line (spills, washing losses, condensate handling etc.) have a larger impact on the treatability and selection of treatment methods than the bleaching effluent itself.

Hence, the treated effluent characteristics depend more on the pulpwood, mill geographical location and pulping process than on the selected bleaching process (ECF or TCF).

A major difference in treatability is, however, noticed between hardwood and softwood BKP mill effluents: the COD removal efficiency for hardwood effluents is commonly above 80% but for softwood effluents it is in the range 60-70%.

Secondary treatment normally eliminates the acute toxicity of the effluent.

In conclusion, with improved bleaching technology resulting in lower effluent loads from the bleach plant, the contribution of organic matter from the unbleached area of the mill becomes more important for the mill effluent treatability and the final discharge levels.

2.7.2 ECF effluents

2.7.2.1 Untreated

Untreated effluent contains suspended solids, dissolved organic matter, AOX, chlorate and nutrients. The effluent also contains coloured material¹⁷ and non biodegradable organic matter.

¹⁶ If the pulpwood is softwood.

¹⁷ Especially high if the pulpwood is eucalypt.

Table 2.10 lists achieved annual average emission levels in primary clarified effluent from kraft mills employing ECF bleaching. The guideline ranges according to [IPPC BREF, 2001] are also given for reference. These mills to a large extent use AMT as can be inferred from the low treated effluent loads.

Table 2.10 Achieved annual average emission levels before secondary treatment (after primary clarification) from BKP mills employing ECF bleaching

Mill	Furnish %		COD kg/ADt	N _{tot} kg/ADt	P _{tot} kg/ADt	AOX kg/ADt
	SW	HW				
1	90	10	45	0.25	0.06	0.15
2	70	30	28	0.24	0.04	0.1
3	100		34	0.3	0.04	0.25
4	50	50	40	0.28	0.035	0.35
IPPC	n.a.	n.a.	30-45	0.3-0.4	0.04-0.06 ¹⁾	<0.4

Notes:
1. For eucalypt, the P_{tot} is much higher, 0.04-0.25 kg/t, or as an average, 0.1 kg/t.

Sources: [IPPC BREF, 2001], ÅF-Process.

2.7.2.2 **Treatability**

Effluent from bleached kraft pulp mills can be treated by a two or three stage process. The first two stages remove the suspended solids, dissolved organic matter, AOX and nutrients. Other compounds can be reduced in the third step, if necessary, for discharge into the local recipient.

Primary treatment

Suspended solids such as fibres and bark particles are usually removed by sedimentation in a primary clarifier. This process also protects the subsequent stage from disturbance due to accumulation of inert matter. Other process steps prior to secondary treatment are neutralisation, cooling and flow equalisation (surge capacity).

Secondary treatment

Biodegradable organic pollutants are usually treated in this stage by an activated sludge process. This consists of two main units; the aeration tank and the secondary clarifier. These systems remove all dissolved BOD and total suspended solids (TSS). However, the removal of some of these suspended solids in the primary clarifier is worthwhile as it increases the secondary system efficiency and decreases production of sludge. Small quantities of finely suspended material are easily handled. They become enmeshed with the biological solids. The effluent is aerated and generates a large quantity of micro-organisms in the form of bio-floc (activated sludge). The concentration of these micro-organisms is kept high through internal recirculation of sludge from the subsequent stage. The retention

time in effluent treatment for kraft pulp mill system is of the order of 15-50 hours.

Aeration and mixing are provided by mechanical aeration equipment such as surface aerators, submerged turbine aerators, fins bubble aerators and jet aerators. Pure oxygen systems with covered bioreactors are some times used, e.g. when there are special requirements regarding low emissions of odorous compounds or space constraints.

The sludge is separated from the water in the secondary clarifier. The main portion of this sludge is recycled to the aeration tank, but a certain amount must be removed from the system as excess sludge.

The activated sludge process is the most common secondary treatment process for new installations in the kraft pulp industry. Aerated stabilisation basins are still common in existing installations although many have been modified to extended contact time activated sludge or similar facilities. The selector technique (a pre-treatment stage which aims to select a certain culture of micro-organisms) has resulted in better sludge characteristics, giving more stable operation and less carry-over of bio-floc. The discharge of nutrients is also substantially reduced.

Treatment efficiency varies between 85-98% BOD removal, 60-80% COD removal and 40-65% AOX removal. Phosphorus is reduced by 40-85% and nitrogen by 20-50% (calculated on net incoming amounts before addition of nutrients). Overall TSS removal for the primary and secondary stages is around 85-90%.

Aerated lagoons were used in the past as the secondary treatment process. However, since the discharges of organic matter (measured as BOD and COD), suspended solids and nutrients are higher than those from modern activated sludge plants, this technology can no longer be regarded as AMT.

Table 2.11 lists achieved annual average emission levels in secondary treated effluent from kraft mills employing ECF bleaching. The guideline ranges according to [IPPC BREF, 2001] are also given for reference. These mills to a large extent use AMT as can be inferred from the low treated effluent loads.

Table 2.11 Achieved annual average emission levels after secondary treatment from BKP mills employing ECF bleaching

Mill	Furnish %		COD kg/ADt	BOD kg/ADt	TSS kg/ADt	N _{tot} kg/ADt	P _{tot} kg/ADt	AOX kg/ADt
	SW	HW						
1		100	5	<0.2	0.6	0.09	0.02	0.07
2	50	50	18	n.a	2	0.3	0.03	0.1
3	100		14	n.a	0.6	0.16	0.035	0.1
4	100		10	0.2	n.a	0.14	0.01	0.14
5	30	70	14	0.2	0.2	0.07	0.013	0.17
6		100	11	0.7	n.a	0.2	0.01	0.1
IPPC	n.a.	n.a.	8 - 23	0.3-1.5	0.6-1.5	0.1-0.25	0.01-0.03	(-)-0.25

Sources: Swedish Forest Industries Federation, 2004/ Finnish Forest Industries Federation, 2004/ [IPPC BREF, 2001], ÅF-Process.

Tertiary treatment

In special cases, e.g. particularly sensitive receiving waters, where requirements for low discharges are very stringent, it may be necessary to combine the secondary treatment with chemical coagulation. This constitutes tertiary treatment. Chemicals used are normally aluminium salts, ferric salts, ferrous salts and lime. The chemical treatment gives further reduction of some recalcitrant compounds such as high molar mass degradation products from lignin. A chemical floc is produced by precipitation of organic and inorganic matter. The floc is removed by sedimentation or flotation.

When these chemicals are used, sludge production is very high and the technology is not regarded as AMT unless the recipient is very sensitive. The technology can be used for limited times in order to protect receiving water during unfavourable seasonal conditions. In that case annual sludge production will be more moderate.

The tertiary treatment system at the Tembec Skookumchuk BKP mill in Cranbrook, BC, Canada uses polymer instead of inorganic salts or lime and the sludge from the system is burned in the recovery boiler. Consequently, the sludge from tertiary treatment at this mill does not end up in a landfill.

2.7.2.3 Environmental impact

Physiological disturbances have clearly diminished in fish populations living in pulp mill recipients after switching from molecular chlorine bleaching to ECF or TCF bleaching. However, in some cases, field studies show that fish exposed to ECF bleaching effluents still show a consistent disturbance in liver function, growth and/or reproductive fitness.

All types of effluents (unbleached, TCF, ECF, mechanical), even after treatment, may, in some cases, result in liver function disturbance. The characteristics of the recipient and, in particular, the dilution of the liquid effluent are most likely important factors.

Laboratory tests where organisms at different trophic levels have been exposed to effluents from either ECF or TCF mills do not show a clear pattern in the ecotoxicological response. In some cases, effluents from TCF mills gave less toxic effects but the opposite has also occurred.

Acute toxic effects seldom occur after secondary treatment of any pulp mill effluent.

The overall technical standards of mills and effluent treatment plants seem to be more important than the bleaching technique adopted in explaining the effect pattern.

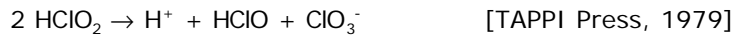
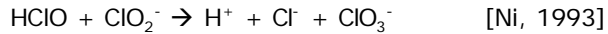
Endocrine disrupting substances (EDS) have attracted particular interest since the 1980s because they may inflict chronic effects on living organisms by interacting with their natural hormonal system and disturb essential life functions such as reproduction and growth. Since about 1996, pulp mill effluents have been implicated as a possible source of EDS. The conclusion so far, made by several research groups (see Section 2.8-“Environmental impact of ECF and TCF bleaching”) working on EDS in relation to pulp and

paper mill effluents, is that EDS are probably not chlorinated organic compounds.

2.7.2.4 Removal of chlorate

About 26% of the ClO_2 charged oxidises to chlorate ions (ClO_3^-) in a D stage.

Reported mechanisms for chlorate formation are:



If the bleaching sequence includes ozone, oxidation of HClO , HClO_2 and ClO_2^- to chlorate is enhanced. Ozone can be applied in the first stage of a sequence as ZD or DZ. In ZD prebleaching, chlorate is formed more quickly than in a DZ sequence. In DZ prebleaching, chlorate formation can be managed by having a sufficient retention time for the D stage so that the residual chemicals are minimised. In practice, most mills have opted for the ZD option. Despite the enhanced oxidation, either sequence results in significantly reduced chlorate formation compared to an ECF sequence without ozone because of the lower ClO_2 charge.

Because chlorate ions do not react with lignin, their formation results in a loss of oxidative power for the ClO_2 .

Chlorate is most likely toxic to all aquatic plants. Brown algae, e.g. bladderwrack, seem to be the most sensitive to chlorate. The concentration at which the toxic effect sets in depends on the species and also the concentration of other inorganic ions in the water, notably nitrate. The toxic effect of chlorate is due to a competitive uptake with nitrate. Plants normally take up nitrate as a nutrient but if chlorate is present they will take up this as well. The lower the nitrate level the higher the risk for a chlorate uptake.

The toxic level of chlorate to bladderwrack in the Baltic Sea is 20-30 $\mu\text{g/L}$.

Hence, concentrations of chlorate above these levels may result in the loss of large brown algae, such as kelps, which are common in many parts of the Australian marine environment [Rosemarin, 1986], [Rosemarin, 1994].

Biological reduction of chlorate

The biological reduction of chlorate was first observed in aerated lagoons in Sweden. It was then discovered that the reduction was achieved by bacteria specialised in chlorate reduction in a reaction similar to denitrification. The reaction requires low oxygen concentration, i.e. anoxic environment. The key factors are redox potential (-200 to -300 mV), easy biodegradable organic matter, sufficient retention time, adjusted temperature and a sufficient amount of bacteria.

In aerated lagoons there will commonly be natural or designed zones with low aeration and sufficient retention time for chlorate reducing bacteria to develop spontaneously. Chlorate reduction efficiencies in the range 80-99% can be achieved in aerated lagoons.

In activated sludge systems the treatment starts with an anoxic zone. Part of the return sludge is recirculated to this zone and the rest of the return sludge is led to the aeration tank. Within weeks the chlorate reducing bacteria develop and removal rates of 90-99% can be achieved.

Chlorate removal can be achieved also in moving bed systems using the same principle as for activated sludge systems. Even if the moving bed itself is operated under aerobic conditions, there are sufficient anoxic zones within the carriers for the chlorate reduction. The concentration gradient over the biofilm provides the driving force to transport chlorate into the anoxic zone of the biofilm on the carrier.

Biological chlorate removal is sensitive to fast variations of the chlorate concentration as the amount of bacteria self adjust to the actual chlorate concentration. For instance, the bacteria need about one day to adjust for a 50% increase in chlorate levels. In the meantime, the discharge of chlorate initially increases by 50% to successively drop as a sufficient amount of bacteria builds up.

Effluents from hardwood and softwood pulping and bleaching display the same chlorate reduction efficiencies.

Table 2.12 Chlorate discharges from selected BKP mills employing ECF bleaching

(as annual averages in kg/t)

Mill	Treatment method	Chlorate discharge	Reduction% ¹⁾
A	Chemical (SO ₂)	3.5	10
B	Chemical (SO ₂)	2.5	30
C	Chemical (SO ₂)	1.5	60
D	Aerated lagoon	0.6	80
E	Aerated lagoon	0.1	98
F	Aerated lagoon	0.02	99
G	Activated sludge	0.5	90
H	Activated sludge	0.2	95
I	Activated sludge	0.1	97
J	Moving bed	0.3	95
Notes:			
1. The reduction is calculated as chlorate entering the effluent treatment compared to the discharge after treatment.			

Sources: Swedish Forest Industry Federation, 2004/ ÅF-Process.

2.7.2.5 Removal of chelants

In most cases no chelants are used in ECF bleaching, but if they are used, the charge is 0.1-1 kg/ADt.

Chelants need to be added into the bleaching sequence if a pressurised peroxide stage or in some case an atmospheric peroxide stage is used in order to remove the heavy metals that naturally enter mills with the raw wood chips.

However, in most ECF sequences chelants are not required. Chelants are discussed further under TCF Effluents in Section 2.7.3.4.

2.7.2.6 **Atmospheric emissions**

The main emissions sources to the atmosphere from kraft pulping are the recovery boiler, the lime kiln, the power boiler, the CNCG incinerator and the CNCG emergency incinerator. The three most common air emission issues are total reduced sulfur (TRS) compounds (i.e. odorous compounds) and the oxides of nitrogen and sulfur (NO_x and SO_x). Kraft pulp mills also release particulate matter into the atmosphere.

If the kraft pulp is bleached, these sources are for all practical purposes identical whether ECF or TCF bleaching is employed.

Two additional emissions sources to the atmosphere in ECF kraft mills are the ClO_2 plant environmental scrubber and the bleach plant scrubber, which may occasionally emit minor amounts of either inorganic or organic chlorinated compounds, or both.

Collection and scrubbing with alkaline scrubbing solutions of residual chlorinated compounds from the bleaching chemical preparation plant and the bleach plant is standard practice in ECF kraft mills and this technique is considered AMT.

2.7.2.7 **Solid wastes**

Various solid wastes are generated in kraft pulp mills. These include saltcake from chemical recovery, bark and wood residue from wood handling, dust from boilers and furnaces, rejects, ash, and sludge from effluent treatment (fibre sludge and secondary sludge), miscellaneous material (e.g. building material) and small amounts of hazardous waste that require special handling.

There is no difference between BKP mills employing either ECF or TCF bleaching in these respects and therefore the amounts, composition, handling etc. of the solid wastes are comparable.

A recent method of disposal for secondary biosludge begins with dewatering in a centrifuge followed by mixing with weak black liquor. The mixture is then screened, evaporated and finally burned in the recovery boiler. For this process to be implemented, the risk for disturbances caused by the accumulation of NPE in the recovery process must be carefully evaluated.

Another disposal method for the sludge from effluent treatment is to stabilise it by a drying and composting process, then utilise it as a soil conditioner. Secondary sludge has low water permeability and has sometimes been used as cover material on old landfills. Secondary sludge may also be dewatered, mixed with either fibre sludge or bark, or both and burned in the power boiler.

2.7.2.8 **Removal of dioxins/furans from effluent**

Knowledge on the fate of dioxins/furans in effluent treatment plants is at present rather limited. Unpublished data in Scandinavia indicate that 50-70% separation of dioxins/furans occurs in biological treatment systems. The dioxins/furans are transferred from the water phase onto the biological sludge and thus follow the sludge to the final sludge handling.

A mill study of the fate of incoming dioxins with the raw water reported that 97% of the dioxins/furans are transferred to the sludge. This mill has an activated sludge treatment and a tertiary treatment with chemical precipitation with metal salts. In this report it seems that only 10-70% of the different dioxins/furans are separated in the biological stage and the majority of the separation occurs in the tertiary treatment up to the total separation of 97% [Nakamata, 2004].

Another mill study (at two mills) found that after biological treatment more than 90% of the 2,3,7,8-TCDD/F was adsorbed onto the suspended solids and was subsequently transferred to the sludge or discharged with the suspended solids in the effluent [Amendola, 1989].

2.7.2.9 **Status of Swedish studies investigating dioxins in receiving environment of ECF mills**

[Olsson, 2005a] measured dioxin concentration in fish muscle from perch (*Perca fluviatilis*) and viviparous blenny (*Zoarces viviparous*) collected along gradients outside 5 Swedish pulp mills employing ECF bleaching. A few km outside one of the mills the TEQ concentration of dioxins was 0.8 pg/g fresh weight. Compared to the concentration measured 5 km outside the mill in the mid 1980s, the concentration was around 20 times lower. Chlorine bleaching was discontinued in 1992.

That study shows that TEQ concentrations of dioxins in fish muscle collected from "unpolluted" reference areas were between 0.26 and 0.36 pg/g fresh weight. Concentrations in fish muscle collected close to the mills were between 0.3 and 0.9 pg/g fresh weight or between 1.2 and 2.5 times the reference concentrations. The authors discuss several possible reasons for the elevated concentrations. According to the authors, the most likely sources for the measured PCDD/ PCDF include the raw material used in pulping, bleaching and contaminated sediments outside the mills.

From the given data it is not possible to decide which hypothesis is the most probable. Several other substances, including DDT, PCB and HCB, are also found in elevated concentrations in fish collected closer to the mills. None of these other substances are actively handled by the mills, which lends some support to the hypothesis that the sediments are a source of contamination. Apart from the explanations given by the authors, several other factors may be important, including hydro-morphological, chemical and ecological conditions in the systems.

Traces of dioxin were detected in late 2005 in tank deposits in the chlorine dioxide plant of a Swedish BKP mill. Subsequent research and investigations uncovered two additional BKP mills had the same problem. The process used in all cases is Cellchem's Hydrogen Peroxide Atmospheric (HP-A®)

process (http://www.cellchem.com/docs/products-services/chlorine_dioxide.htm).

To the best knowledge of the authors of this report, no dioxins have been emitted to the environment from this source.

2.7.2.10 **American and Canadian emissions of dioxins from ECF mills**

Most North American BKP mills analyse and report on dioxin discharges regularly, typically several times annually. Most American and all but one Canadian mills in the early 2000s reported "non-detect" on 2,3,7,8 TCDD (at 10 pg/L in the bleach plant effluent for the US and 15 pg/L in the treated effluent for Canada) and roughly half had occasional detection of 2,3,7,8 TCDF.

All Canadian mills except one were employing ECF bleaching, whereas only about $\frac{2}{3}$ of the US mills were employing ECF bleaching at the time of the survey [McCubbin, 2001].

A recent update of the dioxin survey [McCubbin, 2006] reports that in the USA, 55 of the 80 or so bleached kraft mills determine the concentrations of 2,3,7,8 TCDF and 2,3,7,8 TCDD in bleach plant effluent regularly, but few report data on the concentrations of these substances in the effluent as discharged to the receiving water after biological treatment. The legal detection limit (minimum level) for 2,3,7,8 TCDD and 2,3,7,8 TCDF is 10 pg/L, and virtually all the analyses report values less than this level. However, there is insufficient data available to calculate the margin by which bleach plant discharges are below the legal detection limit.

A first approximation, on the basis that bleach plant effluent flows are typically around $\frac{1}{3}$ of the total mill effluent flow and at least some of the dioxins will be retained in the effluent treatment plant sludge, suggests that treated effluents discharged from American mills may contain less than about 2-3 pg/L of 2,3,7,8 TCDD.

Virtually all Canadian mills are at present authorised by Environment Canada to reduce sampling, analysis and reporting of dioxin and furan discharges to once annually, and virtually all analyses are undetectable at the regulatory levels of 15 pg/L for 2,3,7,8 TCDD and 50 pg/L for 2,3,7,8 TCDF.

Environment Canada verifies that mills report discharges as required, but does not maintain a database of actual values, since all are considered "non-measurable".

It is clear that discharges of PCDD/ PCDF in Canada and the US are dramatically below the levels of the early 1990s, but there is insufficient data available to quantify the current discharge levels.

2.7.3 TCF effluents

2.7.3.1 Untreated

In TCF bleaching the bleaching chemicals are oxygen based and do not contain the chloride ion unless it is an impurity in the chemical (e.g. NaOH). The trend in TCF and ECF mills alike is to use less water in increasingly closed systems. However, TCF and ECF mills have the same NPE entering with their pulpwood¹⁸ and water. This includes an array of heavy metals, chloride and potassium ions. These combine with organic and inorganic material in the mill systems and form scales and deposits in tubes and on equipment leading to operational upsets and a need to shut down to carry out cleaning cycles.

These problems are equally difficult to handle in BKP mills employing either ECF or TCF bleaching, hence, bleaching effluent recycle to chemical recovery must include some treatment and purge of NPE.

Chloride and potassium ions are soluble and enter the liquor circuits in both ECF and TCF mills and the lower concentration in the TCF mills has not proved to be an advantage.

The following table lists achieved annual average emission levels in primary clarified effluent from BKP mills employing TCF bleaching. The guideline ranges according to [IPPC BREF, 2001] are also given for reference. These mills to a large extent use AMT as can be inferred from the low treated effluent loads.

Table 2.13 Achieved annual average emission levels before secondary treatment (after primary clarification) from BKP mills employing TCF bleaching

Mill	Furnish %		COD kg/ADt	N _{tot} kg/ADt	P _{tot} kg/ADt
	SW	HW			
1	100		35	0.4	0.05
2	70	30	32	0.3	0.04
3	100		38	0.3	0.05
4	100		28	n.a.	0.025
IPPC	n.a.	n.a.	30-45	0.3-0.4	0.04-0.06 ¹⁾
Notes: 1. For eucalypt, the P _{tot} is much higher, 0.04-0.25 kg/t, or as an average, 0.1 kg/t.					

Sources: Swedish Forest Industries Federation, 2004/ Finnish Forest Industries Federation, 2004/ [IPPC BREF, 2001].

¹⁸ Eucalypt, in particular, has a high content of phosphorus and may have a high content of chloride.

2.7.3.2 Treatability

As was discussed earlier, there is no significant difference in treatability of ECF and TCF mill effluents in a biological treatment facility. Other parameters such as pulpwood, place of growth of the pulpwood, effluents from the unbleached line (spills, washing losses, condensate handling etc.) have a larger impact on the treatability and selection of treatment methods than the bleaching effluent.

Recycling the filtrates from TCF bleaching to the chemical recovery cycle may create problems and various options for filtrate recycle have been tried:

- The acid filtrates, which do not contain a large quantity of organic matter, can be discharged. Only the alkaline filtrates are recycled.
- A portion of the acid filtrates is recycled directly to the recausticising system. Many heavy metals and other materials that are dissolved in the recycled acid bleach effluent will be precipitated as hydroxides, due to the high pH, and will then be separated within the recausticising system and consequently those substances will be removed prior to the fibre line. This is not a total solution since only a relatively small amount of water can be handled in this way.
- The acid filtrates are treated separately in an internal purification stage. The purified water is returned to the bleach plant as washing water. Purification methods such as ultrafiltration, evaporation and chemical treatment can be used.

In mills where effluent is recycled, controlled purges are required for chloride, potassium, sulfur, phosphorus, silica, aluminium, calcium, magnesium, manganese and iron. These are all present in the pulpwood and build up in a closed or partially closed system. There are currently no mills in the world that operate with completely closed filtrate and liquor systems. Many mills have closed the loop to some extent with partial recycle of bleach plant effluent.

The following table lists achieved annual average emission levels in secondary treated effluent from kraft mills employing TCF bleaching. The guideline ranges according to [IPPC BREF, 2001] are also given for reference. These mills to a large extent use AMT as can be inferred from the low treated effluent loads.

Table 2.14 Achieved annual average emission levels after secondary treatment from BKP mills employing TCF bleaching

Mill	Furnish		COD kg/ADt	BOD kg/ADt	TSS kg/ADt	N _{tot} kg/ADt	P _{tot} kg/ADt	AOX kg/ADt
	SW	HW						
1		100	13	n.a	0.7	0.24	0.07	0.005
2	70	30	7	n.a	0.3	0.1	0.005	0
3	100		21	n.a	n.a	0.3	0.03	0
4	100		5	0.2	n.a	0.05	0.007	0
IPPC	n.a.	n.a.	8 - 23	0.3-1.5	0.6-1.5	0.1-0.25	0.01 - 0.03	(-)-0.25

Sources: Swedish Forest Industries Federation, 2004/ Finnish Forest Industries Federation, 2004/ [IPPC BREF, 2001], ÅF-Process.

2.7.3.3 Environmental impact

The overall conclusion from the review of recent studies of environmental impact of bleached kraft mill effluents confirms that neither ECF nor TCF bleaching gives clear environmental advantages.

It is noted that EDS have also been shown to occur in the effluent from a BKP mill employing TCF bleaching [Larsson, 2002], [Förlin, 2004]. See also Section 2.8 – “Environmental impact of ECF and TCF bleaching”.

2.7.3.4 Removal of chelants

Chelating agents, ethylene-diamine-tetra-acetic acid (EDTA) and diethylene-triamine-penta-acetic acid (DTPA) are applied because of good sequestering properties, i.e. their ability to suppress the activity of the dissolved transition metal ions without precipitation. These metal ions are able to catalyse the decomposition of hydrogen peroxide into radicals. TCF bleaching is only possible by treating the pulp with EDTA or DTPA (or other similar chelants) before the hydrogen peroxide stage. Therefore, effluents from TCF bleach plants have increased concentrations of chelants. There is concern about the ability of chelants to remobilise toxic heavy metals out of sediments and their biodegradability.

Chelant charge in TCF bleaching is normally about 2 kg/ADt.

The chelant DTPA is not degraded in biological treatment but may be adsorbed onto the biological sludge. About 10-30% of the DTPA is separated from the water phase in this way. According to [SSVL, 1981], 20-50% of DTPA can be separated with chemical precipitation with metal salts. These data relate to mechanical pulp bleaching but it is believed that a similar effect can occur in effluents from chemical pulp bleaching (ÅF-Process, internal data from bleach plant effluents, 2001).

The chelant EDTA is resistant to aerobic biodegradation in an activated sludge plant operated under “normal” conditions (about 10% reduction at pH 7 and short sludge age). EDTA does not adsorb onto sludge so it passes through the treatment plant without significant removal. EDTA is however biodegradable under special conditions. If the pH is higher than 8 and the sludge age (retention time of the biosludge in the biological treatment) is long enough (>20 days), the reduction will be about 75% as an annual average.

Since the removal rate depends on the biology of the system, it is sensitive to rapid and major changes in effluent composition. Normal monthly averages can be 90-99% but when the activity of the biological system is upset, the removal rate can drop to 40-50% for a month before the system has recovered [van Ginkel, 1997], [Virtapohja, 1997], [van Ginkel, 1999], (ÅF-Process file data).

The chelants contain about 8% of nitrogen and contribute to the N_{tot} discharge from the mill. Biodegradation of EDTA increases the release of nitrogen in the activated sludge plant which is of benefit since it replaces otherwise added nutrient nitrogen. This may lead to an overall reduction in the discharge of nitrogen to the environment.

2.7.3.5 **Atmospheric emissions**

The main emissions sources to the atmosphere from kraft pulping are the recovery boiler, the lime kiln, the power boiler, the CNCG incinerator and the CNCG emergency incinerator.

If the kraft pulp is bleached, these sources are for all practical purposes identical whether ECF or TCF bleaching is employed.

Ozone is manufactured on site and its production rate matches the process requirements. Any excess ozone (either from the generator or the bleaching stage) is fed through a catalytic bed to be destroyed and the resulting oxygen is returned to the O stage.

2.7.3.6 **Solid wastes**

The solid waste generated in a kraft pulp mill operation originates from the wood handling (sand and wood residues), chemical recovery (grits and sludge), ash from boilers and sludge from effluent treatment (primary sludge, secondary sludge and tertiary sludge, if present) and miscellaneous material (e.g. building material).

There is no difference between BKP mills employing either ECF or TCF bleaching in these respects and therefore the amounts, composition, handling etc. of the solid wastes are comparable.

TCF biosludge and fibre sludge have not been commonly tested to date and therefore, minimal data have been generated. The bleach plant itself does not generally produce solid waste. Rather, solid wastes are produced from other areas of the mill (see above).

2.8 ENVIRONMENTAL IMPACT OF ECF AND TCF BLEACHING

2.8.1 Conclusions reported in studies carried out in the 1990s and early 2000s

The environmental effects of bleach plant effluents and whole mill effluents have been assessed in several reports that have reviewed and analysed a large number of investigations, field studies, research work and chemical analyses carried out during the 1990s.

One outstanding review report is that by the Darmstadt Technical University (DTU) [Hamm, 2002], which reviewed 70 literature peer-reviewed references published on this topic between 1989 and 2001 (most were published in the latter half of the 1990s).

The main conclusions reported in these studies are as follows:

- Treated wastewater from well-managed pulp and paper mills employing ECF bleaching is virtually free of dioxin and persistent bioaccumulative toxic compounds.
- The other chlorine-containing organic compounds resulting from ECF bleaching have a composition similar to that of natural compounds, degrade naturally, do not persist in the environment and present a negligible environmental risk to aquatic ecosystems.
- The toxicity of the whole mill effluent from modern mills is generally very low and shows no correlation to the levels of AOX from ECF bleaching.
- There is no evidence available to indicate that further reductions of effluent AOX from the average level of 0.5 kg/ADt (in 2002) would result in any demonstrable environmental benefit.
- There is no international consensus on appropriate AOX discharge limits.
- In global terms, if mills currently using molecular chlorine were to switch to ECF bleaching, a greater reduction in AOX would be achieved than if mills currently using ECF bleaching sequences switched to TCF sequences.
- There is no systematic difference in effect intensity or effect pattern between the whole mill effluents from mills employing ECF or TCF bleaching.
- There is no indication of a difference between ECF and TCF bleaching in terms of acute and chronic toxic effects on aquatic eco-systems.
- Biological toxicity tests carried out at the Mercer International Rosenthal BKP mill in Blankenstein, Germany, while producing both ECF and TCF pulps, indicate no difference in ECF and TCF effluent quality.
- The remaining environmental effects of modern mills (e.g. sub-lethal toxicity to aquatic organisms) cannot be predicted from the bleaching sequence alone. Future evaluations of these environmental effects should focus also on other unit operations within the mill (e.g. wood handling, cooking, washing, screening, spill and foul condensate handling).
- A secondary effluent treatment is a prerequisite for both ECF and TCF wastewaters to minimise long term toxic impacts on aquatic ecosystems.
- The ECF and TCF bleaching processes are considered BAT in [IPPC BREF, 2001].

- Organic halogen (OX) content of pulp is a suitable parameter for assessing the aquatic eco-friendliness of ECF pulp production.
- ECF pulps have better paper-making properties than TCF pulps.
- TCF bleaching offers no advantage over ECF bleaching in terms of reducing or eliminating an effluent discharge.

Three studies have addressed the issue of toxicity of ECF and TCF effluents particularly well:

- Nelson, Stauber *et al.* compared the toxicity of ECF and TCF effluents from bleaching of eucalypt kraft pulps using a suite of marine bioassays developed by the National Pulp Mills Research Program (Australia). The untreated TCF effluents were more toxic than the ECF effluent, possibly due to residual peroxide in the TCF effluents. While secondary treatment reduced toxicity, both the ECF - D(EO)DD - and the TCF - (XQ)(EOP)(EPN)¹⁹ - effluents were still found to be toxic in the sensitive sea urchin fertilisation and scallop larval abnormality tests [Nelson, 1995], [Stauber, 1996].
- More recently, Munteer *et al.* found that for activated sludge treated ECF - D(EO)DD - and TCF - Q(OP)(ZQ)(PO) - bleaching effluents of Brazilian eucalypt kraft pulp, Microtox® toxicity was consistently eliminated from both effluents, whereas chronic toxicity to uni-cellular green freshwater alga *Selenastrum capricornutum* was reduced but not removed during treatment [Munteer, 2002].

2.8.2 Conclusions reported in recent studies

A considerable amount of work has been carried out recently in Canada on the impact of pulp and paper mill effluents on the reproductive capacity of fish.

Because there are no TCF BKP mills in Canada, all the work to date has been on mills either using chlorine-containing bleaching chemicals or on mechanical pulp mills. However, there is growing evidence that endocrine disrupting substances (EDS) are either derived from wood or are chemical or bio-degradation by-products of naturally occurring chemicals, and not organochlorine compounds. Consequently, the impacts are likely to be the same whether the mills use ECF or TCF bleaching sequences.

¹⁹ Xylanase/EDTA; oxygen alkali extraction with peroxide; alkali extraction with peroxide and nitrilamine; peroxide.

The following is a review of the conclusions reported in selected studies published on this topic in the technical literature:

2.8.2.1 **Mixed function oxygenase (MFO) enzymes**

Physiological responses occur in fish when fish are exposed to pulp mill effluents. The main biological responses attributable to mill effluents are a reduction in the fishes' reproductive capacity and the induction of mixed function oxygenase (MFO) enzymes in their liver. Of these responses, the most serious is diminished reproductive capacity [Carey, 2002]. MFO induction can be taken as a possible indicator of toxicity but its biological significance has not been elucidated [Kovacs, 2001].

2.8.2.2 **Endocrine disrupting substances**

Any external agent that upsets or interferes in a specific way with the endocrine system²⁰ is called an EDS.

Chemicals such as insecticides, fungicides, surfactants, polychlorinated biphenyls (PCB), chlorodibenzodioxins and synthetic hormones are known to affect the endocrine system.

In the case of pulp and paper mill effluent, the issue of EDS has exclusively involved their potential to affect fish [Tatum, 1995].

The World Health Organisation considers the following changes in fish to be examples of endocrine disruption: delayed sexual maturity; reduced egg production, gonad size and sex hormone levels; and alterations in the expression of secondary sexual characteristics [Damstra, 2002].

Canadian studies of fish caught near pulp and paper mills found the fish to have reduced levels of hormones in the blood, reduced gonad size, and delayed sexual maturation [Munkittrick, 1991], [Munkittrick, 1992], [Munkittrick, 1994]. Other work [Kovacs, 1995a], [Larsson, 2000] suggested that mill effluents could possibly create a bias towards more males than females by altering the sex ratio of embryos and larvae.

EDS in pulp and paper mill effluents causing these physiological effects have not been identified [Kovacs, 2006a], [Kovacs, 2006b]. Laboratory studies and field studies have shown that BKP mill effluent is improved in terms of its physiological effects on fish when mills:

- Reduce black liquor losses and black liquor carry-over into the bleach plant.
- Convert from bleaching with molecular chlorine and hypochlorite to ECF bleaching.
- Improve "handling" of evaporator condensates.
- Install or improve secondary (biological) effluent treatment [Kovacs, 2001].

²⁰ The endocrine system in animals and humans controls development, growth, behaviour and other physiological functions. The system consists of the endocrine glands (pituitary and thyroid glands, pancreas, adrenal gland and male and female gonads) and the hormones which these glands produce.

2.8.2.3 Environmental impact

Even if the impact of converting to ECF bleaching on effluent quality has not been specifically identified because other changes in the mills were undertaken at the same time, several researchers have concluded that chemicals other than those created by ECF bleaching are probably responsible for the physiological effects in fish [Pryke, 1996], [Kovacs, 1996], [O'Connor, 1993], [O'Connor, 1994], [NCASI, 1990], [Carey, 2002]. This conclusion was based, in part, on the following observations:

- Research has shown that MFO inducing compounds are likely to be natural compounds related to wood furnish [Martel, 1997a], [Martel, 1997b] and not compounds such as dioxins.
- Laboratory studies with effluent taken from a BKP mill before and after the mill converted its bleaching sequence from $D_{55}C_{45}(EO)HDP$ to $D(EO)DP$ showed that the differences in *Ceriodaphnia* reproductive capacity or in liver MFO enzyme activity in rainbow trout were insignificant [Kovacs, 2001].
- When process changes made at two BKP mills which resulted in improved effluent quality, as assessed by *Ceriodaphnia* reproductive capacity and by liver MFO enzyme activity in rainbow trout, were compared, the common element at the two mills was a reduction in black liquor losses [Kovacs, 2001].
- Reverse osmosis treatment of evaporator condensate (whose main contaminant is methanol) used as wash water and dilution water on the second post-oxygen delignification washer in a BKP mill without biological treatment essentially removed the impact of mill effluent on plasma testosterone levels in male and female mummichogs (*Fundulus heteroclitus*) exposed to the 1% effluent for periods of 30 and 57 days. Also, the final effluent was no longer acutely toxic to *Daphnia magna* and rainbow trout. Prior to the RO treatment of condensates, the final effluent was acutely toxic and produced significant reductions in plasma testosterone levels in female mummichogs [Dubé, 2002].
- It appears possible that natural wood substances with estrogenic and androgenic properties could exist in pulp mill effluents [Martel, 2004]. The products of microbial degradation of phytosterols have been shown to cause masculinisation of fish although the actual phytosterols themselves had no effect [Howel, 1989]. Some 300 plant species have been found to contain phytosterols with estrogenic properties [Hughes, 1988]. Δ -sitosterol, a potential EDS [MacLatchy, 1995], has been found in measurable quantities in the final effluents of 22 American pulp and paper mills [Cook, 1997]. Other potential EDS which have been found in mill effluents are genistein [Kiparissis, 2001] and stilbenes [Hewitt, 2001].
- Based on existing evidence, the effect of mill effluents on reproductive indicators does not appear to be dependent on the type of manufacturing process or the type of effluent biotreatment used. This could suggest a common origin of causative agent(s) such as those originating from wood or additives or their biodegradation products. However, just as there is evidence that effects can be caused by effluents from mills using different processes, there is also evidence for the absence of effects in relation to effluents from other mills using the same processes. At present it is unclear why effluents from mills using the same processes have different quality. In field studies, the actual

receiving environment could be an important factor [Kovacs, 2006a], [Kovacs, 2006b].

- While the types of manufacturing process or biotreatment do not appear to be critical factors regarding effluent-related effects, there is some evidence that the way a mill operates can be an important factor. For example, it is known that changes in mill operating conditions, such as “good housekeeping” (e.g. spill control, staff education), improved condensate handling and biotreatment, as well as modernised bleaching processes have improved effluent quality, albeit not to a point that was considered to result in the removal of all effects. The specific changes in operating conditions or combination of changes that can eliminate the residual effects attributed to mill effluents remain to be identified [Kovacs, 2006a], [Kovacs, 2006b].

Work is continuing to identify either sources or causes, or both, for the toxicological effects of pulp and paper mill effluents in the aquatic eco-system and to evaluate remedial in-plant and ex-plant technologies [Kovacs, 2006a], [Kovacs, 2006b]. While it cannot be stated conclusively at present that ECF and TCF bleaching sequences are equivalent in terms of their impact on the aquatic eco-system, the research results outlined above, which indicate that either naturally-occurring wood substances or their chemical or biodegradation by-products, or both, rather than chlorinated organic compounds, are responsible for physiological effects in fish, appear to be pointing in that direction.

2.9 PROCESS CLOSURE OF THE BLEACH PLANT

2.9.1 Historical perspective and perceptions

Process closure seeks to decrease the fresh water use and effluent discharge. The difficulty of reducing water use is clearly stated by Aracruz in their 2005 Annual Report and Sustainability Report: "The quality of pulp is directly related to the quantity of water used in the manufacturing process because washing is a fundamental stage to obtain a high quality product, which is particularly indispensable for paper that comes into direct contact with skin or food".

Developing a closed-cycle or zero discharge BKP mill has been the goal of researchers and operating companies for many years. There was significant research and development activity in this area in the 1930s, 1950s, 1970s and 1990s.

Liquid effluents from bleaching are the most problematic stream when considering closure, and present the last major technical hurdles to a fully closed-cycle BKP mill.

Initially TCF developers claimed that this technology was the best way towards closure. For example, in Södra Cell's marketing material for ozone bleached softwood TCF pulp in 1994 (Södra Cell, No Ordinary Ghost Story, 1994) states "...all the signs indicate that the route to a closed-cycle bleaching plant is also via TCF". This point was illustrated with a picture of a pulp mill in a bottle.

This concept was also embraced by environmental groups, for example: "The elimination of chlorine based chemicals allows mills to close the loop and reuse large amounts of water"... "the presence of any chlorinated compounds make the water impossible to reuse, as it will corrode equipment" (Greenpeace - The Medium is The Message, 1994).

And the concept was also included in a World Bank guidance document: "It is generally not practical to recover chlorinated organics in effluent since the chloride content causes excess corrosion" (World Bank - Pollution Prevention and Abatement Handbook - Part III Pulp and Paper Mills (Draft) 1 September 1997).

Similar statements are also made in submissions commenting on proposed BKP mills today.

These statements on the TCF bleaching process are incorrect.

Both Södra in Sweden and Louisiana Pacific (now Evergreen Pulp) in the USA fully expected to be able to recycle all bleaching filtrates from their TCF bleach plants, in the 1990s. They were unsuccessful. Additionally Champion Paper Company demonstrated at Canton, NC, USA that chlorinated organics from bleaching filtrates can be returned to the recovery cycle, without causing corrosion or other difficulties.

2.9.2 Actual results

To examine the role of ECF and TCF technologies in bleach plant closure it is useful to review necessary technologies to achieve full closure. Key technologies that go beyond AMT and are used to progress towards a closed-cycle BKP mill are:

- Recycle of alkaline bleaching effluent, i.e. (EO) or (EOP) recycle.
- Recycle of acidic bleach plant effluent.
- Recycle of all bleach plant effluent.
- Secondary or extended evaporator condensate stripping for reuse in bleaching.
- Use of special evaporation techniques for bleaching and other mill effluents.
- Use of "kidneys" to purge chlorides, alkaline earth materials (Ca, Mg, Mn) or other non-processes elements (Al, silica).

Alkaline bleaching filtrates are being recycled from TCF and ECF mills today. This practice is common with TCF mills, but not as common in ECF mills.

Table 2.15 Bleach plant filtrate recovery practices at paper grade BKP mills

Mill	Wood Type	Sequence or Bleaching Agents Used	Filtrates Recovered ^a	Biological Treatment?
Blue Ridge Paper Canton, NC, USA	SW	OD(EOP)D	D, EOP	Yes
	HW	OD(EO)D	EO	
International Paper Franklin, VA, USA	SW	OZED	Z, E	Yes
Evergreen Pulp Samoa, CA, USA	SW	OQQPQ(PO)	P, PO	No
Smurfit Munksjö Aspa Bruk, Sweden	SW	OQ(PO)	Q, PO	Yes (2005) ^{b)}
		OQ(PO)DD	O, PO	
M-Real Sverige AB Husum, Sweden	SW	O, D, E, P	Acid, alkaline	Yes (2005)
	HW	O, Z, E, P, D	All - part time	
SCA Östrand, Sweden	SW	OQQ(OP)(ZQ)(PO)	Alkaline	Yes
Södra Cell Mörrum, Sweden	SW, HW	O, Paa, P, Q, D	Alkaline	Yes (2002)
Södra Cell Värö, Sweden	SW	O, Paa, P, Q	Alkaline	Yes (2002)
Stora Enso Skoghäll, Sweden	SW	O(PO)DQ(PO)	PO	Yes
Metsä-Botnia Rauma, Finland	SW	O(ZQ)(PO)(ZQ)(PO)/PO	PO	Yes
Kymmene Pietarsaari, Finland	HW Line	O, Z, D, P	Alkaline from TCF only	Yes
	SW Line		None recovered	Yes

Notes:

- All mills in this table recover filtrates from oxygen delignification.
- Treatment of selected effluents.

Sources: ÅF Process, [Beca AMEC, 2004].

The original intent for many of these mills was to completely eliminate bleach plant effluents. However, mills have generally found that incremental benefits diminish and technical challenges increase as the degree of closure increases. Complete closure appears to be considerably more difficult to achieve than expected, and most mills have found that operations can be sustained only under partially closed conditions. Additionally, several of the mills in Sweden have concluded that partial closure coupled with biological treatment of the remaining effluent represents a more optimal solution than full closure, and have installed treatment facilities.

In addition to the mills listed in Table 2.15, there are three essentially closed-cycle bleach plants in operation in Sweden at mills that bleach a portion of their total pulp production. In each of these, a small bleach plant was added to an existing brown paper and board mill in order to produce white top liner. Alkaline filtrates from bleaching are recycled countercurrently to brownstock washing. The neutral or acidic filtrate is returned for washing brownstock on the unbleached portion of the production lines in two of the mills, and in the third it is concentrated in a low temperature evaporation stage with the concentrate added to the black liquor concentrators (crystallisers). The bleached pulp production represents only 20% of production in two of the mills, SCA Munksund and Kappa Kraftliner Piteå (formerly AssiDomän Lövholmen). In the third mill, Korsnäs, Frövi, formerly AssiDomän Frövi, 40% of production is bleached. The small capacity of these bleach plants relative to the total capacity of the brownstock system and chemical recovery facilities provides favourable circumstances for recovering bleaching filtrates that cannot be taken advantage of at paper grade BKP mills where all of the pulp is bleached.

Partial closure of the bleach plant (and other mill systems), leads to increased concentrations of organics²¹ (dissolved wood compounds) and inorganics, often called non-process elements (NPE). Consequences of this can be increased corrosion in digesters, evaporators and recovery boilers; depression of recovery boiler capacity and efficiency; scaling and deposits in bleach plants, digesters and evaporators; increased consumption of chemicals; and variable pulp quality. In addition, the efficiency of a Q stage in removing transition metal ions is reduced by extensive system closure [KAM report A100, 2003]. Before implementing a closure strategy, the consequences for mill operations (e.g. mill uptime, construction materials, mill personnel safety and pulp quality) have to be carefully analysed.

Much of the technology development associated with kraft mill bleach plant closure involved extensive water use reduction and has been coupled to an understanding of NPE behaviour. This means focusing on mitigating undesirable consequences such as scale deposits, corrosion, loss of bleaching efficiency, increased evaporative loads, reduced production capacity, and loss of operational flexibility. These issues have caused many companies to reconsider the role of process closure in minimising effluent impacts. In many cases, the optimal solution has been found to be a high degree of closure down to 15 m³/ADt coupled with external biological treatment of the remaining process effluent.

²¹ Both the fibrous and non-fibrous fractions of wood are organic substances, to the chemist. However the term "organics" is widely used in the pulp industry to refer to the non-fibrous material only, and is so used in this report.

Examples include SCA Östrand, M-Real Husum, Södra Cell Mörrum and Värö, and Metsä-Botnia Rauma. It appears that there are no bleach plants at paper grade BKP mills that operate fully closed on a continuous basis.

The adverse effects of NPE and the particular elements responsible for these effects are summarised in the following table.

Table 2.16 Adverse effects of NPE

Adverse effects	Elements responsible
Scaling and deposits	Al, Si, Ca, Ba
Depression of recovery boiler capacity and efficiency	K, Cl
Corrosion	K, Cl
Inerts in the lime cycle	P, Mg, Al, (Si)
Inefficient peroxide bleaching	Mn, Fe, Cu
Environmental impact	N, P, Cd, Pb

Source: [KAM report A100, 2003].

Kraft mill bleach plant effluent flows usually range from 10 to 30 m³/ADt in modern mills. Many European mills have flows between 15 and 25 m³/ADt. Few mills have bleach plant effluent flows under 10 m³/ADt. There are still many mills having bleach plant effluent flows above 30 m³/ADt.

Table 2.17 Main strategies for bleach plant closure

<ul style="list-style-type: none"> • Increased recycle of filtrates within the bleach plant. This results in reduced fresh water consumption and bleach plant effluent flows, however, it does not lead to a reduction of specific emissions like AOX and COD on a mass basis (e.g. kg/ADt) • Recycle of bleach plant filtrates to the chemical recovery system. Usually only alkaline bleach plant filtrate is recycled, but a few mills recycle acid filtrate. The filtrate can be used as partial replacement of wash liquid in the fibrelime brown stock washing, or directly recycled to the chemical recovery area <p>The fresh water consumption and effluent flow may also decrease, but not necessarily</p>
--

Sources: ÅF-Process/ AMEC.

Currently, ECF effluents can be recycled to chemical recovery but only when there is provision made for increased chloride removal from the chemical recovery system. This is due to the build-up of chloride ions (Cl⁻) and in some cases potassium (K).

Since TCF bleach effluents contain virtually no chloride, the problems associated with chloride in TCF bleaching are less than those in ECF bleaching when bleach plant effluent is recycled, but generally increased purging is also required [Gleadow, 1996].

The difficulty in managing the problems with NPE (need for their control and removal) and with increased concentrations of organic and inorganic compounds is the same or greater in TCF bleaching when compared with ECF bleaching since NPE have a greater impact on pulp quality and

brightness in TCF bleaching. In some mills, the build-up of metal levels (particularly Mn) due to filtrate recycle is so high that H₂O₂ bleaching, an important part of any TCF sequence, loses effectiveness and this makes strength and brightness targets unobtainable. Bleaching with ClO₂ is not subject to this limitation.

The COD loads of BKP mill bleach plant effluents at a kappa number of 8-12 to the bleach plant and with no recovery of bleach plant filtrates are as follows:

- Hardwoods: about 20-30 kg/ADt for ECF bleaching and 20-35 kg/ADt for TCF bleaching.
- Softwoods: about 25-35 kg/ADt for ECF bleaching and 25-40 kg/ADt for TCF bleaching.

Partial recovery of bleach plant filtrates has the potential to reduce COD emissions by about 30%.

Table 2.18 Adverse effects of partial bleach plant closure

The accumulation of dissolved solids causes a considerable increase in the consumption of bleaching chemicals
Difficulty in reaching target brightness particularly for peroxide bleached pulps
Variable pulp quality, particularly for TCF pulps
pH adjustments with H ₂ SO ₄ and NaOH may be costly because of the considerable buffer capacity of the pulp. The sodium-sulfur (Na-S) balance of the mill may, therefore, be disrupted
Partial closure of the bleach plant and other mill systems leads to increased concentrations of organic and inorganic compounds, also including NPE, resulting in increased corrosion, scaling and deposition within the bleach plant and other mill areas Buffer storage capacity for filtrates is necessary to absorb transient and upset conditions
Increased likelihood of precipitation of calcium oxalate (CaC ₂ O ₄), calcium carbonate (CaCO ₃) and barium sulfate (BaSO ₄). Calcium oxalate precipitates at pH < 8 while CaCO ₃ precipitates at pH 8-12. Barium sulfate precipitates over the entire technically interesting pH range (2-12)
A control strategy for water management in the plant has to be developed and implemented
Additional evaporation plant capacity and additional recovery boiler capacity may have to be installed

Sources: AMEC/ [KAM Report A100, 2003].

More research is therefore needed to find "kidneys" (e.g. ion exchange or precipitation) to avoid the build-up of unwanted species (e.g. mineral constituents or NPE) that may impair the bleaching process, the equipment or the product.

Both ECF and TCF bleaching have significant challenges to overcome before achieving complete bleach plant filtrate recycle.

Recycle of alkaline filtrates is practised by both ECF and TCF mills. It is likely a little easier for TCF mills to recycle alkaline filtrates, due to lower chloride levels in these filtrates. There are, however, demonstrated technologies successfully applied in a number of mills for controlling chloride levels in the kraft recovery system.

Recycling of acidic filtrates is practiced in one ECF mill (Blue Ridge Canton, NC, USA). It is likely easier to recycle acidic filtrates in ECF mills, as in TCF mills build-up of metals results in ineffective bleaching. Both ECF and TCF mills must overcome Ca- and possibly Ba-based scales associated with acid filtrate recycle.

Separate evaporation of TCF bleach plant filtrates is practised at Korsnäs, Frövi, Sweden. Laboratory and pilot work has demonstrated that the technique could possibly be applied to both ECF and TCF filtrates, but condensate treatment and scale deposition are among the technical challenges to be resolved.

Extended evaporator condensate treatment is more generally applied in TCF mills, and is a critical part of the metals management strategy in bleaching. This technique can be applied in both ECF and TCF mills. Care must be taken in modern mills with reuse of evaporator condensates because of their recently identified role as a likely source of pulp mill chronic toxicity (due to extractive components such as stilbenes and terpenes). These components appear to be present at the same levels in ECF, TCF and unbleached kraft mills.

2.9.3 Conclusions

Both ECF and TCF bleaching offer paths to process closure. Based on current knowledge, the degree of closure in TCF mills can be only partial whereas ECF mills are more likely to offer full bleaching closure.

As of Q2 2006 there are no paper grade bleached kraft mills that operate fully closed on a continuous basis, more specifically there are no bleach plants in paper grade BKP mills that operate fully closed on a continuous basis.

The principal impediment to closure in a BKP mill is the recycle of bleach plant effluents, which typically comprise about half of the total effluent volume. For ECF mills the prime concern has been the build-up of chloride in the chemical recovery cycle, with secondary concerns with pulp quality and mill operability. For TCF mills the prime concern has been pulp quality (strength and brightness) with secondary concerns in operability, and potassium and chloride build-up in the recovery system. Both ECF and TCF bleaching closure can cause operating difficulties with increased chemical consumptions, poorer pulp quality and provide challenges in minimising deposition and scaling on equipment.

2.10 BLEACHING CHEMICAL PREPARATION

The most commonly used chemicals for bleaching of chemical pulps are ClO_2 , O_2 , O_3 and H_2O_2 . Other common chemicals used in bleaching are NaOH (caustic soda) and H_2SO_4 . Chlorine dioxide and O_3 have to be produced on site due to their instability. Hydrogen peroxide, O_2 , NaOH and H_2SO_4 can be purchased and delivered to the mills.

2.10.1 Chlorine dioxide preparation

Chlorine dioxide must be generated on site because it is unstable as a gas and can only be stored as a solution of approximately 1% in water. Gaseous ClO_2 decomposes to Cl_2 and O_2 and this decomposition is explosive at 300 mm Hg partial pressure.

There are a number of possible reactions to produce ClO_2 and some technologies can produce up to 0.7 tonnes of by-product Cl_2 per tonne of ClO_2 in the generator off-gas while others produce very small amounts.

There are two proven modern processes that can accomplish this. These processes reduce sodium chlorate (NaClO_3) with either methanol (CH_3OH) or H_2O_2 in the presence of H_2SO_4 to form ClO_2 .

Table 2.19 gives details of the manufacturers, trade names and number of operating or sold installations for these processes up to Q2 2006.

Table 2.19 Methanol and hydrogen peroxide based chlorine dioxide generator installations

Process description	ERCO Worldwide ²²			Cellchem ²³		
	Trade name	First year installed	Total installed to Q2 2006	Trade name	First year installed	Total installed to Q2 2006
Methanol	R8	1989	91	SVP-Lite	1987	64
Methanol with neutral saltcake	R10	1995	3	SVP-SCW	1995	11
Combined	R8/R10	1993	22	SVP-Lite/SCW	1995	1
Hydrogen Peroxide	R11	2000	1	SVP-HP	1992	6
Combined	R8/R11	-	-	SVP-Lite/HP	1996	3
Combined	R10/R11	-	-	SVP-SCW/HP	2003	1

Sources: Cellchem, ERCO Worldwide.

²² ERCO Worldwide is a Division of Superior Plus of Calgary, AB, Canada.

²³ Cellchem is an engineering and contracting department within the Bleaching Chemicals Europe division of Eka Chemicals AB, Stockholm, Sweden.

The entire generating system is operated under vacuum by means of a steam ejector, or a liquid ring vacuum pump.

Chlorine dioxide is absorbed in chilled water in the absorption tower and stored in ClO_2 solution tanks (with typical retention time of 8 hours).

The ClO_2 solution storage tanks are vented to an off-gas scrubber by a fan. Likewise, any remaining traces of ClO_2 in the off-gas from the ClO_2 absorption tower are absorbed in chilled water in a scrubber.

As shown in Table 2.19, the methanol process (ERCO R8/ R10 and Cellchem SVP-Lite/ SVP-SCW) is the dominant modern method for generation of chlorine dioxide with low chlorine content.

There are a few installations using H_2O_2 as the reducing agent (ERCO R11 and Cellchem SVP-HP). The advantage of this method is that the risks associated with methanol handling as an additional hazardous chemical are eliminated whereas H_2O_2 is also used as a bleaching chemical. In all other respects the process conditions and the unit operations are similar to those used in the generation of ClO_2 using methanol.

By-product sodium (Na) and sulfur (S) from the generation of ClO_2 in the form of either neutral or acid sodium sulfate (Na_2SO_4 or saltcake) can generally²⁴ be returned to the pulp mill for chemical make-up and there is no effluent.

2.10.1.1 **Integrated chlorine dioxide plants**

Conventional integrated chlorine dioxide plants (IDP) generally consist of:

- A ClO_2 plant which generates sodium chloride (NaCl) solution, ClO_2 solution and Cl_2 gas from NaClO_3 solution and hydrochloric acid (HCl) solution.
- An NaClO_3 electrolytic cell plant which generates NaClO_3 solution and hydrogen (H_2) gas from NaCl.
- A hydrogen chloride (HCl) plant which generates HCl solution from H_2 gas and Cl_2 gas.

The only external inputs to the IDP are water, electricity and make-up Cl_2 gas.

Sometimes the source of Cl_2 gas for the HCl plant is a chlor-alkali electrolytic cell plant which generates Cl_2 gas, NaOH solution, H_2 gas and NaCl purge from NaCl and water. In this case the only external inputs to the IDP are water, electricity and NaCl.

IDP do not require NaClO_3 , acids, and reducing agents as raw materials, hence present advantages in terms of chemical supply and handling, especially in relatively isolated areas, but typically generate ClO_2 solutions contaminated with 0.22 kg Cl_2 /kg ClO_2 .

The low-chlorine IDP is a recent development proposed by Chemetics, a division of Aker Kværner Canada Inc. of Vancouver, BC to address this contamination issue [Ma, 2000]. Chemetics claims this type of plant generates ClO_2 solutions with 0.02 kg Cl_2 /kg ClO_2 , a contamination level

²⁴ This will depend on the particular mill chemical balance.

similar to that achieved by the methanol- and hydrogen peroxide-based ClO_2 generators.

Three low-chlorine IDP are currently operating:

- Hai Nan Jiang Lin, Hainan Province, PRC (70 t/d ClO_2 capacity). Start-up Q4 2004.
- PT. Indah Kiat Pulp & Paper, Perawang, Indonesia (50 t/d ClO_2 capacity). Start-up Q1 2005.
- PT. Lontar Papyrus Pulp & Paper, Jambi, Indonesia (25 t/d ClO_2 capacity). Start-up Q1 2005.

Due to the relatively short operating time of these installations and the consequent lack of consistent track record for low Cl_2 contamination of the ClO_2 solution, the low-chlorine IDP is at present considered to be an emerging technology.

2.10.2 Ozone preparation

The main purpose of using O_3 is to provide more delignification power. Ozone activates the fibres towards H_2O_2 and this results in higher brightness and lower H_2O_2 consumption.

Ozone is produced from dry air or O_2 by the application of high voltages (10-20 kV) across two electrodes separated by the reactant gas. Ozone is unstable and its yield is fairly low with a high level of unreacted O_2 in the product gas. A modern O_3 generator fed with O_2 uses about 10-15 MWh/t O_3 generated.

Ozone bleaching has very high investment costs due to the high costs of O_3 generators and auxiliary equipment. Since the O_3 concentration will be only about 10-16% O_3 in O_2 , fairly large volumes of O_2 are required. Thus, the operating cost is rather high due to a relatively high cost of O_2 as well as to the relatively high power consumption [Jaakko Pöyry, 1997], [Finnish BAT report, 1997], [Fuhrmann, 1998].

2.10.3 Other bleaching chemicals

Other bleaching chemicals are normally purchased:

- Hydrogen peroxide as 50% solution.
- Oxygen is mainly purchased but there are a few mills in Europe which generate O_2 on site. Several North American mills with O_2 activated sludge treatment plants have installed O_2 generators.
- Peracetic acid is used as bleaching chemical in a few pulp mills with TCF bleaching sequences. The electricity requirement for the production of Paa is about 3 MWh/t of product. This bleaching chemical is a valuable complement in a stage preceding H_2O_2 where it can replace O_3 . Full brightness can be achieved even when the unbleached pulp has a relatively high kappa number. The drawback with Paa is its high cost.

2.11 PULP QUALITY AND MARKETABILITY

ECF and TCF bleaching processes have been extensively studied in the laboratory under controlled conditions. An analysis of pulp produced with the same set of woodchips, under exactly the same pulping conditions and then either ECF or TCF bleached can provide an accurate comparison of how the bleaching method affects pulp properties, however, it is more meaningful to examine the properties of market pulps [Button, 2005].

Tables 2.17 and 2.18 on the following pages present the data for bleached eucalyptus kraft pulp (BEKP) and northern bleached softwood kraft pulp (NBSKP), respectively.

These pulps are produced in different areas of the world and display different properties. There are many possible reasons for this observation including climate, harvest age and maturity, wood species, processing conditions including the bleaching sequence, and customer requirements.

It is, therefore, apparent that this analysis is influenced by many more factors than ECF and TCF bleaching processes alone and it is not possible to generalise about which bleaching process is superior with respect to pulp properties.

This section examines selected softwood and hardwood market pulps, presents data from specific mill installations and then gives some concluding remarks regarding ECF and TCF bleached pulp properties.

2.11.1 Properties of hardwood market pulps produced in different regions

A representative selection of market BEKP from various regions was analysed according to standard procedures. Three pulps are ECF bleached and the 4th pulp is TCF bleached.

Table 2.17 Market BEK pulp properties

Region	Central Coast Brazil – ECF	Southern Brazil – ECF	South-east Asia - ECF	Iberian – TCF
Wood Species	<i>E. Grandis</i> and assorted hybrids	<i>E. Globulus</i> , <i>E. Grandis</i> and some hybrids	<i>E. Camaldulensis</i>	<i>E. Globulus</i>
Brightness (%)	89.8	88.4	87.2	87.6
Opacity (%)	78.2	81.2	82.8	77.8
Application	Premium facial tissue	Printing and writing paper Premium tissue	Book papers. Advantageous if used in bleached board, cover stock or bulk sensitive grade	Heavier weight printing and writing grades, especially coated paper
Properties suitable for application	Tactile softness when layered on the surface	Used in lightweight grades due to high fibre count ²⁵ and low coarseness. This produces a soft velvety feel to tissue	Exceptional bulk and opacity qualities	Does not develop tactile softness. Useful in mills that co-refine long and short fibres due to refining resistance
Distinct attributes	Brightness and cleanliness are above average. The pulp is short fibred. Freeness is high but bulk is low at a given tensile strength	Known for its fibre uniformity, low fines and good burst and tensile strength properties when properly refined. Good printed opacity in	High bulk and opacity. It is a softer pulp and would not tolerate hard refining. Reasonable brightness, cleanliness and purity	These fibres resist hard refining without becoming shorter or collapsing

²⁵ Since hardwood fibres have much lower mass than that of softwood fibres, their fibre count, or reciprocal of mass, is much higher.

Region	Central Coast Brazil – ECF	Southern Brazil – ECF	South-east Asia - ECF	Iberian – TCF
		lightweight paper		

Source: [Nanko, 2005].

The physical and optical properties of the market BEKP were tested at different freeness levels achieved by applying increasingly higher refining energy. In general, the tensile and tear indices of hardwood pulp increase with refining. Of the 4 pulps compared, the Iberian TCF pulp reaches the highest level of tensile strength, and the Central Coast Brazilian pulp reaches the highest tear strength. This pulp also achieves the best combination of these two properties, which is an advantage to papermakers. Overall, the TCF pulp's strength properties compare with the 3 ECF BEKP market pulps, however, although the TCF pulp had the best tensile strength at low levels of refining, it was an average performer at higher levels of refining, for tear strength and other properties.

The market pulp data analysis of 4 eucalypt pulps shows that the TCF bleached pulp does not perform quite as well as the 3 ECF bleached pulps. It has very good refining properties and bulk but its other properties are generally below average as demonstrated by the low light scattering coefficient, low zero span tensile strength (or fibre strength), and the high coarseness.

The properties of the TCF bleached Iberian pulp may be partially due to the late harvest of the pulpwood (harvested at 20-24 years old rather than the usual 7-12 years). Tree age causes greater fibre diversity in the raw material. Mature fibres have thicker walls and are longer and larger in diameter, therefore more resistant to refining.

2.11.2 Properties of softwood market pulps produced in different regions

A representative selection of market NBSKP from various regions was analysed. Four of the five pulps are ECF bleached and the 5th pulp is TCF bleached.

Table 2.18 Market NBSK pulp properties

Region	Coastal British Columbia – ECF	Québec – ECF	Maritimes & New England – ECF	Siberian – ECF	Eastern Europe – TCF
Wood Species	Douglas fir	Black spruce	Black, red and white spruce, eastern hemlock, balsam fir, red and white pine	Pine, spruce, European larch	Pine and spruce
Brightness (%)	88.9	89.2	88.0	89.0	89.1
Opacity (%)	74.4	74.7	72.0	72.6	74.5
Application	Fibre-reinforced cement	Facial tissue, printing and writing paper as well as coated and uncoated paper	Tissue	Converting and packaging grades	Reinforcement fibre
Properties suitable for application	High loft (fibre resilience) with good absorbency. Reasonably high tensile strength	Excellent wet tensile strength, good smoothness and “crumple”	Produces a dense/tight/high holdout heavily calendered paper	Inherent high strength	Acceptable blend of tensile, TEA, burst, fold and tear strength properties
Distinct attributes	Douglas fir exhibits the highest tear strength of any NBSK pulp. Tensile breaking lengths are average	High tensile strength and high fold property is a characteristic of this pulp. It has very high fibre strength. Tear strength at given tensile breaking length are highest. A very good reinforcement pulp	Freeness and bulk are lower than for other NBSK pulps. High tensile ratings are readily obtained on refining. The balance between tear and tensile strengths is average	High bulk at a given tensile strength. Tear strength is lower than for other NBSK pulp. Aesthetic qualities are poor but the customers do not require them	High fibre strength. Does not take extensive refining well – tensile breaking length and freeness drop significantly. ISO brightness levels are competitive with ECF counterparts

Source: [Nanko, 2005].

The physical and optical properties of the market NBSKP were tested at different freeness levels achieved by applying increasingly higher refining energy. The following conclusions could be made:

- At high refining energies the Coastal British Columbia and Québec pulps exhibit very high tear strength. The Eastern European TCF pulp has average tear strength when compared to the other NBSK market pulps.
- Aside from the Coastal British Columbian pulp, all of the pulps have very similar tensile breaking lengths that increase steadily with refining. The TCF pulp is slightly different as its tensile strength drops off with a high amount of refining.
- When refining softwood, tensile strength increases, but tear strength decreases. Therefore, there has to be a trade-off between the two properties. The Québec pulp has the highest tear strength of the NBSK pulps but this occurs at a low tensile index. The tear-tensile curve for the Eastern European TCF pulp is relatively flat which allows a satisfactory balance of tear and tensile strength.

The NBSK TCF bleached pulp performs well in comparison with the strength properties of the ECF bleached NBSK pulps analysed. It is competitive in its brightness and opacity properties and is not lacking in any particular area of the common pulp properties examined.

2.11.3 Mill cases

A few mills with experience in various pulp bleaching sequences, particularly TCF bleaching, are discussed below.

2.11.3.1 Kymmene Pietarsaari, Finland

Kymmene (formerly Wisaforest) Pietarsaari is a two-line integrated kraft mill. Hardwood pulp is TCF and ECF bleached on Line 1. Since the same pulpwood is used to produce both pulps, the property comparison is more representative than that of pulps from different regions.

The data in Table 2.20 were recorded from Line 1 in 1996.

Table 2.20 Kymmene Pietarsaari Line 1 pulp property data

Property	ECF bleached pulp	TCF bleached pulp
Brightness (%ISO)	89	89
Dirt count, mm ² /kg	4	3
Kappa number	1.5	2.5
Viscosity, dm ³ /kg	950	750
Fibre length, mm	0.85	0.85
Refined pulp		
Revolutions	650	900
Tensile index, Nm/g	70	70
Tear index, mNm ² /g	7.8	7.8
Freeness, °SR ²⁶	26	25
Sheet density, kg/m ³	785	780

Source: [McCubbin, 1996].

The total pulp capacity at this mill was 580 000 ADt in 1996 and TCF pulp production capacity was up to 50% of the total. These data show that the ECF and TCF bleached pulps produced are equal in brightness (89% ISO) and strength, provided the refining energy is increased by about 50% for the TCF bleached pulp [McCubbin, 1996].

The bleaching sequence on Line 2, where softwood is processed, is D(EOP)DP. Ozone and TCF bleaching are no longer used for softwood in order to optimise pulp quality. Since 2004, when the new high-pressure recovery boiler was installed, the bleach plant filtrates are no longer recycled to chemical recovery to minimise corrosion and the detrimental effect of chloride on recovery boiler capacity and efficiency.

The two hardwood sequences are A(Z/Q)(OP)(Z/Q)P for TCF and A(Z/D)(OP/P)Z/DP for Wisa ECF (see also Table 2.8). Most production is sold to UPM Kymmene paper mills.

(Source: Notes from mill visit, P Gleadow, 29 September 2005).

2.11.3.2 Evergreen Pulp, Samoa, CA, USA

Evergreen Pulp (formerly Louisiana Pacific Samoa Pulp Mill) was at the forefront of TCF and closed-cycle bleaching development in the USA in the 1990s.

Evergreen trialled TCF bleaching in 1992, and by 1994 had fully converted to TCF bleaching. Louisiana Pacific gave many presentations on this technology, which was funded under the US Department of Energy NICE3 program. Feature sheets from that time are still available (<http://www.tamarpulpmill.info/tcfmill.pdf>).

²⁶ Dewatering resistance in degrees Schopper Riegler.

Samoa is the only American kraft mill without biological treatment as it successfully negotiated a special provision of the Clean Water Act (Section 301(m)) to exclude it from this requirement.

The mill last made bleached pulp (TCF) in November 2004, and, while retaining the capability, has no current plans to make TCF in the future. It describes itself as follows: “Evergreen Pulp, Incorporated is the largest unbleached kraft pulp mill in North America, with 3 grades of unbleached kraft pulp” (www.evergreenpulp.com).

Although Louisiana Pacific was a pioneer, it was unsuccessful in fully recycling filtrates from bleaching. It took many years to produce pulp close to market brightness, and the mill was unable to successfully manufacture and sell the pulp at a sustainable price.

The sequence used on softwood was Q(EOP)PPP with later pressurisation of one of the P stages and additional chelation QQPQ(PO).

The early trials produced pulp at 60-70% brightness. This was subsequently improved over the years to 87-88% brightness. Comparative pulp properties of the softwood fully bleached pulp (sequence (CD)(EO)HDED) and the TCF bleached pulps follow:

Table 2.21 Evergreen Pulp, Samoa property data

	Fully Bleached	TCF	TCF
Sequence	(CD)(EO)HDED	OQQPQ(PO)	OQ(EOP)PPP
Date	1988	2004	1994
Fibre (mixed species)	Douglas Fir/Redwood/Spruce/Pine Fir		20%Redwood/ 80%Fir
Properties at 250 mL CSF			
Burst Factor	80	57	70
Tensile	10.7 km	8.6 km	9.8 km
Tear factor	118	104	130
Density, kg/m ³	660	700	-
Tappi	90.9	87	85
Brightness, %			
Opacity, %	63	65	-

Sources: [Samoa, 2004], [Econotech, 1988] and [Jaegel, 1995].

Comparatively, TCF pulp produced at Samoa had lower tear, burst and brightness than the previously produced pulp using a chlorine-based sequence. It is understood that similar wood species (50% Douglas fir 30% redwood and 20% other softwoods) were run for the 1988, and 2004 sequences, with a slightly different mix in 1994. Chip quality variations may also account for some differences in pulp properties.

2.11.3.3 Mercer International Rosenthal Mill, Germany

A comparison was carried out between ECF and TCF bleached pulp produced at the Rosenthal mill from identical softwood raw material. The tests showed that to obtain the same tensile index the TCF pulp had to be refined to 29-31°SR while the ECF pulp required only refining to 21-23°SR²⁷. Both

²⁷ A lower SR value indicates a higher pulp freeness.

the unrefined and the refined tear indices of ECF pulp were higher than those of TCF pulp and the tear loss with refining of TCF pulp is more rapid than that of ECF pulp.

Mercer Rosenthal concluded that the brightness, the tensile and tear strength of the ECF pulps were higher than those of the TCF pulps. The TCF pulps needed more refining energy to reach a certain strength level. [Hamm, 2002].

Consequently, these results are in disagreement with those presented in Section 2.11.2.

2.11.4 Concluding remarks

2.11.4.1 Kappa number ranges for full brightness

The typical oxygen-delignified pulp kappa number range to attain full brightness (about 90% ISO) for ECF bleached pulps is 9-12 for hardwoods and 11-14 for softwoods.

Fully bleached ECF pulp is typically of high quality, i.e. it has high strength (burst, tear, tensile and viscosity), cleanliness, and brightness stability.

The typical oxygen-delignified pulp kappa number range to attain full brightness (about 90% ISO) for TCF bleached pulps is 8-10 for hardwoods and 9-12 for softwoods.

2.11.4.2 Pulp yield

The level of delignification in cooking, the cooking process and oxygen delignification determine the final yield [Chirat, 2005] and [Johansson, 2005].

The yield loss in bleaching is in the range 1-3% (on wood) and is most likely independent on whether an ECF or TCF sequence is employed. There is a tendency for increased yield loss if alkaline peroxide bleaching is carried out. This is particularly noticeable in the bleaching of hardwood pulps [Bergnor-Gidnert, 2006].

Because TCF bleached pulps tend to have lower oxygen-delignified pulp kappa number, they have a lower overall bleached yield than ECF bleached pulps [Bergnor-Gidnert, 2006].

If ozone is used in one of the bleaching stages, the yield can be up to 6-10% lower than that of ECF bleached pulp. However, not all mills experience such large losses in pulp yield when carrying out TCF bleaching. These losses are primarily due to overextending cooking in the digester.

2.11.4.3 Pulp brightness

According to present knowledge it is difficult to achieve full brightness (+90% ISO) with alkaline peroxide based TCF sequences, e.g. Q(OP)Q(PO), on softwood pulps. If acid stages are included in the bleach sequence, e.g. Paa, and in particular Z, a full brightness can be reached but then it is difficult to get high pulp strength [KAM Report A100, 2003], [Bergnor-Gidnert, 2006].

2.11.4.4 Residual lignin and brightness reversion

Brightness reversion for ECF and TCF bleached pulps is a complex issue which has not been completely elucidated so far. The current state of knowledge can be summarised as follows [Bergnor-Gidnert, 2006]:

- There are large differences between softwood and hardwood pulps.
- Cooking conditions affect the brightness stability of the fully bleached pulp.
- The HexA content is probably the most important factor but there are several other "precursors" for reversion.
- The role of oxidised carbohydrates is most likely underestimated in reversion.
- The handling of the bleached pulp from the drying machine to final use is of importance.
- Either the wood species or clone, or both are of importance.
- The method used to evaluate reversion affects the results and the ranking of different pulps.

In general hardwood pulps show higher brightness reversion than softwood pulps and ECF pulps lower than TCF pulps. ECF bleaching as such is no guarantee for low reversion since factors like clone or handling of the pulp are of great importance.

Despite a few applications of hot acid stages in the Brazilian and South African BEKP mills, adoption of acid hydrolysis as a standalone stage (A_{hot} , $(AD)_{hot}$ and D_{HT}) for the selective removal of HexA has not been widespread [Eiras, 2003] and is debatable as an environmental measure. Hence, these stages are at present considered to be an emerging technology

As seen previously, hot acid stages (A_{hot} , $(AD)_{hot}$ and D_{HT}) may break down and remove HexA to save bleaching chemicals and reduce brightness reversion [Vuorinen, 1996], [Lachenal, 1998], [Ragnar, 2004].

The effect of a final P stage on pulp brightness reversion has not been conclusively clarified, as demonstrated by the following:

A final P stage can reduce the amount of remaining quinoid structures which are possible "precursors" for brightness reversion [Mateo, 2004], [Süss, 2005], [Lachenal, 2005].

A final P stage can also result in a lower residual OX content in the pulp, which is also a possible "precursor" for brightness reversion [Eiras, 2005a], [Eiras, 2005b].

Other workers have drawn a partly different conclusion. They have shown that a final P stage gives lower brightness reversion than a D stage in dry ageing, the reverse was true in moist ageing [Björklund, 2005].

A larger quantity of residual lignin often remains in TCF bleached pulp than in ECF bleached pulp because H_2O_2 delignifies less than ClO_2 and O_3 . Consequently, TCF bleached pulp usually has higher brightness reversion than ECF bleached pulp [Beca AMEC, 2004]. Also, a higher proportion of carbonyl (C=O) and carboxyl groups (COOH) (photoreceptors) account for the accelerated brightness reversion characteristics of TCF bleached pulps [Panchapakesan, 1995].

2.11.4.5 Other considerations

TCF bleached pulps tend to have lower viscosity, higher content of acid COOH groups in the hemicelluloses, higher content of residual lignin and extractives and in general show a lower strength potential than ECF bleached pulps at the same brightness [Hamm, 2002].

The overall conclusion from the review of the papermaking properties of ECF and TCF pulps is the following:

- At the same brightness the ECF pulps demonstrate higher tensile strength than the TCF pulps.
- For use as reinforcing pulp in lightweight papers, the ECF pulp gives the papermaker more flexibility and better possibility to reach the desired paper characteristics. The same flexibility can be reached using TCF pulps but then at the expense of the brightness level [Hamm, 2002].

An investigation of the change in characteristics of ECF and TCF softwood pulps during accelerated aging showed that the TCF bleached pulps had lower initial brightness and displayed only slightly higher yellowing than the ECF bleached pulps. Moreover, the TCF bleached pulps showed a more rapid decline in burst, folding and tensile strength compared to the ECF bleached pulps [Käßberger, 1998].

Both ECF and TCF bleached pulp quality parameters improve if the a kraft mill fibreline is well optimised and tuned. ECF bleached pulp is, however, of better quality than TCF bleached pulp. This applies especially to general pulp strength properties and is independent of how well the mill is operated. This is more accentuated for pine/ spruce kraft pulp properties than for eucalypt kraft pulp properties. Furthermore, to keep an even quality, ECF pulp production is more “forgiving” than TCF pulp production (ÅF-Process, 2006).

The following is a summary of the strength characteristics of eucalypt and pine BKP at comparable operation of the mill:

- Eucalypt kraft pulp: TCF pulp strength properties²⁸ are 90-100% of those for ECF pulp.
- Pine kraft pulp: TCF pulp strength properties are 85-95% of those for ECF pulp (ÅF-Process, 2006).

²⁸ Eucalypt pulp strength properties are arguably not the most important parameters, whereas light scattering coefficient, opacity and parameters promoting formation are more important.

ECF bleached pulp dominates the world bleached chemical pulp market. Data shows a widening gap between ECF and TCF bleached pulp production. ECF bleaching continues to grow whereas TCF, at approximately 5% of the world market at present (Q2 2006), is declining. There are mills originally built with the intention of producing TCF bleached pulp that have converted or plan to convert to ECF bleaching with the capability of producing TCF bleached pulp as required (ÅF-Process, 2006).

TCF bleaching has continued to develop, for example Södra no longer uses ozone to produce TCF softwood pulps, and Kymmene has similarly discontinued the use of ozone. Södra and Kymmene indicated strength concerns with ozone during mill visits carried out in 2005 and advised they are developing better alternative bleaching techniques. All major companies that pioneered kraft TCF bleaching in their fibrelines have recently purchased, built or plan to build new ECF capacity. This includes Metsä-Botnia, Kymmene and ENCE (ÅF-Process, 2006).

2.12 ECF AND TCF BLEACHING CHEMICAL SAFETY ISSUES

2.12.1 Aim of the risk assessment

The aim of this risk assessment is to compare ECF and TCF bleaching from the viewpoint of workplace hazard and hazards outside the mill fence. The assessment is a risk inventory (not a complete risk assessment) with focus on differences between modern ECF and TCF bleaching processes.

The probability of the occurrence of an accident and its consequences are evaluated on a scale from 1 to 5 using a risk matrix which quantifies the potential adverse effects on human health, life and environment (Table 2.22).

For each identified risk an evaluation is made of the probability for an accident to occur and for the extent of adverse effects that may be caused.

The adverse effects to the environment resulting from this assessment are estimated for a "recipient of average sensitivity".

Table 2.22 Risk assessment matrix for ECF and TCF bleaching processes

		Consequences				
		Small	Limited	Serious	Very serious	Catastrophic
Probability		1	2	3	4	5
Very probable	5					
Probable	4					
Less likely	3					
Unlikely	2					
Very unlikely	1					

Consequences for human health and environment

Human life and health	Slight discomfort	Lasting discomfort/ A few injuries	Serious discomfort/ A few serious injuries	5-10 deaths/ Several serious injuries	More than 20 deaths/ 100 serious injuries
Contamination	No cont./ Localised effects	Simple cont./ Localised effects	Simple cont./ Widespread effects	Heavy cont./ Localised effects	Heavy cont./ Widespread effects
Environmental impact ^{a)}	Local/ Short term	Local/ Medium term	Local/ Long term	Regional/ Short term	Regional/ Medium term

Notes:

a) Local impact – within ca. 1 km/ Regional - within ca. 10 km/ Short term – ca. 1 month/ Medium term – ca. 6 months/ Long term – ca. 36 months.

Source: ÅF-Process.

Probability definitions

Very probable	More than once in a year
Probable	Once in 1 to 10 years
Less likely	Once in 10 to 100 years
Unlikely	Once in 100 to 1 000 years
Very unlikely	Less than once in 1 000 years

Source: ÅF Process.

This risk assessment template is widely used, among others by the Swedish Rescue Services Agency and UNEP. There is no generally defined standard describing which action(s) should be taken for any identified risk, rather, the type of industry/ site and the safety policy of the facility should guide further action. The colour codes below, related to the risk matrix, are typically used in pulp mills.

	Very critical. Risk mitigating measures have to be taken immediately.
	Serious. Risk mitigating measures have to be investigated and taken in the future.
	Low risk. Risk mitigating measures have low priority.

Source: ÅF Process.

2.12.2 Differences between ECF and TCF bleaching from a risk perspective

A main factor in the safety assessment for the two bleaching methods is the chemicals used and how they are generated, transported, stored and handled.

The following table lists differences and similarities regarding the use of chemicals for the two bleaching methods.

Table 2.23 Chemicals used in ECF and TCF bleaching

Chemicals	ECF	TCF
NaClO ₃ / ClO ₂	Yes	No
H ₂ O ₂	Low charge	High charge
O ₂	Similar charge	Similar charge
CH ₃ OH	Yes	No
O ₃	Occasional use - low charge	Common use - high charge
EDTA, DTPA	Occasional use	Yes
NaOH/ H ₂ SO ₄	Not specific for the bleaching process	Not specific for the bleaching process
Paa (CH ₃ COOOH)	No	Occasional use

Source: ÅF-Process.

The use of chlorine based chemicals is unique for ECF bleaching, hence, so are the safety aspects connected with the handling of NaClO₃, ClO₂ and CH₃OH.

The use of O₃ is typical for the TCF process. Ozone is sometimes used in the ECF process but in this report it is considered as a typical TCF chemical. Hydrogen peroxide, EDTA and DTPA are also regarded as typical TCF chemicals. Peracetic acid is only used in TCF bleaching even if its use is limited.

Sodium hydroxide and H₂SO₄ are widely used in pulp and paper mills outside the bleaching process. These chemicals are therefore not considered relevant to a specific safety assessment of the bleaching processes.

2.12.3 Risk characteristics of the most important bleaching chemicals and raw materials

2.12.3.1 Risk codes and phrases

Risk codes and phrases are used to characterise the safety issues connected to hazardous chemicals and other hazardous materials. The relevant risk codes and phrases are shown in the following table.

Table 2.24 Risk codes and phrases

Risk code	Risk phrase
R7	May cause fire
R8	Contact with combustible material may cause fire
R9	Explosive when mixed with combustible material
R10	Flammable
R11	Highly flammable
R20	Harmful by inhalation
R21	Harmful in contact with skin
R22	Harmful if swallowed
R23	Toxic by inhalation
R24	Toxic in contact with skin
R25	Toxic if swallowed
R26	Very toxic by inhalation
R34	Causes burns
R35	Causes severe burns
R36	Irritating to eyes
R37	Irritating to respiratory system
R39	Danger of very serious irreversible effects
R50	Very toxic to aquatic organisms
R51	Toxic to aquatic organisms
R53	May cause long-term adverse effects in the aquatic environment
R65	Harmful: may cause lung damage if swallowed
R66	Repeated exposure may cause skin dryness or cracking
R67	Vapours may cause drowsiness and dizziness
R68	Possible risk of irreversible effects

Source: ÅF-Process.

2.12.3.2 Sodium chlorate NaClO₃ (solid and water solution)

Sodium chlorate is transported both as crystal form and as water solution. Used as minimum 99% by weight to be dissolved in water to concentration 650- 710 g/L NaClO₃.

Table 2.25 Risk codes and physical properties for NaClO₃

Risk codes	R9/ R22/ R51/ R53
Solubility in water	96 g/100 g water

Source: ÅF-Process.

Hazard: Self igniting with organic substances. Strong oxidiser.

Human health: Crystal form: Local irritation to skin and eyes. Inhalation may cause irritation to respiratory tract, high concentration may be fatal. 15 mg/m³ (OSHA PEL), 10 mg/m³ (TLV Value for dust - IUCLID).

Environment: Easily biodegradable. Probably not bioaccumulating. Toxic to water-living organisms.

2.12.3.3 Chlorine dioxide ClO₂ (water solution)

Chlorine dioxide is used as a diluted chilled water solution (8-10 g/L). Chlorine dioxide slowly decomposes in water solution.

Table 2.26 Risk codes and physical properties for ClO₂

Risk codes	>25%:R25- 34-50 0,3%- 3%: R36
Boiling point	-11°C
Vapour pressure	3 mm Hg at 30°C
Solubility in water	0.8% (wt) at 10°C
Explosion limits	10-100 % (Vol)

Source: ÅF-Process.

Hazard: Non flammable. Strong oxidiser. Concentrated vapours may explosively decompose on shock, friction, concussion or heating.

Human health: Irritation to skin and eyes, strong respiratory irritant. Exposure limit: IDLH = 5 ppm.

Environment: No information.

2.12.3.4 Methyl alcohol (methanol) CH₃OH

Used as concentrated.

Table 2.27 Risk codes and physical properties for CH₃OH

Risk codes	R11/ R23/ R24/ R25/ R39
Boiling point	64.7°C (337.8 K)
Solubility in water	Fully miscible
Explosion limits	LEL=73 g/m ³ , UEL=590 g/m ³
Flash point	11°C

Source: ÅF-Process.

Hazard: Highly flammable.

Human health: Toxic by inhalation, ingestion or skin absorption. May pose reproductive hazards. Ingestion may be fatal. Exposure may cause eye, kidney, heart and liver damage. Irritant. Exposure limit: IDLH = 6 000 ppm.

Environment: Probably easily biodegraded and not bioaccumulating. Low toxic effect to water-living organisms.

2.12.3.5 Ozone O₃

In bleaching ozone is added to the chemical mixer as a gas.

Table 2.28 Risk codes and physical properties for O₃

Risk codes	R8/ R26/ R36/ R37/ R50
Boiling point	-169°C
Solubility in water	0.5% (Wt)

Source: ÅF-Process.

Hazard: Non flammable. Strong oxidiser.

Human health: Local irritation to skin and eyes, inhalation problems. Exposure limit: IDLH = 5 ppm.

Environment: Easily biodegraded. Probably not bioaccumulating. Toxic to water-living organisms.

2.12.3.6 Hydrogen peroxide H₂O₂ (20-60%)

Table 2.29 Risk codes and physical properties for H₂O₂

Risk codes	R8/ R34
Boiling point	150°C
Solubility in water	Miscible

Source: ÅF-Process.

Hazard: Non flammable. Strong oxidiser. Decomposes naturally into oxygen and water.

Human health: Local irritation to skin and eyes, inhalation problems. Exposure limit: IDLH = 75 ppm.

Environment: Not bioaccumulating. Affects water-living organisms.

2.12.3.7 Peracetic acid (CH₃COOOH)

The data below is for hydrogen peroxide <43% (stabilised).

Table 2.30 Risk codes and physical properties for CH₃COOOH

Risk codes	R7/ R10/ R20/ R21/ R22/ R35/ R50
Boiling point	105°C
Solubility in water	Miscible

Source: ÅF-Process.

Hazard: May explosively decompose on shock, friction, or concussion. May explode on heating. The substance is a strong oxidiser and reacts violently with combustible and reducing materials. Explodes spontaneously at 110°C.

Human health: Local irritation to skin and eyes. Inhalation: Cough, laboured breathing, shortness of breath. TLV not established.

Environment: Easily and quickly biodegraded. Not bioaccumulating. Very toxic to water-living organisms (short term effect).

2.12.3.8 EDTA and DTPA

Human health: No human health hazards.

Environment: No acute toxicity.

2.12.3.9 Oxygen

Human health: No human health hazards.

Environment: No acute toxicity.

2.12.4 Risk assessment

2.12.4.1 ECF bleaching

Sodium chlorate NaClO₃

NaClO₃ can be delivered either in crystal form, which is most common, or in a water solution. The transport can be carried out either by boat, train or truck.

Sodium chlorate solution is normally stored in large tanks.

The identified risks are:

- Spill of NaClO₃ solution during transportation.
- Spill of NaClO₃ in crystal form when unloading.
- Spill of NaClO₃ solution when unloading.
- Rupture of or major leak from the NaClO₃ solution storage tank.
- Fire caused by self ignition in contact with organic substances.

Scenario 1: Spill of NaClO₃ solution during transportation	
Description	Rupture of the container
Consequence	<u>Human health risk:</u> Low effect <u>Environmental risk:</u> Toxic to water-living organisms if emitted to a recipient <u>Consequence level:</u> 2
Probability	2

Scenario 2: Spill of NaClO₃ in crystal form when unloading	
Description	Container with NaClO ₃ is dropped at unloading. Rupture of the container. Airborne particles are spread
Consequence	<u>Human health risk:</u> Inhalation may cause irritation and respiratory tract damage <u>Environmental risk:</u> Low effect. Clean-up <u>Consequence level:</u> 1
Probability	3

Scenario 3: Spill of NaClO₃ solution when unloading	
Description	Pipe or hose rupture when unloading. Operator mistake. Overflow due to full storage tank. Self ignition in contact with organic substances (clothes)
Consequence	<u>Human health risk:</u> Burns <u>Environmental risk:</u> Sodium chlorate solution and fire water toxic to water-living organisms if emitted to the recipient <u>Consequence level:</u> 2
Probability	3

Scenario 4: Rupture of or major leak from the NaClO₃ solution storage tank	
Description	Spill of major amount of NaClO ₃ solution caused by tank or pipe rupture
Consequence	<u>Human health risk:</u> Burns caused by self ignition in contact with organic substances (clothes) <u>Environmental risk:</u> Toxic to water-living organisms if emitted to the recipient. Toxic to the biological step in the effluent treatment <u>Consequence level:</u> 3
Probability	1

Scenario 5: Fire caused by self ignition in contact with organic material	
Description	Spill of sodium chlorate causes fire by self ignition in contact with organic material. Toxic fire smoke
Consequence	<u>Human health risk:</u> Toxic by inhalation. Burns caused by self ignition in contact with organic material (clothes) <u>Environmental risk:</u> Fire water to the recipient and the effluent treatment plant. Toxic to water-living organisms if emitted to the recipient. Toxic to the biological stage in the effluent treatment <u>Consequence level:</u> 3
Probability	2

Methanol CH₃OH

Transportation of methanol can be carried out either by boat, train or truck. Methanol is normally stored in tanks in separate buildings, well protected with gas and fire alarms and extinguishing systems.

The identified risks are:

- Spill of methanol during transportation.
- Spill of methanol, leak from methanol tank or pipes.
- Fire and/or explosion caused by methanol leak from methanol tank and ignition.

Scenario 6: Spill of methanol during transportation	
Description	Accident during transportation. Spill of methanol due to tank rupture. Ignition may lead to fire
Consequence	<u>Human health risk:</u> Inhalation of fire smoke may cause irritation and respiratory tract damage, high concentration may be fatal <u>Environmental risk:</u> Methanol and fire water toxic to water-living organisms if emitted to a recipient <u>Consequence level:</u> 2
Probability	1-2

Scenario 7: Spill of methanol, leak from methanol tank or pipes	
Description	Spill of methanol from tank or pipe rupture etc. Methanol to the recipient
Consequence	<u>Human health risk:</u> Low effect <u>Environmental risk:</u> Toxic to water-living organisms if emitted to the recipient. Toxic to the biological step in the effluent treatment plant <u>Consequence level:</u> 3
Probability	2

Scenario 8: Fire and/or explosion caused by methanol leak from methanol tank and ignition	
Description	Leak from methanol tank or pipes. Fire and/or explosion caused by ignition. Toxic fire smoke
Consequence	<u>Human health risk:</u> Burn damage. : Inhalation of fire smoke may cause irritation and respiratory tract damage, high concentration may be fatal <u>Environmental risk:</u> Fire water toxic to water-living organisms if emitted to the recipient <u>Consequence level:</u> 3
Probability	1

Production of ClO₂/ ECF bleaching process

Chlorine dioxide solution is also stored in large tanks. The tanks are placed in containment bunds.

Bleaching towers are used for the bleaching step. The reaction time is one hour or more which amounts to a considerable total amount of chlorine dioxide in water solution.

The identified risks are:

- Spill of ClO₂ solution from storage tanks, pipes, bleaching tower.

Scenario 9: Spill of ClO₂ solution from storage tanks, pipes, bleaching tower	
Description	Spill of large volumes of ClO ₂ solution due to rupture of the storage tanks, pipes, bleaching tower etc. Chlorine dioxide then gasses off
Consequence	<u>Human health risk:</u> Inhalation may cause irritation and respiratory tract damage, high concentration may be fatal <u>Environmental risk:</u> Low environmental risk <u>Consequence level:</u> 3
Probability	2

2.12.4.2 TCF bleaching

Hydrogen peroxide H₂O₂

Transportation of peroxide is carried out either by boat, train or truck. Hydrogen peroxide is normally stored in tanks, well protected with alarm systems and containment bunds.

The identified risks are:

- Spill of H₂O₂ during transportation.
- Spill from H₂O₂ tank or pipes.
- Explosion and fire caused by H₂O₂ spills and leaks.

Scenario 1: Spill of H₂O₂ during transportation	
Description	Accident during transportation. Spill of H ₂ O ₂ due to tank rupture. May cause fire with combustible material
Consequence	<u>Human health risk:</u> Inhalation of H ₂ O ₂ may cause irritation and respiratory tract damage, high concentration may be fatal <u>Environmental risk:</u> Acute toxic to water-living organisms if emitted to a recipient. Short term effects. Not bio accumulating <u>Consequence level:</u> 2
Probability	1

Scenario 2: Spill from H₂O₂ tank or pipes	
Description	Spill from H ₂ O ₂ tank or pipes with peroxide. May cause fire
Consequence	<u>Human health risk:</u> Inhalation of H ₂ O ₂ and/or fire smoke may cause irritation and respiratory tract damage, high concentration may be fatal <u>Environmental risk:</u> Acute toxic to water-living organisms if emitted to a recipient. Short term effects. Not bioaccumulating <u>Consequence level:</u> 2
Probability	2

Scenario 3: Explosion of H₂O₂ in the tank	
Description	Increased temperature, due to fast decomposition, fire or other reason, causes explosion. Hydrogen peroxide vapour can detonate above 70°C
Consequence	<u>Human health risk:</u> Inhalation of H ₂ O ₂ may cause irritation and respiratory tract damage, high concentration may be fatal. Explosion injury <u>Environmental risk:</u> Acute toxic to water-living organisms if emitted to a recipient. Short term effects. Not bioaccumulating <u>Consequence level:</u> 3
Probability	1

Peracetic acid (CH₃COOOH)

Transportation of peracetic acid can be carried out either by boat, train or truck. Peracetic acid is normally stored in tanks, well protected with alarm systems and containment bunds.

The identified risks are:

- Spill of peracetic acid during transportation.
- Spill from peracetic tanks and pipes.
- Fire/explosion caused by decomposition.

Scenario 4: Spill of peracetic acid during transportation	
Description	
Consequence	Human health risk: Inhalation may cause irritation and respiratory tract damage, high concentration may be fatal Environmental risk: Acute toxic to water-living organisms if emitted to a recipient. Short term effects. Not bioaccumulating Consequence level: 2
Probability	1

Scenario 5: Spill from peracetic acid tank or pipes	
Description	Spill from peracetic acid or pipes with peroxide. May cause fire
Consequence	Human health risk: Inhalation may cause irritation and respiratory tract damage, high concentration may be fatal Environmental risk: Acute toxic to water-living organisms if emitted to a recipient. Short term effects. Not bioaccumulating Consequence level: 2
Probability	2

Scenario 6: Explosion of peracetic acid in the tank	
Description	May explosively decompose on shock, friction, or concussion. May explode on heating
Consequence	Human health risk: Inhalation may cause irritation and respiratory tract damage, high concentration may be fatal. Explosion injury Environmental risk: Acute toxic to water-living organisms if emitted to a recipient. Not bioaccumulating Consequence level: 3
Probability	1

Production of ozone O₃/TCF bleaching process

Ozone is produced on site. The reaction time between pulp and O₃ is just a few seconds. Thus the total amount of O₃ in the bleaching system is low.

The identified risks are:

- Spill of ozone solution in water from pipes, bleaching tower.

Scenario 7: Leak of ozone in water	
Description	Due to rupture of the reactor, pipes etc an outflow of water with bleaching chemicals can happen. Ozone then gasses off
Consequence	<u>Human health risk:</u> Inhalation may cause irritation and respiratory tract damage, high concentration may be fatal <u>Environmental risk:</u> No environmental risk <u>Consequence level:</u> 3
Probability	2

2.12.5 Safety assessment for ECF and TCF bleaching

The result of the risk assessment is shown in the risk matrix in the following tables. The numbers in the matrix refer to the risk scenarios as defined and evaluated in the preceding sections.

The 9 risk scenarios identified for ECF bleaching are presented in Table 2.31.

Table 2.31 Risk matrix for ECF bleaching

		Consequence				
		1	2	3	4	5
Probability	5					
	4					
	3	2	3,7,9			
	2		1,6	5		
	1			4,8		

Source: ÅF-Process.

The 7 risk scenarios identified for TCF bleaching are presented in Table 2.32.

Table 2.32 Risk matrix for TCF bleaching

	Consequence				
	1	2	3	4	5
Probability	5				
	4				
	3				
	2		2, 5	7	
	1		1, 4	3, 6	

Source: ÅF-Process.

All the risks identified in the evaluation of TCF and ECF bleaching are in the low risk area in the risk matrix where additional risk mitigating measures normally can be regarded to have low priority. All risk scenarios are either “less likely” or “unlikely” or “very unlikely” to occur, i.e. the probability for their occurrence is once in 10 years to once in over 1000 years. Even though there are two more risk scenarios identified for ECF bleaching and the probability level for some ECF scenarios is slightly higher than for TCF, the overall risk levels for the two processes may be considered comparable.

2.12.6 ECF and TCF bleaching from an OH&S perspective

A literature review of epidemiological studies on the health effects on workers in elemental chlorine free (ECF) pulp mills and totally chlorine free (TCF) pulp mills was carried out for the Commission in 2005 [Driscoll, 2005].

The review focused on ECF mills since there were no studies comparing the health and safety of workers in ECF mills to workers in TCF mills. Therefore, direct comparison between these two mill types was not possible. Instead, exposures common to the two mill types, and exposures specific to one mill type, were identified.

A wide variety of common exposures occur in both ECF and TCF pulp mills. The main difference between plant types is that ECF workers are exposed to ClO₂, possibly organochlorines and in some mills a little O₃. In contrast, TCF plants do not use ClO₂ and have O₃, peroxides as and possibly Paa as the main bleaching agents used in its place.

Several chemicals emitted to air in pulp mills are known to be strong respiratory irritants. The main ones are ClO₂ and O₃ but also H₂O₂, Paa, sulfur dioxide (SO₂) and other organic sulfur compounds are known respiratory irritants. There is thus good evidence that work in ECF and TCF mills increases the risk of having respiratory symptoms such as cough and wheeze, decreases lung function, and increases the risk of reporting symptoms consistent with asthma or with having been diagnosed with adult-onset asthma.

The pathological effects of exposure to these irritants are likely to be primarily due to the level of exposure, rather than to the type of respiratory irritant involved, since all are very powerful irritants. The level of respiratory problems in the workforce will, therefore, depend on how well contained and maintained the process is rather than on whether the process uses ClO_2 or O_3 . Therefore, no significant differences should be expected in the level of respiratory symptoms or disorders in workers from ECF mills compared to TCF mills, provided that the level and extent of leaks are similar.

The one area of difference between ECF mills and TCF mills that may lead to differing risks relates to organochlorines. These are produced during bleaching in ECF mills, but do not occur in significant quantities in TCF processes. Organochlorines have been associated with a wide range of health effects. To the extent that considerable exposure to organic chlorinated compounds may occur in ECF mills, then workers at those plants can be expected to have an increased risk of developing some cancers, compared with workers at TCF mills.

In modern ECF bleaching the formation of organochlorines is typically about 20 times lower than in chlorine bleaching and the ones formed have on average a low degree of chlorination. The level of volatile organochlorines from ECF bleaching is also very low. Due to the design of the mills e.g. enclosed equipment, vented air from the bleach plant being scrubbed, effluents conveyed in pipes, there is a very low exposure of workers to these compounds.

This conclusion corroborates the statement by Driscoll that pulp and paper mill workers have been found to have a lower total mortality from all causes and from all cancers compared to the general population.

The Driscoll review and the discussion of the extremely low potential for exposure to organochlorines in ECF mills leads to the tentative conclusion that the risk level for any health effects from working in ECF and TCF mills is comparable.

3 CONVENTIONS RELEVANT TO THE DEBATE ON ECF AND TCF BLEACHING

3.1 UNITED NATIONS ENVIRONMENT PROGRAMME – CHEMICALS

UNEP - Chemicals is the centre for all chemicals-related activities of the United Nations Environment Programme. The goal of this program is to make the world a safer place from toxic chemicals. This is achieved by helping governments take global actions for the sound management of chemicals, by promoting the exchange of information on chemicals, and by helping to build the capability of countries around the world to use chemicals safely.

3.1.1 Stockholm Convention on persistent organic pollutants (POP)

The Convention is an international treaty adopted in 2001 in Sweden by 151 countries aimed at restricting and ultimately eliminating the production, use, release and storage of all intentionally produced POP (i.e. industrial chemicals and pesticides). It also seeks the continuing minimisation and, where feasible, ultimate elimination of the release of unintentionally produced POP (UPOP) such as dioxins and furans.

In June 2002, an Expert Group on best available techniques (BAT) and best environmental practices (BEP) was established to develop guidelines on BAT and provisional guidance on BEP directed towards the reduction or elimination of releases of UPOP like PCDD, PCDF, hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB).

The Convention came into force on 17 May 2004 and Australia ratified the treaty on 20 May 2004.

Two meetings of the Conference of the Parties have been held since the Convention came into force [www.pops.int]:

- The first meeting (CoP-1) was held in Punta del Este, Uruguay, from 2 to 6 May 2005.
- The second meeting (CoP-2) was held in Geneva, Switzerland from 1 to 5 May 2006.

The most recent relevant publication of the Expert Group programme is the "Draft Guidelines on best available techniques and provisional guidance on best environmental practices relevant to Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants", Revised working draft version 25 April 2006 [www.chem.unep.ch/pops], [www.pops.int], [UNEP, 2006].

These Draft Guidelines, which were presented at CoP-2, define best available techniques (BAT) as "...the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for release limitations designed to prevent and, where that is not

practicable, generally to reduce releases of chemicals listed in Part I of Annex C and their impact on the environment as a whole”.

In this regard:

- “Techniques” includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned.
- “Available” techniques means those techniques that are accessible to the operator and that are developed on a scale that allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages.
- “Best” means most effective in achieving a high general level of protection of the environment as a whole.
- “Best environmental practices” means the application of the most appropriate combination of environmental control measures and strategies.
- “New source” means any source of which the construction or substantial modification is commenced at least one year after the date of:
 - a) Entry into force of this Convention for the Party concerned; or
 - b) Entry into force for the Party concerned of an amendment to Annex C where the source becomes subject to the provisions of this Convention only by virtue of that amendment.

Since Australia ratified the treaty on 20 May 2004, any source built or substantially modified after 20 May 2005 would be considered a “new source”.

The text of the Draft Guidelines following CoP-2 were unavailable at the time of writing of this report.

3.1.2 Unintentional formation and release of chlorinated dioxins and furans

Annex C – “Unintentional production” of Article 5 – “Measures to reduce or eliminate releases from unintentional production” of the Stockholm Convention states that potential sources for formation and release of these chemicals to the environment are the following sources in the pulp and paper industry:

- Production of pulp using molecular chlorine or chemicals generating molecular chlorine for bleaching.
- Fossil fuel-fired utility and industrial boilers.
- Firing installations for wood and other biomass fuels.

3.1.3 Minimising or eliminating dioxins and furans

Annex C also provides general guidance on preventing or reducing releases of the chemicals listed. BAT and BEP should be applied and useful measures could include the following of relevance to pulp mills:

- Replacement of feed materials which are POP or where there is a direct link between the materials and releases of POP from the source (precursors).
- Minimisation of these chemicals as contaminants in products.
- Avoiding molecular chlorine or chemicals generating molecular chlorine for bleaching.

When constructing new facilities or significantly modifying existing facilities using processes that release chemicals listed in Annex C, priority consideration should be given to alternative processes, techniques or practices that have similar usefulness but which avoid the formation and release of such chemicals. In cases where such facilities will be constructed or significantly modified, in addition to the prevention measures outlined in section A of Part V the following reduction measures could also be considered in determining best available techniques:

- Use of improved methods for flue-gas cleaning such as thermal or catalytic oxidation, dust precipitation, or adsorption.
- Treatment of residuals, wastewater, wastes and sewage sludge by, for example, thermal treatment or rendering them inert or chemical processes that detoxify them.
- Process changes that lead to the reduction or elimination of releases, such as moving to closed systems.
- Modification of process designs to improve combustion and prevent formation of the chemicals listed in Annex C, through the control of parameters such as incineration temperature or residence time.

3.1.4 Comments and consequences for the pulp and paper industry

Chlorine dioxide itself does not produce chlorinated compounds. Hypochlorous acid (HClO) which is an intermediate formed by chlorine dioxide in bleaching does however produce chlorinated compounds although to a very low extent. The probability for formation of chlorinated organic compounds with several chlorine substitutions, like TCDD or TCDF is extremely low.

According to best available knowledge today, the concentration of 2,3,7,8-TCDD in effluents from ECF bleaching and particularly "ECF light" bleaching (with low charge of ClO₂) is undetectable using present sampling and analytical techniques (i.e. at low pg/L or ppq level). The same applies to 2,3,7,8-TCDF as long as the concentration of the precursor DBF is low. Hence, ECF bleaching minimises the probability for the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF.

As the ECF and TCF bleaching processes are considered BAT in [IPPC BREF, 2001] and acceptable for use in pulp bleaching in [UNEP, 2006], they should also be acceptable for pulp bleaching according to:

- BAT and BEP as defined in Article 5 and qualified in Annex C of the Convention.
- General prevention measures relating to BAT and BEP as defined in Annex C of the Convention.

In Annex C to the Convention process changes such as moving to closed systems are recommended. This may however lead to build up of non-process elements such as chloride in the systems which could increase any formation of TCDD and TCDF in the recovery boiler.

3.2 1992 Rio Declaration on Environment and Development and Agenda 21

3.2.1 The Rio Principles

As a general comment it can be stated that the Rio Declaration, its principles etc. constitute recommendations and guidelines for the individual States to implement and enforce. Companies and corporations should in the first place responsibly follow the applicable laws and regulations in the country concerned and may in addition also decide on their own rules of conduct that may well be inspired by documents like the Rio Declaration.

In the following some Principles taken from Annex 1 of the Rio Declaration on Environment and Development (Rio de Janeiro, 3-14 June 1992) are cited and discussed from a technology and technology development perspective.

Principle 9

“-- improving scientific understanding through exchanges of scientific and technological knowledge, and by enhancing the development, adaptation, diffusion and transfer of technologies, including new and innovative technologies.”

Principle 10

“Environmental issues are best handled with the participation of all concerned citizens, at the relevant level. At the national level, each individual shall have appropriate access to information concerning the environment that is held by public authorities, including information on hazardous materials and activities in their communities, and the opportunity to participate in decision-making processes. States shall facilitate and encourage public awareness and participation by making information widely available. Effective access to judicial and administrative proceedings, including redress and remedy, shall be provided.”

Principle 12

“--- Environmental measures addressing transboundary or global environmental problems should, as far as possible, be based on an international consensus. ”

Principle 15

In order to protect the environment, the precautionary approach shall be widely applied by States according to their capabilities. Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation.

Principle 16

“National authorities should endeavour to promote the internalization of environmental costs and the use of economic instruments, taking into account the approach that the polluter should, in principle, bear the cost of pollution, with due regard to the public interest and without distorting international trade and investment.”

3.2.2 Comments and consequences for the pulp and paper industry

The technical and scientific community in the pulp and paper industry can be regarded as transparent and open for exchange of information both with regard to information on the environmental impact of operations, on the formation and/or release of various organic and inorganic compounds that may be of importance to environmental impact and on technical solutions to reduce any impact. These aspects are openly presented and discussed at international conferences and in peer reviewed papers. The Rio Principle 9 can therefore be regarded as fulfilled to a high degree in the industry.

In most of the major pulp and paper producing countries, including Australia, Principle 10 is well served by the various proceedings that will have to be passed and information that should be supplied in order to obtain or renew an environmental permit for a pulp and paper mill. Community and stakeholder participation is in those countries actively encouraged and sought.

The release of non or slowly degradable material into the biosphere such as TCDD and TCDF is an example of Principle 12. These specific compounds have now been covered by the Stockholm Convention.

Principles 15 and 16 are to a large extent being considered in most national environmental legislations, including that of Australia.

3.3 Ramsar Convention of the Parties

3.3.1 The Convention, Montreaux records and Wetlands Strategies

The Convention on Wetlands, signed in Ramsar, Iran, in 1971, is an intergovernmental treaty which provides the framework for national action and international cooperation for the conservation and wise use of wetlands and their resources. There are presently 150 Contracting Parties to the Convention, with 1591 wetland sites, totalling 134 million hectares, designated for inclusion in the Ramsar List of Wetlands of International Importance.

The Convention's mission is "the conservation and wise use of all wetlands through local, regional and national actions and international cooperation, as a contribution towards achieving sustainable development throughout the world".

The Convention uses a broad definition of the types of wetlands covered in its mission, including swamps and marshes, lakes and rivers, wet grasslands and peatlands, oases, estuaries, deltas and tidal flats, near-shore marine areas, mangroves and coral reefs, and human-made sites such as fish ponds, rice paddies, reservoirs, and salt pans.

The Contracting Parties shall formulate and implement their planning so as to promote the conservation of the wetlands included in the Ramsar List, and as far as possible the wise use of wetlands in their territory.

The Montreaux Records of Ramsar contains "a record of Ramsar sites where changes in ecological character have occurred, are occurring or are likely to occur" and are maintained in consultation with the Contracting Parties concerned.

Within the framework of the Ramsar Convention several countries have formulated National Wetlands Strategies.

3.3.2 Comments and consequences for the pulp and paper industry

The Ramsar Convention does not cover any technical details for the protection and preservation of Wetlands and has thus no comments about ECF and TCF bleaching. The possible implication for the pulp and paper industry is that when a plant is located at or planned to be located at a Ramsar site (or any other site with particular protection) the proper precautions must be taken in order to safeguard the environmental values that are the subject of the site.

3.4 UN World Summit Nairobi 2002

The UN World Summit on Sustainable Development in Johannesburg, South Africa, 2002 was focused on sustainable development in general and can be seen as a follow-up on the Stockholm 1972 and Rio 1992 Conferences. The Plan of Implementation that was annexed to the proceeding of the Conference mainly reinforces the recommendations from the Rio Summit but regarding “technical issues” places more emphasis on energy conservation and sustainable energy generation.

It is also stressed that industry has an important role in poverty eradication and sustainable natural resource management. Relevant authorities at all levels should take sustainable development considerations into account in decision-making, including on national and local development planning, investment in infrastructure, business development and public procurement.

The approach that the polluter should, in principle, bear the costs of pollution, with due regard to the public interest and without distorting international trade and investment was highlighted in the Annex as well as the use of environmental impact assessment procedures.

As far as the pulp and paper industry is concerned, it can be concluded that there are no additional consequences as compared to the Rio 1992 proceedings.

3.5 1998 Wingspread Statement

The Wingspread house was built in 1939, in Racine, Wisconsin, USA. Frank Lloyd Wright designed the Wingspread house for the family of H.F. Johnson, Jr., who lived there from 1939 to 1959. In 1959, Mr Johnson established The Johnson Foundation, designating Wingspread as its educational conference facility.

The Foundation has since sponsored thousands of conferences on a wide range of issues. At the Wingspread Conference on Precautionary Principle, in 1998, a definition was agreed upon: “When an activity raises threats of harm to human health or the environment, precautionary measures should be taken even if some cause and effect relationships are not fully established scientifically”.

The concept has its origin in the German environmental policy and it was probably at the 2nd International Conference on the Protection of the North Sea, in 1987, that the “principle” first was introduced into an official, binding convention between nations. Soon after this, the idea was widely accepted in several countries and received strong support among environmental groups globally.

4 GUIDELINES AND REGULATIONS RELEVANT TO THE DEBATE ON ECF AND TCF BLEACHING

4.1 EUROPEAN UNION

The EU Directive "Integrated Pollution Prevention and Control" (the IPPC Directive) aims at achieving integrated prevention and control of pollution from a number of industry activities including the pulp and paper industry. It defines measures designed to prevent or, where that is not practicable, to reduce emissions to air, water and land from these activities, including measures concerning waste, in order to achieve a high level of protection of the environment taken as a whole.

The IPPC Directive was published in 1996 (Council Directive 96/61/EC) and is a legally binding document for all EU member states. To assist in the application of the Directive a number of BAT reference documents (BREF) have been compiled. The BREF for the pulp and paper manufacture sector was finalised in December 2001 [<http://eippcb.jrc.es>], [IPPC BREF, 2001].

The BREF states that both ECF and TCF bleaching technology are regarded as BAT. The BREF further states that there is no clear difference in the toxic effect pattern and effect intensity between effluents from mills using low-kappa ECF (chlorate reduced) and TCF bleaching.

4.2 EUROPEAN COUNTRIES

Some European countries have promulgated national discharge limits that apply to all pulp and paper mills within the country. Permitting authorities can set stricter limits based on site specific environmental conditions. Emission limits can be specified in terms of concentration (mg/L), specific load (kg/ADt) or mass load (kg/day, kg/h). Some countries have set different limits for different types of pulp and paper operations, furnishes and end products. Other countries have set general limits that apply to the industry as a whole irrespective of product or mill type. Some countries have no national standards or guidelines but base limits on technological and economically feasible measures on a case-by-case basis considering environmental conditions.

Table 4.1 summarises current national discharge limits for new bleached kraft pulp mills in Austria, France and Germany. Belgium, Denmark, Finland, Norway and Sweden do not have national limits [IPPC BREF, 2001].

Table 4.1 Discharge limits for new bleached kraft pulp mills in Austria, France and Germany

Parameter	Austria	France		Germany
		Softwood	Hardwood	
COD	20 kg/ADt	50 kg/ADt	25 kg/ADt	25 kg/ADt
BOD ₅	2 kg/ADt	3 kg/ADt	2 kg/ADt	30 mg/L
TSS	2.5 kg/ADt	5 kg/ADt	5 kg/ADt	no limit – part of COD
AOX	0.25 kg/ADt	1 kg/ADt	1 kg/ADt	0.25 kg/ADt
Notes:				
1 Germany and Austria require 4 out of every 5 daily measurements to be below the permitted maxima.				
2 In France, the AOX limit is an annual average limit. All others are monthly average limits. The daily limit is twice the monthly limit.				

Source: [IPPC BREF, 2001].

4.2.1 Swedish emission limits for kraft pulp mills

There are no national or provincial guidelines for emissions from kraft pulp mills in Sweden. Limits are set by the Environmental Court (Miljödomstolen) on an individual basis for each mill.

BKP mills employing both ECF and TCF bleaching processes have only one set of emissions limits.

If there were different limits, those limits would be difficult to follow up and enforce, as, e.g., ECF pulp may be produced on one fibre line and TCF pulp on a parallel fibre line with the liquors from both lines mixed and, after evaporation, burned in a common recovery boiler.

4.2.2 Finnish air emission limits for kraft pulp mills

The situation in Finland is the same as in Sweden.

4.3 UNITED STATES OF AMERICA

The U.S. Environmental Protection Agency (USEPA) in April 1998 promulgated the Final Pulp and Paper Cluster Rule to protect human health and the environment by reducing toxic releases to the atmosphere and aquatic environment from U.S. pulp and paper mills [USEPA, 1998].

These guidelines are widely known as the "Cluster Rule", because they were designed to coordinate air and water discharge rules.

The Cluster Rule consists of:

- **Preamble** - Explains EPA's rationale for developing the final air and water Cluster Rule.
- **Final air rule** (Amends 40 CFR Part 63 and Part 261) – which includes maximum achievable control technologies (MACT) I emissions from non-combustion sources of pulping and bleaching operations at chemical and semi-chemical pulp mills.
- **Final water rule** (Amends 40 CFR Part 430) - which includes best available technology (BAT)²⁹ limits from mills in Subpart B (Bleached paper grade kraft and soda) and best management practice (BMP) requirements.
- **Final air rule** which includes MACT II emissions from combustion sources at kraft, soda, semi-chemical, and sulfite mills, including recovery boilers, smelt dissolving tanks, and lime kilns (12 January 2001)³⁰.

4.3.1 USEPA Cluster Rule and its position on ECF v TCF

During the investigative and consultative process leading up to the adoption of the Cluster Rule (circa 1989-92), the USEPA investigated mills using TCF bleaching sequences. The Agency identified more than 15 mills worldwide producing TCF kraft paper grade pulps. Since the pulps produced by these mills had lower brightness than market kraft pulp grades (75-80% ISO v 88-90% ISO), the Agency concluded that there was insufficient evidence at that time to demonstrate that TCF bleaching processes could produce the full range of market pulps currently produced by the ECF bleaching process [USEPA-821-R-93-019, 1993]. Consequently, the Agency determined that TCF was not BAT [US EPA, 1998], pg. 18543.

The EPA believed that eventually TCF processes would be developed to provide a full range of bleached kraft market pulps and for this reason, the Agency evaluated the performance of TCF mills with the objective of establishing discharge limits for mills that chose to employ TCF bleaching processes. The Agency conducted effluent sampling programs at two unidentified mills in an attempt to characterise the treated effluent from BKP mills using a TCF bleaching sequence – at a US mill producing TCF-bleached softwood kraft pulp and at a Nordic mill producing bleached hardwood and softwood pulps in two bleaching lines that alternated between ECF and TCF bleaching sequences. The Agency was unable to collect treated effluent samples at either mill. The US mill did not have a secondary effluent

²⁹ BAT is defined as the best control and treatment measures that have been or are capable of being economically achieved.

³⁰ 66 FR 3180, <http://www.epa.gov/ttn/atw/pulp/pulppg.html>

treatment system and therefore only bleach plant filtrates were collected and in the case of the Nordic mill, treated effluent samples representing TCF pulp production could not be obtained because effluents from the TCF and ECF bleaching lines were combined prior to treatment. Finished pulp brightness at the time of effluent sampling was 83% ISO at the Nordic mill and 79% ISO during the first sampling program at the US mill and 83% ISO during a second sampling program. Neither chloroform nor chlorinated phenolic compounds were detected in any of the samples collected from the two mills. Dioxin, furan and AOX were not detected above the analytical minimum level in samples collected during full TCF operations at the US mill. However, dioxin was detected in one sample of bleach plant filtrate taken from the Nordic mill at concentrations just above the analytical minimum level when the mill was bleaching without chlorine or chlorine-containing compounds. Furan was not detected. EPA believed this result was "unique" to the operation of that particular mill and the Agency did not conclude from this result that TCF bleaching generates dioxin [US EPA, 1998], pg. 18543.

In fact, EPA determined that the TCF bleaching process does not generate dioxin, furan, chloroform or chlorinated phenolic compounds and therefore did not specify discharge limits for these pollutants for mills choosing to use a TCF bleaching process. However, although the sampling programs at the two TCF mills discussed above indicated that AOX concentrations were consistently below minimum detection limits in the bleach plant filtrates, the Agency set an AOX limit for TCF mills at "minimum level", which for AOX is 20 µg/L.

Table 4.2 compares the “New Source Performance Standards” for ECF and TCF bleached market kraft pulp mills that commenced discharging an effluent after 15 June 1998.

Table 4.2 NSPS for ECF and TCF bleached market kraft pulp mills in the USA

Bleaching process	Parameter	Units	Daily maximum	Monthly average	Sample point	Sample frequency
ECF	AOX	kg/ADUt	0.476	0.272	Final Effluent	Daily
	BOD ₅	kg/ADt	4.52	2.41	Final Effluent	Daily
	TSS	kg/ADt	8.47	3.86	Final Effluent	Daily
	pH	-	see Note 1	n/a	Final Effluent	Continuous
	TCDD	pg/L	<ML	n/a	Bleach Plant Filtrate ³¹	Monthly
	TCDF	pg/L	31.9	n/a	Bleach Plant Filtrate	Monthly
	Chloroform	g/ADUt	6.92	4.14	Bleach Plant Filtrate	Weekly
	12 Chlorinated Phenolic Compounds	µg/L	<ML	n/a	Bleach Plant Filtrate	Monthly
TCF	AOX	µg/L	<ML	n/a	Final Effluent	not specified
	BOD ₅	kg/ADt	4.52	2.41	Final Effluent	Daily
	TSS	kg/ADt	8.47	3.86	Final Effluent	Daily
	pH	no units	see Note 1	n/a	Final Effluent	Continuous
	TCDD	not specified	not specified	not specified	not specified	not specified
	TCDF	not specified	not specified	not specified	not specified	not specified
	Chloroform	not specified	not specified	not specified	not specified	not specified
	12 Chlorinated Phenolic Compounds	not specified	not specified	not specified	not specified	not specified

Note 1. pH within the range of 5.0 to 9.0 at all times.
Note 2: n/a means not applicable.
Note 3: ML means minimum level. Minimum levels are given in Table 4.9

Source: US EPA Federal Register FR 63, pp 18656-18657.

³¹ This requirement is more restrictive than that included in the [EELG, 2004] where the limits are 10 pg/L for 2,3,7,8 TCDD and 30 pg/L for 2,3,7,8 TCDF as sampled in the treated effluent. It is proposed that, similar to the American NSPS, the Commission consider the adoption of the limits for 2,3,7,8 TCDD 2,3,7,8 TCDF as sampled in the bleach plant effluent.

Table 4.3 lists the “minimum levels” determined by the USEPA to be those levels at which the analytical system gives recognisable signals and an acceptable calibration point.

Table 4.3 Minimum Levels for specific pollutants as determined by the USEPA

Pollutant	Units	Minimum Level
2,3,7,8-TCDD	pg/L	10
2,3,7,8-TCDF	pg/L	10
Tric hlorosyringol	µg/L	2.5
3,4,5 - Trichlorocatechol	µg/L	5.0
3,4,6 - Trichlorocatechol	µg/L	5.0
3,4,5 - Trichloroguaiacol	µg/L	2.5
3,4,6 - Trichloroguaiacol	µg/L	2.5
4,5,6 - Trichloroguaiacol	µg/L	2.5
2,4,5 - Trichlorophenol	µg/L	2.5
2,4,6 - Trichlorophenol	µg/L	2.5
Tetrachlorocatechol	µg/L	5.0
Tetrachloroguaiacol	µg/L	5.0
2,3,4,6 - Tetrachlorophenol	µg/L	2.5
Pentachlorophenol	µg/L	5.0
AOX	µg/L	20

Source: US EPA Federal Register FR 63, pg. 18638.

4.4 CANADA

4.4.1 Federal and provincial liquid effluent limits

The Canadian federal government has adopted one set of regulations which specify discharge limitations for BOD₅, TSS, toxicity, 2,3,7,8-TCDD and 2,3,7,8-TCDF in effluent from all pulp and paper operations regardless of age, process, or product. More stringent site specific standards can be set, if necessary, to protect the receiving environment. The limits are measured in the final effluent (i.e. the effluent discharged directly into the environment including process water, gas scrubbing water, boiler blowdown water, washdown water, cooling water, and leachates from landfills and wood chip and hogfuel storage piles).

The federal standards apply to all pulp and paper mills in Canada. The individual provinces may adopt these standards or set more stringent standards. Table 4.4 summarises the federal discharge limits.

Table 4.4 Federal pulp and paper effluent standards

Parameter	Unit	Maximum daily limit	Maximum monthly average of daily measurements
BOD ₅	kg/ADt	12.5	7.5
TSS	kg/ADt	18.75	11.25
Toxicity	LC ₅₀ ¹ %	100	
2,3,7,8-TCDD ²	pg/L	15	
2,3,7,8-TCDF ²	pg/L	50	
Notes: 1. LC ₅₀ means the concentration of the effluent at which more than 50% of the Rainbow trout are killed when exposed to it for a 96-hour period. Undiluted effluent is referred to as 100% concentration. 2. The toxicity measurement is made in a grab sample of effluent. All other test are performed on a 24-hour composite sample. 3. The BOD ₅ and TSS values are multiplied by a "reference production rate" (RPR) to obtain a daily and monthly mass loading limit. The RPR is defined for any one year as the average of the 90 th percentile of the daily production of finished product at the mill for the previous three years.			

Source: [Beca AMEC, 2004].

In addition to a monthly toxicity test using rainbow trout, weekly toxicity tests must also be carried out using *Daphnia magna* as the test species. In the case of daphnia, 50% or more must survive 48-hour exposure in undiluted effluent to pass the test. Failure to pass is not an offence. The test is used to indicate potential problems.

The federal *Pulp and Paper Mill Defoamer and Wood Chip Regulation* contains two additional requirements for pulp and paper mills:

- Pulp mills using the chlorine bleaching process cannot use defoamers unless they contain and 10 ppb or less by weight dibenzo-p-dioxin and 40 ppb or less by weight dibenzofuran.
- Wood chips cannot be imported for, sold to, or used in a pulp mill if they are made from wood treated with polychlorinated phenols.

The Canadian *Pulp and Paper Effluent Regulations* require the operator of any pulp and paper mill in Canada discharging into an aquatic receiving environment to undertake environmental effects monitoring (EEM) studies at regular intervals. The first, second and third EEM cycles EEM reports were submitted in 1994, 2000 and 2004. The fourth cycle report will be submitted in April 2007.

4.4.1.1 Québec (QC)

The province of Québec has issued standards for the final effluent from existing and new pulp and paper mills. The standards for new mills (i.e. mills whose construction was completed on or after 22 October 1992) are summarised in Table 4.5.

Table 4.5 Québec pulp and paper effluent standards for new mills

Parameter	Unit	Maximum daily limit	Maximum monthly average of daily measurements
BOD ₅	kg/ADt	4.0	2.5
TSS	kg/ADt	6.0	3.0
AOX	kg/ADt	0.30	0.25
Hydrocarbons	mg/L	2.0	n/a
pH	-	between 6.0 and 9.5	
Temperature	°C	65	
Toxicity	LC ₅₀ ² %	100	
Chlorinated dioxins and furans	pg/L TEQ ³	15	
PCB ⁶	mg/L	3.0	
Notes:			
1. The BOD ₅ , TSS and AOX values are multiplied by the average production to obtain a daily and monthly mass loading limit. The average production is defined as the sum of the daily production for each of the last 30 days divided by 30.			
2. LC ₅₀ means the concentration of the effluent at which more than 50% of the Rainbow trout are killed when exposed to it for a 96-hour period. 100% concentration means undiluted effluent.			
3. The toxicity equivalent (TEQ) is calculated using the International toxicity equivalency factors according to the NATO scheme (1988) with undetectable measurements equated to zero.			
4. All tests are performed on effluent immediately prior to its discharge into the receiving environment.			
5. The toxicity measurement is made in a grab sample of effluent. Temperature and pH are measured continuously. All other test are performed on a 24-hour composite sample.			
6. PCB is the total concentration of all 10 congeners (mono- to deca-chloro-biphenyls).			

Source: [Beca AMEC, 2004].

4.4.1.2 Alberta (AB)

The province of Alberta does not have provincial guidelines or standards for pulp and paper mill effluent. Standards are set on a mill-by-mill basis.

Alberta-Pacific, Boyle, AB is a greenfield bleached kraft pulp mill which began operation in 1993. It utilises all of the BAT technology identified in [USEPA, 1998] and [IPPC BREF, 2001] except TCF bleaching. It produces hardwood and softwood pulp in campaigns. More than 85% of its production is hardwood pulp. It was the first purposely built ECF mill in the world.

In addition to having to meet Canadian federal government discharge standards, the Al-Pac mill must also meet effluent standards imposed by the province of Alberta. These standards are summarised in Table 4.6.

Table 4.6 Effluent standards for a BAT bleached kraft pulp mill in Alberta

Parameter	Units	Maximum daily limit	Maximum monthly average of daily measurements
BOD ₅	kg/day	4,500	2,250
	kg/ADt	3.0	1.5
TSS	kg/day	9,000	4,500
	kg/ADt	6.0	3.0
AOX	kg/day	1,390	818
	kg/ADt	0.927	0.545

Table 4.6 Effluent standards for a BAT bleached kraft pulp mill in Alberta (continued)

Parameter	Units	Maximum daily limit	Maximum monthly average of daily measurements
Colour	kg/day	185,500	104,000
	<i>kg/ADt</i>	<i>127</i>	<i>69</i>
pH	-	between 6.0 and 9.5	
Toxicity	LC ₅₀ ^{2%}	100	
2,3,7,8-TCDD	pg/L	15	
2,3,7,8-TCDF	pg/L	50	
Total resin ³² and fatty acids	mg/L	2.0	
Floating solids	-	Not present except in trace amounts	
Visible foam	-	Not present except in trace amount s	
Oil & other substances	-	Not present in sufficient amounts to create a visible film or sheen	
Notes:			
<ol style="list-style-type: none"> 1 "Legal" standards for BOD₅, TSS, AOX and colour are specified in kg/day. The italicised numbers are computed from the legal standards using a nominal production rate of 1 500 ADt/d. The italicised numbers are shown for illustrative purposes only. 2 LC₅₀ means the concentration of the effluent at which more than 50% of the Rainbow trout are killed when exposed to it for a 96-hour period. 100% concentration means undiluted effluent. All tests are performed on effluent immediately prior to its discharge into the receiving environment. 3 Toxicity is measured in a grab sample of effluent. pH is measured continuously. Floating solids, visible foam and oil & other substances are visual checks. All other test are performed on a 24-hour composite sample. 			

Source: [Beca AMEC, 2004].

4.4.1.3 British Columbia (BC)

Regulations

British Columbia has issued pulp and paper effluent regulations which apply mainly to mills in existence prior to 1990. Mills that have been built or extensively modernised since 1990 must meet more stringent discharge requirements. These requirements are established on a mill-by-mill basis.

³² Resin acids would not be present in the effluent when hardwood is processed.

The Celgar Pulp Company bleached softwood³³ kraft pulp mill at Castlegar, BC was essentially replaced in the early 1990s by a modern mill which incorporates all of the BAT identified in [USEPA, 1998] and [IPPC BREF, 2001] except TCF bleaching.

The effluent standards that the Celgar mill must meet are summarised in Table 4.7.

Table 4.7 Effluent standards for a BAT bleached kraft pulp mill in British Columbia

Parameter	Units	Maximum daily limit	Maximum monthly average of daily measurements
BOD ₅	kg/day	6,000	n/a
	<i>kg/ADt</i>	<i>5.0</i>	n/a
TSS	kg/day	6,000	n/a
	<i>kg/ADt</i>	<i>5.0</i>	n/a
AOX	kg/day	n/a	600
	kg/ADt	0.6	0.5
pH	-	between 6.5 and 8.5	
Toxicity	LC ₅₀ ^{3%}	100	
2,3,7,8-TCDD	pg/L	15	
2,3,7,8-TCDF	pg/L	50	
Temperature	°C	40	
Notes:			
1 n/a means not applicable.			
2 "Legal" standards on BOD ₅ and TSS are specified in kg/day. The italicised numbers are computed from the legal standards using a nominal production rate of 1200 ADt/d. The italicised numbers are shown for illustrative purposes only. The "legal" monthly average AOX standard is specified in both kg/day and kg/ADt.			
3 LC ₅₀ means the concentration of the effluent at which more than 50% of the Rainbow trout are killed when exposed to it for a 96-hour period. 100% concentration means undiluted effluent.			
4 The toxicity measurement is made in a grab sample of effluent. pH and temperature are measured continuously. All other tests are performed on a 24-hour composite sample. All tests are performed on effluent immediately prior to its discharge into the receiving environment.			

Source: [Beca AMEC, 2004].

³³ Strictly speaking, this BKP mill should not be mentioned in this report, however, it is included here as an example of BAT kraft mill built in the 1990s.

Scientific basis for AOX effluent standard in British Columbia

In 1992, the Province of British Columbia (BC) modified the *Pulp and Paper Mill Liquid Effluent Control Regulation* to require the elimination of AOX discharges from bleach plants by 31 December 2002. In effect this would have required all existing chemical pulp mills in the province to convert their bleaching processes to TCF. The cost of converting the 25 bleach plants in the 14 chemical pulp mills operating in the province at that time would have crippled the industry. In December 2001, the Province appointed a Scientific Advisory Panel to review the scientific basis of this requirement. After reviewing the available scientific literature, receiving submissions from a number of stakeholders, and reviewing mills' performance data and design features, the Panel concluded that there was no evidence that the current level of AOX being discharged by the mills, which averaged less than 0.5 kg/ADt on an annual basis, presented a demonstrable risk to the ambient aquatic environment that could be attributed to AOX.

This conclusion was based on the following evidence considered by the Panel [Carey, 2002]:

- The discovery in the late 1980s that biota in provincial waters receiving effluent from pulp mills contained elevated levels of POP (such as 2,3,7,8-TCDD and 2,3,7,8-TCDF) led to the establishment of consumption advisories and fishery closures. By the mid-1990s most, if not all BC mills had adopted ECF bleaching and all mills (mainly coastal mills) not having secondary treatment of effluent had installed such facilities. With these, and other miscellaneous technological improvements, annual average AOX discharges dropped from around 6.5 kg/ADt in 1988 to below 0.5 kg/ADt and by the late 1990s most of the closures and consumption advisories noted above had been lifted. The Panel felt that those few closures and consumption advisories remaining probably related to historical organochlorine discharges since they were for organisms (crabs) that live directly on the bottom of receiving water bodies where they could be exposed to contaminated sediment that had been deposited prior to the changes made to the mills' processes. The Panel concluded that the process modifications implemented by BC mills during the 1990s were generally effective in reducing organochlorine concentrations in biota to acceptable levels and that there would be no benefits with respect to limitations on consumption of receiving water biota due to organochlorine contamination from further reductions in AOX discharged.
- In the past, when mills used large amounts of Cl_2 and NaClO to bleach pulp, there was a general tendency for mills having high AOX discharge levels to also discharge large amounts of 2,3,7,8-TCDD and 2,3,7,8-TCDF. However, for the AOX levels achieved by BC mills in the mid-1990s, the Panel was unable to find any evidence that there was a correlation between the discharge of AOX (expressed as kg/ADt pulp) and the discharge of PCDD/PCDF (expressed as ng TEQ/ADt pulp).
- Since the installation of secondary treatment facilities in all BC mills by the mid-1990s, BC mills have passed, with few exceptions, the standard regulatory test for acute toxicity (the 96hrLC₅₀ test using Rainbow trout fingerlings). The few exceptions were not AOX related. The Panel concluded, therefore, that further reductions in AOX discharges were unnecessary to meet regulatory acute lethality requirements. Furthermore, the Panel did not identify any published peer-reviewed

scientific information demonstrating a link between AOX and acute toxicity of mill effluents.

- Sub-lethal toxicity data for effluent from seven BC bleached kraft pulp mills discharging into fresh water, obtained during the federally mandated Cycle 2 Environmental Effects Monitoring (EEM) program (1997-2000), did not correlate with the mills' AOX discharge levels (expressed as mg/L). The best correlation had an R^2 value of 0.107 which was considered to be far too low to be significant. The Panel concluded, therefore, that there was no cause-effect link between AOX and sub-lethal toxicity measured by the three test organisms (fish, *Ceriodaphnia*, and plants) used in the EEM program. An examination of EEM sub-lethal toxicity data (*Ceriodaphnia*) collected at 5 Ontario BKP mills also found no relationship (R^2 less than 0.05) between sub-lethal toxicity and AOX concentration.

Based on the conclusions reached by the Scientific Advisory Panel, on 5 July 2002, the Minister of Water, Land and Air Protection issued a news release which said:

"A new scientifically based limit to control AOX discharges from pulp mills that protects the environment and ensures a viable future for the pulp industry has been enacted by cabinet, Water, Land and Air Protection Minister Joyce Murray announced today. This decision is scientifically sound and will give British Columbia the strongest industry-wide standard for AOX discharges in Canada. The decision by the previous government to require zero AOX discharge from BC pulp mills by 31 December 2002 had no scientific basis and would have resulted in huge costs to the pulp and paper industry with no demonstrable environmental benefits. Under the change to the Waste Management Act's Pulp Mill Effluent Control Regulation, a new monthly average limit of 0.6 kg/ADt pulp, down from the current 1.5 kg/ADt, has been set for bleached kraft pulp mill effluent. A monthly average limit of 1.0 kg/ADt has been set for the province's one bleached sulfite pulp mill. The new industry-wide standards are the strongest of any regulation in Canada".

4.5 WORLD BANK GROUP

Pulp and paper industry projects that solicit and use financing from the World Bank Group (WBG) must comply with their "...policies and guidelines, which emphasise pollution prevention, including the use of cleaner production technologies".

Design and operating emission levels are established through an environmental assessment process on the basis of the country legislation and with the WBG's "Pollution Prevention and Abatement Handbook 1998" [PPAH, 1999], section Pulp and Paper mills.

WBG's air emission limits are generally referenced to guidelines from the World Health Organisation (WHO), the EU, and the USEPA. The WHO guidelines are solely based on health considerations whereas the EU and USEPA standards also reflect technological and economical feasibility.

The WBG incorporates consideration of all of these issues to ensure that ambient guidelines are an effective part of the environmental management system.

4.5.1 Pollution Prevention and Abatement Handbook

In the PPAH, guidance is given as to the technology to use and emission numbers to strive for in order to be eligible for WB financing of projects. The following are excerpts from the Handbook with relevance for the use of ECF and TCF bleaching:

Industry description and practices

In modern mills, oxygen is normally used in the first stage of bleaching. The trend is to avoid the use of any kind of chlorine chemicals and employ "total chlorine-free" (TCF) bleaching. TCF processes allow the bleaching effluents to be fed to the recovery boiler for steam generation, thereby reducing the amount of pollutants discharged.

Elemental chlorine-free (ECF) processes, which use chlorine dioxide, are required for bleaching certain grades of pulp. *The use of elemental chlorine for bleaching is not recommended.* Only ECF processes are acceptable, and, from an environmental perspective, TCF processes are preferred.

Pollution prevention and control

Reduce bleaching requirements by process design and operation. Use the following measures to reduce emissions of chlorinated compounds to the environment:

- Before bleaching, reduce the lignin content in the pulp (kappa number of 10) for hardwood by extended cooking and by oxygen delignification under elevated pressure.
- Optimize pulp washing prior to bleaching.
- Use TCF or at a minimum, ECF bleaching systems.
- Use oxygen, ozone, peroxides (hydrogen peroxide), peracetic acid, or enzymes (cellulose-free xylanase) as substitutes for chlorine-based

-
- bleaching chemicals; recover and incinerate maximum material removed from pulp bleaching.
 - Where chlorine bleaching is used, reduce the chlorine charge on the lignin by controlling pH and by splitting the addition of chlorine.

Key issues

The key production and control practices that will lead to compliance with emissions guidelines can be summarised as follows:

- Prefer total chlorine-free processes, but at a minimum, use elemental chlorine-free bleaching.
- Reduce the use of hazardous bleaching chemicals by extended cooking and oxygen delignification.
- Aim for zero-effluent discharge where feasible. Reduce wastewater discharges to the extent feasible. Incinerate liquid effluents from the pulping and bleaching processes."

Table 2 "Liquid Effluents from New Pulp and Paper Manufacturing", column "Parameter maximum value" states that an AOX of 2 kg/t is acceptable but the aim should be 0.4 kg/t in retrofits and 0.2 kg/t for new mills. A note to Table 2 states that "Molecular chlorine should not be used in the process."

4.5.2 International Finance Corporation

The International Finance Corporation (www.ifc.org) is the private sector arm of the WBG.

Its mission is to promote sustainable private sector investment in developing countries, helping to reduce poverty and improve people's lives.

The creation of IFC in 1956 represented the first step by the global community to foster private sector investment in developing nations.

IFC provides loans, equity, structured finance and risk management products, and advisory services to build the private sector in developing countries.

IFC has 178 member countries, which collectively determine its policies and approve investments.

IFC is currently using two sets of guidelines for its projects:

- The environmental guidelines contained in the [PPAH, 1999].
- The Environmental, Health, and Safety Guidelines (EHS) that it has been preparing since 1993 on an ongoing basis and for which there are no parallel guidelines in the [PPAH, 1999].

The EHS are technical reference documents that address IFC's expectations regarding the industrial pollution management performance of its projects. They are designed to assist managers and decision makers with relevant industry background and technical information. This information supports actions aimed at avoiding, minimising, and controlling environmental, health, and safety (EHS) impacts during the construction, operation, and decommissioning phase of a project or facility.

The IFC is currently undertaking the comprehensive review and update of the EHS. As part of this process, the total body of the EHS included in

Part III of the [PPAH, 1999] and on the IFC website is being updated. The result of the process will be a new set of World Bank Group Environmental, Health, and Safety Guidelines.

The draft updated EHSG will be posted on IFC's website in a staggered fashion as they become available starting in June 2006, and each draft will be available for comment for a minimum of 60 days.

4.5.3 Comments and consequences for the pulp and paper industry

It should be kept in mind that the PPAH was published in 1999 and probably researched and written from 1995 and onwards. The statement "the trend is to avoid the use of any kind of chlorine chemicals and employ "total chlorine-free" (TCF) bleaching" is thus not quite relevant in 2006 when TCF bleaching accounts for less than 5% of the global production capacity of bleached chemical pulp and there has in fact been a reduction in total TCF capacity over the last years.

Another statement in the PPAH "TCF processes allow the bleaching effluents to be fed to the recovery boiler for steam generation, thereby reducing the amount of pollutants discharged" was a high expectation of the 1990s, however, the recycling of bleach effluents from TCF processes has proven equally difficult to manage as from ECF processes.

Zero-effluent discharge from kraft pulping is at present (Q2 2006) not a feasible option and the possible recycle and incineration of bleach effluents (from ECF and TCF bleaching alike) is limited.

The PPAH states that "ECF processes are acceptable, and, from an environmental perspective, TCF processes are preferred". Except for the statements discussed above there is no further evidence given to support this preference in the text.

5 SPECIFIC ISSUES RAISED IN THE WWF REPORT ON ARAUCO VALDIVIA

This report includes references to a number of issues raised in [WWF, 2005].

The following sections address a few specific additional issues raised in [WWF, 2005].

5.1 Hazard profile of chlorine dioxide

Recommendation 58 of the [WWF, 2005] states "In relation to the ECF technology, it should be noted that all bleaching chemicals are potent oxidisers, and as a result they present hazards to workers and nearby residents. When compared over a full range of characteristics, oxygen-based chemicals are less dangerous overall than chlorine dioxide (ClO₂). Both chronic and acute toxic effects can result from ClO₂ exposure including irritation of the eyes, nose, and throat, coughing, wheezing and breathing difficulties (possibly delayed), pulmonary edema, possible chronic bronchitis and asthma. This, along with the chloroform and similar by-products from ECF bleaching, contribute to the hazard profile of chlorine dioxide".

Comment

The risk and health assessment of ECF and TCF bleaching (reported in section 2.12) concludes that the overall risk levels for the two processes may be considered comparable. Similarly, the risk level for any health effects from working in ECF and TCF mills is comparable.

5.2 Increased concentration of dioxins in the Baltic Sea near ECF mills during 1979-2000

Recommendation 60 of the [WWF, 2005] states "For more than ten years, pulp companies have stated that the ECF process does not result in significant discharge of dioxins into the environment as a result of improved processes and bleaching methods. However, a new study, released in June 2005, shows increased concentration of dioxins in the Baltic Sea marine environment near ECF pulp plants during 1979-2000. According to the research group, this indicates ongoing pollution rather than leakage from sediments, which was a common hypothesis. The study links the increased dioxin levels with chlorine dioxide bleaching as one possible source. The results of that study have taken the whole industry by surprise and a new research program has been initiated by the Swedish Environmental Protection Agency and forest industries".

Comment

The WWF has misinterpreted the study by [Olsson, 2005a].

It is possible that dioxin levels have increased in fatty fish from the Bothnian Sea during the period 1979-2000, although the number of measurements has been insufficient from a statistical point of view. However, this

increase has not been observed in fish from ECF pulp mill primary recipients but in herring (*Clupea harengus*) collected at one station in the southern part of the Bothnian Sea [Olsson, 2003].

One hypothesis among others (e.g. oligotrophication and thereby less biological dilution) to explain this increase in dioxin levels raised by [Olsson, 2003] was an ongoing pollution in the catchment area of the Bothnian Sea.

Consequently, a study was initiated to measure dioxin levels in stationary fish (perch and eelpout) from pulp mill recipients. The results from this study have so far [Olsson, 2005a] shown low levels of dioxins although somewhat higher in the recipients compared to the reference areas. The only recipient where it is possible to compare with historical data shows a decrease of dioxins in perch by a factor 20 during the last 15 years. These results are thus in conflict with those for pelagic herring and indicate a dramatic reduction in dioxin discharges from the pulp mill compared to the situation in the 1980s.

5.3 Catalytic oxygen bleaching

Recommendation 62 of the [WWF, 2005] states "Several mills in the world produce high quality TCF pulp, and many more are capable of doing so. Many reports support the view that TCF is the best option, specifically from an environmental point of view. The European pulp industry is very interested in the research concerning catalytic bleaching with oxygen gas conducted at the Helsinki Technical University. According to researcher Tuula Lehtimaa, there is pressure on the industry to switch to TCF bleaching. Catalytic oxygen gas bleaching would provide the advantages of traditional TCF technology, while being even more cost-effective than ECF".

Comment

The news article (in Swedish) referenced in the WWF report [Lehtimaa, 2005] explains that catalytic oxygen bleaching (COB) is being investigated at Helsinki Technical University (www.tkk.fi) as a means to increasing oxygen delignification selectivity.

This would allow the kappa number of oxygen delignified kraft pulp to be lower without the serious drawback of strength loss due to carbohydrate attack.

Lehtimaa also says that "The problem with current technology for bleaching with totally chlorine free chemicals (TCF) is that it is primarily suitable for relatively lightly bleached pulp or in cases where lower run-off volumes are desirable for environmental or market reasons" and concludes by saying "Catalytic oxygen gas bleaching would thus provide the advantages of TCF technology while being even more cost-effective than ECF, which is still defined as the best available technology for bleaching".

Another comment made in the news article is: "No one has so far presented an economically feasible alternative for catalytic bleaching on an industrial scale".

Hence, catalytic oxygen bleaching is considered to be an emerging technology.

5.4 Multibio system at SCA Östrand

Recommendations 69 and 70 of the [WWF, 2005] state “Biological treatment systems, such as activated sludge, aerated lagoons, and anaerobic fermentation, can reduce BOD by over 99% and achieve a COD reduction of 50% to 90%. These systems are used worldwide in modern pulp mills. The future in secondary treatment is to minimize the effluent from the bleaching process, decrease the production of sludge and to combine a high COD reduction with low nutrient discharges. This has been recognized by the SCA Östrand mill in Sweden. By minimizing the water usage, they succeeded in closing the bleaching process far more than had previously been possible, and as a result they were able to build the most modern treatment plant, Multibio. By minimizing the water usage, and by using only TCF bleaching and the installation of the Multibio system, the engineers were able to make the secondary treatment plant more compact, as well as less sensitive to process disruptions. The result has been a cost of operation that is lower than traditional treatment, as well as less sludge production. In addition, the lowest levels of water consumption can be reached only with the TCF process”.

Comment

Biological effluent treatment is considered to be AMT for BKP mills. With modern technology it is possible to achieve both high reduction of biodegradable organic matter and low discharge of nutrients.

The biological treatment system can be designed in different ways and the selection of treatment system should be based on a techno-economical evaluation considering the site specific conditions. It is not true that a special type of biological system (e.g. the Multibio process) should be generally superior in comparison to others with respect to removal of COD and other environmental parameters.

5.5 Tertiary treatment

Recommendation 71 of the [WWF, 2005] states “CELCO’s secondary treatment plant should be reconditioned and rebuilt with state-of-the-art technology from an environmental point of view, which would provide greater security in emergency situations and achieve higher parameters than current tertiary treatment. Tertiary treatment could be considered an emergency option only. Tertiary treatment is not a common technique used in modern pulp mills. The reasons are mainly two: a) it is an expensive technique, with the cost of the chemicals being high; and b) it produces large amounts of sludge, which also is expensive and complicated to handle, since the sludge has to be treated as toxic waste. Improperly managed, as appears to be the case here, tertiary treatment increases the overall chemical load on the environment (in this case aluminum sulfate). It should be mentioned that tertiary treatment is not seen as a Best Available Technology (BAT). Only one installation in a modern mill using tertiary treatment has been found, namely Varkaus in Finland. The few other mills using tertiary treatment are in Japan, and were retrofitted with this technology in large part in order to manage effluent colour”.

Comment

While it is agreed that a tertiary treatment stage cannot generally be considered AMT because it requires high chemical dosages and produces large amounts of sludge, in some cases (not only the mills mentioned in Recommendations 70 and 71) it has been considered necessary, due to special local requirements, to include that type of treatment to achieve a lower discharge than can be obtained by only secondary treatment.

It is not possible to design or redesign a secondary treatment system for as high removal efficiency as is achieved with the combined secondary and tertiary treatment. Some type of substances (e.g. high molar mass organic compounds) that are removed in a tertiary treatment cannot be removed by biological methods.

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UNITS AND CONVERSION FACTORS

Units and conversion factors	
m	Micro = 10^{-6}
°C	Degree Celsius
a	Annum, year, 365 days
d	Day, 24 hours
f	Femto = 10^{-15}
h	Hour(s)
m	Metre
kg steam	Assuming a pressure of 2.5 bar in the steam piping, the heat of steam which can be used corresponds to about 0.7 kW _{th} /kg steam or about 2.5 MJ/kg steam
K	Kelvin or absolute temperature
J	Joule. The basic SI unit of energy. It is the quantity of work done when a force of 1 Newton acts through a distance of 1 metre
kWh	Kilowatt hour = 3.6 MJ
L	Litre
m	Milli = 10^{-3}
N	Newton. The basic SI unit of force
n	Nano = 10^{-9}
Pa	Pascal. The SI unit of pressure. It corresponds to a force of 1 Newton applied to an area of 1 square metre
NDm³	Normal dry cubic metre: the volume a gas occupies at atmospheric pressure (101.325 kPa) and 273.15 K (0°C). In this report gas conditions are dry
p	Pico = 10^{-12}
SDm³	Standard dry cubic metre: the volume a gas occupies at atmospheric pressure (101.325 kPa) and 293.15 K (20°C). In this report gas conditions are dry
ppb or mg/L	Parts per billion (10^{-9}) Time scale equivalent: 1 second vs 31.7 years
ppm or mg/L	Parts per million (10^{-6}) Time scale equivalent: 1 second vs 11.6 days
ppq or pg/L	Parts per quadrillion (10^{-15}) Time scale equivalent: 1 second vs 31,709,790 years
ppt or ng/L	Parts per trillion (10^{-12}) Time scale equivalent: 1 second vs 31,710 years
°SR	Schopper Riegler value
t	Metric tonne (10^6 grams)

ABBREVIATIONS AND ACRONYMS³⁴

Abbreviations and acronyms	
%ISO	Brightness unit according to ISO, the International Organisation for Standardisation
£	Less than or equal to
^³	Greater than or equal to
(EO)	Extraction bleaching stage using sodium hydroxide with subsequent addition of oxygen as a reinforcing agent
(EOP)	Extraction bleaching stage using sodium hydroxide with subsequent addition of oxygen and hydrogen peroxide as a reinforcing agents
(EP)	Extraction bleaching stage using sodium hydroxide with subsequent addition of hydrogen peroxide as a reinforcing agent
(OP)	Pressurised peroxide bleaching stage using hydrogen peroxide with oxygen at low peroxide charge
(PO)	Pressurised peroxide bleaching stage using hydrogen peroxide with oxygen at high peroxide charge
<	Less than
>	Greater than
2,3,7,8-substituted PCDD	Any polychlorinated dibenzo-p-dioxin that has the molecular formula $C_{12}H_{8-n}Cl_nO_2$, in which $4 \leq n \leq 8$ and chlorine atoms are located at the 2,3,7,8 positions on the molecule
2,3,7,8-substituted PCDF	Any polychlorinated dibenzofuran that has the molecular formula $C_{12}H_{8-n}Cl_nO$, in which $4 \leq n \leq 8$ and chlorine atoms are located at the 2,3,7,8 positions on the molecule
2,3,7,8-TCDD	2,3,7,8-Tetra Chloro Dibenzo-p-Dioxin (a dioxin). Also named "Seveso dioxin" after the name of the municipality that was most severely affected by a toxic cloud containing 2,3,7,8-TCDD that was accidentally released into the atmosphere following an explosion that occurred in a 2,4,5-trichlorophenol (TCP) reactor of the ICMESA chemical plant on the outskirts of Meda, a small town about 20 kilometres north of Milan, Italy on 10 July 1976. The dioxin cloud contaminated a densely populated area about six kilometres long and one kilometre wide, lying downwind from the site. TCDD is considered to be the most toxic man-made compound and is, e.g., more toxic than cyanide ion, strychnine and nerve gases
2,3,7,8-TCDF	2,3,7,8-Tetra Chloro Dibenzofuran (a furan)
AA	Active alkali or NaOH + Na ₂ S, as g/L Na ₂ O
AD	Air dry (dry solids content of 90% and 10% water)
ADt	Air dry metric tonne of pulp (dry solids content of 90% and 10% water)
AMT	Accepted modern technology is defined in the Tasmanian State Policy on Water Quality Management and Draft Environment Protection Policy (Air Quality) as a "technology which has a demonstrated capacity to achieve the desired emission concentration in a cost-effective manner, takes account of cost-effective engineering and scientific developments and pursues opportunities for waste minimisation"
ANZECC	Australian and New Zealand Environment and Conservation Council
AOX	Adsorbable organic halides measured in wastewaters. In the ECF

³⁴ All acronyms refer to either the singular or the plural form of their expanded version.

Abbreviations and acronyms	
	kraft process, halides are chlorides. AOX measures adsorbable chlorinated organic compounds in effluent from ECF kraft pulp mills
ARMCANZ	Agricultural and Resource Management Council of Australia and New Zealand
ASB	Aerated stabilisation basin (or aerated lagoon); a particular form of secondary effluent treatment
AST	Activated sludge treatment; a particular form of secondary effluent treatment
BAT	Best available techniques (IPPC BREF and UNEP) Best available technology economically achievable (USEPA Final Water Rule)
BEKP	Bleached eucalypt kraft pulp
BEP	Best environmental practices (IPPC Directive)
BFR	Bleach filtrate recycle
BL	Black liquor, a solution of wood lignins, organic compounds, oxidised inorganic compounds (sodium sulfate (Na ₂ SO ₄), sodium carbonate (Na ₂ CO ₃)), and white liquor (Na ₂ S and NaOH)
BMP	Best management practice (USEPA Final Water Rule)
BOD₅/ BOD₇	Biological oxygen demand indicating the amount of biodegradable organic matter in the wastewaters assessed using a standard 5 day or 7 day test
BP	Bleach plant, mill department where pulp is bleached
BPEM	Best practice environmental management; defined in the <i>Environmental Management and Pollution Control Act 1994</i> as "the management of an activity to achieve an ongoing minimisation of the activity's environmental harm through cost-effective measures assessed against the current international and national standards applicable to the activity"
BREF	Best available techniques reference document (IPPC)
BS	Brown stock, the suspension of unbleached pulp
CH₃COOOH	Peracetic acid
CH₃OH	Methanol
Cl₂	Chlorine
ClO₂	Chlorine dioxide
COD	Chemical oxygen demand indicating the amount of chemically oxidisable organic matter in the wastewaters (normally referring to analysis with dichromate oxidation)
CRP	Chloride removal process
CSF	Canadian standard freeness - a measure of the rate at which water drains from a pulp, the smaller the number the slower draining is the pulp
CSIRO	Commonwealth Scientific & Industrial Research Organisation
D	Chlorine dioxide bleaching stage using a water solution of chlorine dioxide (ClO ₂)
DAF	Dissolved air flotation
DPIWE	(Tasmanian) Department of Primary Industries, Water and Environment
DS	Dry solids
DTA	Direct toxicity assessment. The use of toxicity tests to determine the acute and/or chronic toxicity of wastewater discharges or total pollutant loads in receiving waters. Assesses the toxicity of mixtures of chemicals rather than individual chemicals
DTPA	Diethylene triamine penta acetic acid, complexing (chelating) agent

Abbreviations and acronyms	
E	Extraction bleaching stage using sodium hydroxide (NaOH)
E.	<i>Eucalyptus</i> genus
EC₅₀	The concentration of a toxic material that causes a specific effect in 50% of the test organisms in a specified time
ECF	Elemental chlorine free. Bleaching process that uses no chlorine gas, no chlorine water and no sodium hypochlorite as bleaching agents. The only chlorine-containing bleaching agent is chlorine dioxide
EDS	Endocrine disrupting substances
EDTA	Ethylene diamine tetra acetic acid, complexing (chelating) agent
EIA	Environmental impact assessment
EIS	Environmental impact statement
EKP	Eucalypt kraft pulp
EOX	Extractable organic halides (chlorides) measured in wastewaters (following extraction with organic solvents). A common practice in environmental management is to use surrogate parameters when assessing or regulating water quality. Such parameters are used when the complexity of the effluent precludes the identification and quantitation of individual chemical compounds. In the context of the chlorine issue, two surrogate parameters have been developed and have been used, or proposed for use, in regulations. The adsorbable organic halogen (AOX) method determines the quantity of chlorine in a sample which is retained on activated carbon. It is viewed as determining the total quantity of organically bound chlorine. The extractable organic halogen or chlorine (EOX or EOCl) method involves extraction of the aqueous sample with a non-polar solvent. The EOX test is regarded as giving a better indication of potential for bioaccumulation than AOX and typically gives a concentration of a few percent of the AOX value (Axegård, 1986a; 1986b, Earl and Reeve, 1989) implying that most of the components of AOX are hydrophilic, i.e. water soluble
EPA	Environmental Protection Agency/ Authority
EQO	Environmental quality objective
ESP	Electrostatic precipitator
ETP	Effluent treatment plant
F/M	Food to biomass ratio. The amount of substrate (i.e. BOD ₅) in the influent to an AST plant in kg/day divided by the amount of mixed liquor volatile suspended solids (MLVSS) in the aeration basin in kg. The unit of F/M is day ⁻¹
FBK	Fully bleached kraft (i.e. to high brightness, typically 90% ISO)
Fe	Iron
GC	Gas chromatograph/chromatography
GC/MS	Gas chromatography/ mass spectroscopy. Spectroscopy is the study of the interaction of electromagnetic radiation with matter. Nuclear magnetic resonance spectroscopy is the use of the NMR phenomenon to study physical, chemical, and biological properties of matter. As a consequence, NMR spectroscopy finds applications in several areas of science. NMR spectroscopy is routinely used by chemists to study chemical structure using simple one-dimensional techniques. Two-dimensional techniques are used to determine the structure of more complicated molecules. These techniques are replacing x-ray crystallography for the determination of protein structure. Time domain NMR spectroscopic techniques are used to probe molecular dynamics in solutions. Solid state NMR spectroscopy is used to determine the molecular structure of solids. Other scientists have

Abbreviations and acronyms	
	developed NMR methods of measuring diffusion coefficients http://www.cis.rit.edu/htbooks/nmr/inside.htm
GPC	Gel permeation chromatograph/ chroma tography
H₂O₂	Hydrogen peroxide
H₂SO₄	Sulfuric acid
HC	High consistency - pulp concentration in the interval 30-50% dry solid content
HexA	Hexenuronic acids
IDLH	Immediately dangerous to life or health
IDP	Integrated chlorine dioxide plant
IGCC	Integrated gasification combined cycle
IPPC	Integrated Pollution Prevention and Control (European Commission). A regulatory system issued under the auspices of the European Commission that employs an integrated approach to control the environmental impacts of certain industrial activities. It involves determining the appropriate controls for industry to protect the environment through a single permitting process. To gain a permit, operators will have to show that they have systematically developed proposals to apply the "best available techniques" (BAT) and meet certain other requirements, taking account of relevant local factors
I-TEF	International toxicity equivalency factor for PCDD/PCDF (see also Glossary of terms)
IUCLID	International Uniform Chemical Information Database
K	Potassium
KP	Kraft pulp, chemical pulp which has been manufactured using alkaline (NaOH) sodium sulfide (Na ₂ S) as the main cooking chemical
LC	Low consistency - pulp concentration in the interval 3-5% dry solid content
LC₅₀	The concentration of a toxic material that kills 50% of the test organisms in a specified time
LEL	Lower explosive limit
LOD	Limit of detection
LOEC	Lowest observed effect concentration. The lowest concentration of a material used in a toxicity test that has a statistically significant adverse effect on the exposed population of test organisms as compared with the controls. When derived from a life-cycle or partial life-cycle test, it is numerically the same as the upper limit of the MATC
LOQ	Limit of quantitation
MACT	Maximum achievable control technologies (USEPA Final Air Rule)
MATC	Maximum acceptable toxicant concentration. The maximum concentration of a toxic substance that a receiving water may contain without causing significant harm to its productivity or uses as determined by chronic toxicity tests
MBR	Membrane bioreactor
MC	Medium consistency - pulp concentration in the interval 8-15% dry solid content
Mg	Magnesium
MLSS	Mixed liquor suspended solids. The amount of suspended solids (both organic and inorganic) in the system, usually measured in mg/L but also in kg. MLSS is a measure of both volatile and non-volatile SS
MLVSS	Mixed liquor volatile suspended solids. The amount of volatile (organic) suspended solids in the AST system, usually measured in

Abbreviations and acronyms	
	mg/L but also in kg. MLVSS is usually a measure of the amount of biomass but since wood fibre is also volatile, it can be a measure both
Mn	Manganese
MOE	Generic acronym for the ministry responsible for the environment in each of the Canadian provinces
MS MVR	Mass spectrometer/spectrometry Mechanical vapour recompression
Na	Sodium
Na₂CO₃	Sodium carbonate
Na₂S	Sodium sulfide
Na₂SO₄	Sodium sulfate
NaClO₃	Sodium chlorate
NaHS	Sodium bisulfide or hydrosulfide
NaOH	Sodium hydroxide
NCG	Non condensable gases referring to the odorous gases generated in chemical pulping
NMR	Nuclear magnetic resonance. A phenomenon which occurs when the nuclei of certain atoms are immersed in a static magnetic field and exposed to a second oscillating magnetic field. Some nuclei experience this phenomenon, and others do not, dependent upon whether they possess a property called spin. The spin can be thought of as a small magnetic field, and will cause the nucleus to produce an NMR signal http://www.cis.rit.edu/htbooks/nmr/inside.htm
NOEC	No observed effect concentration. The highest concentration of a toxicant at which no statistically significant effect is observable, compared to the controls; the statistical significance is measured at the 95% confidence level
NO_x	The sum of nitrogen oxide (NO) and nitrogen dioxide (NO ₂) expressed as NO ₂
NPE	Non-process elements that can accumulate when closing up the water circuits in pulp mills such as Al, Si, Ca, Mg, Mn
NSPS	New source performance standards for new installations as promulgated by the USEPA. NSPS regulate emissions of pollutants from affected facilities. An affected facility is defined as a facility for which a standard exists and for which construction, reconstruction, or modification is commenced after the standard was promulgated. Sources constructed prior to the promulgation date are not subject to the NSPS until such time as they undergo a modification or reconstruction. A modification is defined as a physical change or a change in the method of operation which results in an increase in emissions of any air pollutant for which the NSPS applies. If an existing facility undergoes reconstruction, it becomes an affected facility regardless of any change in emissions. The USEPA defines reconstruction as the replacement of components of an existing facility or source meeting one of the following characteristics: The replacement has a fixed capital cost greater than 50% of the fixed capital cost that would be required to construct a comparable new facility or source; or The replacement makes it technically or economically feasible to meet the NSPS

Abbreviations and acronyms	
NWQMS	The Australian National Water Quality Management Strategy (NWQMS) aims to achieve the sustainable use of Australia's and New Zealand's water resources by protecting and enhancing their quality while maintaining economic and social development. The NWQMS is a joint strategy developed by two Ministerial Councils — the Agriculture and Resources Management Council of Australia and New Zealand (ARMCANZ) and the Australian and New Zealand Environment and Conservation Council (ANZECC). The Australian National Health and Medical Research Council (NHMRC) is involved in aspects of the strategy that affect public health. The NWQMS aims to meet future needs by providing policies, a process and national guidelines for water quality management
O	Oxygen delignification stage
O₂	Oxygen
O₃	Ozone
OD	Oven dry, the solids content of pulp containing 100% dry solids and 0% water; also called bone dry (BD)
ODt	Oven dry metric tonne of pulp (dry solids content of 100%)
OX	Organic halides measured in pulp. In the kraft process, halides are chlorides
P	Alkaline bleaching stage with hydrogen peroxide (H ₂ O ₂)/ Phosphorus
Paa	Peracetic acid
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls. These are highly toxic and persistent compounds derived from the replacement by Cl radicals of numerous H radicals on biphenyl, which consists of two benzene rings joined by a covalent bond, with the elimination of two H radicals (C ₁₂ H ₁₀)
PCDD	Polychlorinated dibenzo-p-dioxins
PCDF	Polychlorinated dibenzo furans
PEL	Permissible Exposure Limits
pH	Value that represents the acidity or alkalinity of an aqueous solution. It is defined as the negative logarithm of the hydrogen ion concentration of the solution. Measures the acidity (low pH) or alkalinity (high pH) of a solution
PM	Total particulate matter (in flue gases), dust
POP	Persistent organic pollutants. Organic compounds that, to a varying degree, resist photolytic, biological and chemical degradation. The carbon-chlorine bond is very stable towards hydrolysis and the greater the number of chlorine substitutions and/or functional groups, the greater the resistance to biological and photolytic degradation. Chlorine attached to an aromatic (benzene) ring is more stable to hydrolysis than chlorine in aliphatic (straight or branched) structures. As a result, chlorinated POP are typically ring structures with a chain or branched chain framework. By virtue of their high degree of halogenation, POP have very low water solubility and high lipid (fat) solubility leading to their propensity to pass readily through the phospholipid structure of biological membranes and accumulate in fat deposits. They are also semi-volatile, enabling them to be transported over great distances in the atmosphere before deposition occurs. Although many different forms of POP may exist, both natural and anthropogenic, POP which are noted for their persistence and bioaccumulative characteristics include many of the first generation organochlorine insecticides such as dieldrin, DDT, toxaphene and

Abbreviations and acronyms	
	<p>chlordan and several industrial chemical products or by-products including polychlorinated biphenyls (PCB), dibenzo-p-dioxins (dioxins) and dibenzo-p-furans (furans).</p> <p>POP are also noted for their semi-volatility; that property of their physico-chemical characteristics that permit these compounds to occur either in the vapour phase or adsorbed on atmospheric particles, thereby facilitating their long range transport through the atmosphere.</p> <p>While the risk level varies from POP to POP, by definition all of these chemicals share four properties:</p> <ol style="list-style-type: none"> 1. They are highly toxic 2. They are persistent, lasting for years or even decades before degrading into less dangerous forms 3. They evaporate and travel long distances through the air and through water 4. They accumulate in fatty tissue
Q	Acid bleaching stage where a chelating agent, EDTA or DTPA, has been used for the removal of metal ions
RO	Reverse osmosis. The passage through a semipermeable membrane of solvent molecules <i>from a solution into a pure solvent</i> . RO can be achieved by applying to the solution a pressure in excess of its osmotic pressure
S SBK	Sulfur Semi bleached kraft (i.e. to intermediate brightness, typically 70- 75% ISO)
SDT	Smelt dissolving tank
SEPA	Swedish Environmental Protection Agency
SNCR	Selective non-catalytic reduction
SO₂	Sulfur dioxide
SO₃	Sulfur trioxide
SPWQM	State Policy on Water Quality Management 1997
SS	Suspended Solids
SVI	Sludge volume index; Volume in ml occupied by 1 gram of activated sludge after settlement under specified conditions for a specified time, usually 30 minutes
TCF	Totally chlorine free (bleaching). Uses no chlorine-containing bleaching agents
TDS	Total dissolved solids. A measure of the inorganic salts (and organic compounds) dissolved in water
TEF and TEQ	<p>Many regulatory agencies have developed so-called toxicity equivalency factors (TEF) for risk assessment of complex mixtures of PCDD/PCDF. The TEF are based on acute toxicity values from <i>in vivo</i> and <i>in vitro</i> studies. This approach is based on the evidence that there is a common, receptor-mediated mechanism of action for these compounds. However, the TEF approach has its limitations due to a number of simplifications. Although the scientific basis cannot be considered as solid, the TEF approach has been developed as an administrative tool and allows to convert quantitative analytical data for individual PCDD/PCDF congeners into a single toxicity equivalent (TEQ). TEF particularly aid in expressing cumulative toxicity of complex PCDD/PCDF mixtures as one single TEQ value. It should be noted that TEF are interim values and administrative tools for order of magnitude estimates. They are based on present state of knowledge and should be revised as new data gets available. Today there are</p>

Abbreviations and acronyms	
	two schemes applied: the older one are the TEF established by a NATO/CCMS Working Group on Dioxins and Related Compounds as International toxicity equivalency factors (I-TEF) and the most recent scheme established by a WHO/IPCS working group, who re-evaluated the I-TEF and established a new scheme. The TEF for 2,3,7,8-TCDD is 1.0 and that for 2,3,7,8-TCDF is 0.1. For these congeners, the TEF are the same under the two schemes
TKN	Total Kjeldahl nitrogen. The sum of organic nitrogen and ammonia in a water body. High levels of organic nitrogen in water may indicate excessive production or organic pollution from the watershed. Animal and human waste, decaying organic matter, and live organic material like tiny algae cells can cause organic nitrogen enrichment of lake water. TKN is measured in milligrams per litre (mg/L)
TLV	Threshold Limit Values
Total PCDD	The sum of the concentrations of all polychlorinated dibenzo-p-dioxin congeners that have the molecular formula $C_{12}H_{8-n}Cl_nO_2$, in which $4 \leq n \leq 8$
Total PCDF	The sum of the concentrations of all polychlorinated dibenzofuran congeners that have the molecular formula $C_{12}H_{8-n}Cl_nO$, in which $4 \leq n \leq 8$
TRS	Total reduced sulfur meaning the sum of the following reduced foul sulfur compounds generated in the pulping process: hydrogen sulfide, methyl mercaptan, dimethylsulfide and dimethyldisulfide expressed as sulfur (measured as hydrogen sulfide)
TSS	Total suspended solids (in wastewater)
TTA	Total titratable alkali or NaOH + Na ₂ S + Na ₂ CO ₃ , as g/L Na ₂ O
UASB	Upflow anaerobic sludge blanket reactor/process
UEL	Upper explosive limit
UNEP	United Nations Environment Programme
UPOP	Unintentionally produced persistent organic pollutants. Dioxins, furans and, to a limited extent, PCB and pesticides are the POP that may be released from BEKP mills. Dioxins and furans may be released from the recovery boiler and the bleaching process in ECF kraft mills. PCB and pesticide releases may occur via the contamination of raw materials. These POP are called "unintentionally produced POP"
USEPA	United States Environment Protection Agency
VOC	Volatile organic compounds
WBL	Weak black liquor. A dilute solution of wood lignins, organic materials, oxidised inorganic compounds (sodium sulfate (Na ₂ SO ₄), sodium carbonate (Na ₂ CO ₃)), and white liquor (Na ₂ S and NaOH)
WHO	World Health Organisation
WHO-TEF	World Health Organisation toxicity equivalency factor for PCDD/PCDF (see also Glossary of Terms)
WQG	Water quality guideline
Z	Ozone bleaching stage using ozone (O ₃)

GLOSSARY OF TERMS

Glossary of terms	
Abiotic	The non-living components of a system (see biota)
Absorber	Equipment used to carry out gas absorption
Achievable value	When using a particular technique or combination of technologies achievable level means that a certain emission level may be expected to be achieved over a substantial period of time (e.g. a year) in a well designed, well maintained and well operated installation or process using those technologies
Acid	Having a high hydrogen ion concentration (low pH)
Acute toxicity	Toxicity which causes a rapid adverse effect (e.g. death) in a living organism following short-term exposure. Can be used to define either the exposure or the response to an exposure (effect)
Adsorption	The taking up of one substance at the surface of another
Aerobic	Of organisms requiring oxygen for respiration or conditions where oxygen is available
Aesthetic	Aspects of, say, a water body, that can be considered beautiful or pleasant to the senses
Algae	Comparatively simple chlorophyll-bearing plants, most of which are aquatic and microscopic in size
Alkali metals	Consist of the 6 metal elements in group 1 of the periodic table of the elements. The main alkali metals of interest in the kraft process are sodium (Na) and potassium (K)
Alkaline earth metals	Consist of the 6 elements in group 2 of the periodic table of the elements. The main alkaline earth metals of interest in the kraft process are magnesium (Mg), calcium (Ca) and barium (Ba)
Alkalinity	The quantitative capacity of aqueous media to react with hydroxyl ions. The equivalent sum of the bases that are titratable with strong acid. Alkalinity is a capacity factor that represents the acid-neutralising capacity of an aqueous system
Ambient levels	Those in the general environment outside the influence of specific discharges
Amphipods	Invertebrates belonging to the order Crustacea
Anaerobic	Conditions where oxygen is lacking; organisms not requiring oxygen for respiration
Anion	A negatively charge ion. An anion migrates toward the anode in an electrochemical cell
Anionic	Characteristic behaviour or property of an ion that has a negative charge. Anions move to the anode in electrolysis
Anode	The electrode where oxidation occurs
Anoxic selector	A selector (also referred to as selective reactor) is a "mini" bio-reactor placed ahead of the main activated sludge treatment (AST) plant bio-reactor. Selectors in AST plants can have one or more of the following functions: a) prevention of foaming; b) minimisation of the growth of filamentous (bulking or non-settling) bacteria and promotion of the growth of floc-forming (settling) bacteria; c) reduction of chlorate ion (ClO_3^-); d) nutrient removal. The chlorate reduction process is an anoxic process, i.e. it is operated without measurable amounts of dissolved oxygen. The anoxic stage is usually a separate tank before the aeration tank with a retention of the order 5-10

Glossary of terms	
	hours.
Anthropogenic	Produced or caused by human activity
Aquatic ecosystem	Any watery environment from small to large, from pond to ocean, in which plants and animals interact with the chemical and physical features of the environment
Aquifer	An underground layer of permeable rock, sand or gravel that absorbs water and allows it free passage through pore spaces
Assimilative capacity	The maximum loading rate of a particular pollutant that can be tolerated or processed by the receiving environment without causing significant degradation to the quality of the ecosystem and hence the environmental values it supports
Benthic	Referring to organisms living in or on the sediments of aquatic habitats (lakes, rivers, ponds, etc.)
Bioaccumulation	General term describing a process by which chemical substances are accumulated by aquatic organisms from water, either directly or through consumption of food containing the chemicals
Bioassay	A test that exposes living organisms to several levels of a substance that is under investigation, and evaluates the organisms' responses
Bioavailable	The fraction of the total of a chemical in the surrounding environment that can be taken up by organisms. The environment may include water, sediment, soil, suspended particles, and food items
Biomass	All materials that are produced by photosynthesis and potentially useful for the production of organic chemicals or as energy sources
Biota	The sum total of the living organisms of any designated area
Bladderwrack	Bladderwrack is a type of brown algae (seaweed) that grows on the northern Atlantic and Pacific coasts of the United States and on the northern Atlantic coast and Baltic coast of Europe. The main stem of bladderwrack, known as the thallus, is used medicinally. The thallus has tough, air-filled pods or bladders to help the algae float—thus the name bladderwrack. Its Latin name is <i>Fucus vesiculosus</i> and it belongs to the family of kelps
Bleachability	The ease with which pulp is bleached
Bleaching	The process of brightening the fibre by removal or decolourising of the coloured substance
Bleaching efficiency	Some of the oxidising power of a bleaching agent is always wasted in side reactions. Some bleaching agents are more prone than others to undergo wasteful reactions, conversely, some use their oxidising power more efficiently than others. Efficiency is a measure of the degree to which a bleaching agent's oxidising power is used in desirable, kappa reducing reactions
Brightness	Reflectance of blue light from a thick sheet. Sheets having a low brightness appear yellow or brown, those having a high brightness appear white. Brightness may be increased either by decreasing the absorption coefficient (colour intensity) or by increasing the scattering coefficient (e.g. snow vs water)
Brightness reversion	Decrease of brightness of a sheet of pulp or paper due to ageing
Buffer	A solution containing a weak acid and its conjugate weak base, the pH of which changes only slightly on the addition of acid or alkali
Buffer capacity	Amount of acid and/or base that a buffer solution can neutralise

Glossary of terms	
	and still maintain an essentially constant pH. A measure of the relative sensitivity of a solution to pH changes on addition of acids or base
Bulk	The volume of a pulp per unit mass (cm ³ /g). Reciprocal of pulp density (kg/m ³)
Calcination	Decomposition of a solid by heating at temperatures below its melting point, such as the decomposition of calcium carbonate to calcium oxide and CO ₂ (g)
Carbohydrates	Large group of polymer compounds synthesised by plants containing carbon, hydrogen and oxygen, in which the latter 2 elements are usually in the 2:1 proportion of water. Cellulose, sugars and starches are all carbohydrates. The chemistry of carbohydrates is essentially the chemistry of 2 functional groups, the hydroxyl (OH-) and the carbonyl (C=O ²⁻), hence, also technically known as polyhydroxy aldehydes and ketones
Carcinogen	A substance that induces cancer in a living organism
Catalyst	An agent that speeds up a chemical reaction by changing the reaction mechanism to one of lower activation energy
Catchment	The total area draining into a river, reservoir, or other body of water
Cathode	The electrode where reduction occurs
Cation	A positively charge ion. A cation migrates toward the cathode in an electrochemical cell
Cationic	The characteristic behaviour or property of an ion with a positive charge. Cations move to the cathode in electrolysis
Cellulose	Material that forms the framework or cell walls of all plants; the most abundant organic compound in nature. Cellulose is a straight-chain (linear) polysaccharide composed of repeating glucose units, the number of which can vary over a wide range
Chelate	Results from the attachment of chelating agents (multidentate ligands) to a metal ion. Chelates are five- or six-membered rings that include the central metal ion and atoms of the ligands
Chelating agent	A multidentate ligand. It simultaneously attaches to two or more positions in the coordination sphere of a central metal ion. Chelants or chelating agents such as ethylene-diamine-tetra-acetic acid (EDTA) and diethylene-triamine-penta-acetic acid (DTPA) are applied because of good sequestering properties, i.e. their ability to suppress the activity of dissolved transition metal ions without precipitation
Chemical pulp	Fibrous material obtained by removal from the raw material of a considerable part of those non-cellulosic compounds that can be removed by chemical treatment (cooking, delignification, bleaching)
Chronic	Lingering or continuing for a long time; often for periods from several weeks to years. Can be used to define either the exposure of an aquatic species or its response to an exposure (effect). Chronic exposure typically includes a biological response of relatively slow progress and long continuance, often affecting a life stage
Chronic toxicity	Toxicity which results in adverse physiological effects in exposed organisms which appear slowly and persist for long periods following frequent, prolonged, repeated or continuous exposure to a toxicant
Closed-cycle	A mill or industrial plant that has little or no process effluent

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Coarseness	The ratio between a fibre's mass and its length. Generally expressed in either $\mu\text{g}/\text{m}$ or mg/m . Hardwood coarseness can range from 100 to 300 $\mu\text{g}/\text{m}$. Softwood coarseness can range from 300 to 900 $\mu\text{g}/\text{m}$
Complexation	The formation of a compound by the union of a metal ion with a non-metallic ion or molecule called a ligand or complexing agent
Consistency	The weight percent of air dry (or oven dry) fibrous material in a stock or stock suspension. Typical ranges are: low consistency (3-5%, LC), medium consistency (10-15%, MC) and high consistency (30-50%, HC)
Contaminant	Biological (e.g. bacterial and viral pathogens) and chemical (see Toxicants) introductions capable of producing an adverse response (effect) in a biological system, seriously injuring structure or function or producing death
Corrosion	Deterioration of surfaces through erosion processes such as the conversion of metals to oxides and carbonates
Crumple	Capacity for staying wadded
Cytotoxic	Having an adverse impact on cells
Daily production capacity	The weight of products (air dry mass) an installation can produce during one day
Defoamer	Any product that is added to the water-pulp mixture during the manufacture of pulp in a mill to prevent the production of foam or reduce the amount of foam that would otherwise be produced
Detection limit	The smallest concentration or amount of a substance that can be reported as present with a specified degree of certainty by definite complete analytical procedures
Dioxin	Type of organochlorine compound which occurs naturally and is produced in a number of industrial processes
Donnan effect	British chemist whose work was instrumental in the development of colloid chemistry. In electrochemistry, he studied (1911) the electrical potential set up at a semipermeable membrane between two electrolytes, an effect of importance in living cells, known as the Donnan Equilibrium: If diffusible solutes are separated by a membrane that is freely permeable to water and electrolytes but totally impermeable to one species of ion, the diffusible solutes become unequally distributed between the two compartments
Ecologically sustainable development	Development that improves the total quality of life, both now and in the future, in a way that maintains the ecological processes on which life depends
Effluent	A complex waste material (e.g. liquid industrial discharge or sewage) that may be discharged into the environment
Electrical conductivity	The ability of water or a solution to conduct an electric current
Endocrine disrupting substances	Any external agent that upsets or interferes in a specific way with the endocrine system
Endocrine system	The endocrine system in animals and humans controls development, growth, behaviour and other physiological functions. The system consists of the endocrine glands (pituitary and thyroid glands, pancreas, adrenal gland and male and female gonads) and the hormones which these glands produce
Environmental impact or effect	Change in one or several components of the natural environment, that may occur as a result of a particular human activity

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Enzyme	A substance containing protein that catalyses biological reactions
<i>Eucalyptus</i> spp.	The genus <i>Eucalyptus</i> belongs to the family Myrtaceae. Worldwide, Myrtaceae comprises some 140 genera and 3000 species (spp.). In Australia, Myrtaceae is represented by some 75 genera and 1400 species. Myrtaceae is found mainly in Australia, South America and Malesia
Euphotic	Of surface waters to a depth of approximately 80–100 m; the lit region that extends virtually from the water surface to the level at which photosynthesis fails to occur because of reduced light penetration
Euphotic zone	The uppermost layer of a body of water that receives sufficient light for photosynthesis and consequent growth of green plants
Eutrophic	Very biologically productive (in terms of its algal biomass) body of fresh water with relatively high nutrient concentration (>21 µg/L of phosphorus). Frequently resulting in oxygen depletion below the surface layer of a water body
Eutrophication	The over-fertilisation of lakes due to pollution by sewage, runoff from the land, and industrial wastes (inorganic phosphates and nitrates). These compounds act as nutrients, stimulating algal growth to produce huge blooms. Their subsequent decomposition reduces the oxygen content in the water and this leads to the death of the algae themselves and proliferation of bacteria which do not require oxygen and kills most aquatic life
Explosive limit	The explosive limit, also called the explosion limit, of a gas or a vapour, is the limiting concentration (in air) that is needed for the gas to ignite and explode. There are two explosive limits for any gas or vapor, the lower explosive limit (LEL) and the upper explosive limit (UEL). At concentrations in air below the LEL there is not enough fuel to continue an explosion; at concentrations above the UEL the fuel has displaced so much air that there is not enough oxygen to begin a reaction. Concentrations of explosive gases are often given in terms of percent of lower explosive limit (%LEL). Controlling gas and vapour concentrations outside the explosive limits is a major consideration in occupational safety and health. Methods used to control the concentration of a potentially explosive gas or vapour include use of sweep gas, an inert gas such as nitrogen or argon to dilute the explosive gas before coming in contact with air. Use of scrubbers or adsorption resins to remove explosive gases before release are also common. Gases can also be maintained safely at concentrations above the UEL, although a breach in the storage container can lead to explosive conditions or intense fires
Extractives	Compounds extractable from wood with organic solvents. From a physiological standpoint, they can be classified into the following groups: <ol style="list-style-type: none"> 1. Food reserves (fats, fatty acids) 2. Protectants (terpenes, resin acids, phenols) 3. Plant hormones (phytosterols) Composition in <i>E. globulus</i> from Spain is 8.3% hydrocarbons, 13.4% fatty acids, 3% waxes, 32% sterols, 10.8% ketones, 26% sterol esters and 6.5% fats
Fate	Disposition of a material in various environmental compartments (e.g. soil or sediment, water, air, biota) as a result of transport,

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	transformation and degradation
Fats	Triglycerides in which saturated fatty acid components predominate
Fold	The suitability of paper in use to withstand repeated bending, folding and creasing
Fossil fuels	Petroleum, natural gas and coal. These fuels are derived from plant and animal life of millions of years ago
Furan	Type of organochlorine compound which occurs naturally and is produced in a wide variety of oxidation processes
Gas absorption	A unit operation in which a soluble component of a gas mixture is dissolved in a liquid
Green liquor and dregs	Molten inorganic salts, referred to as "smelt", collect in a char bed at the bottom of the recovery furnace. Smelt is drawn off and dissolved in weak wash water in the SDT to form a solution of carbonate salts called "green liquor", which is primarily Na ₂ S and Na ₂ CO ₃ . Green liquor also contains insoluble unburned carbon and inorganic impurities, called "dregs", which are removed in a series of clarification tanks
Guideline trigger values	These are the concentrations (or loads) of the key performance indicators measured for the ecosystem, below which there exists a low risk that adverse biological (ecological) effects will occur. They indicate a risk of impact if exceeded and should 'trigger' some action, either further ecosystem specific investigations or implementation of management/remedial actions
Habitat	The place where a population (e.g. human, animal, plant, microorganism) lives and its surroundings, both living and non-living
Half-life	Time required to reduce by one-half the concentration of a material in a medium (e.g. soil or water) or organism (e.g. fish tissue) by transport, degradation, transformation or depuration
Hardness	The concentration of all metallic cations, except those of the alkali metals, present in water. In general, hardness is a measure of the concentration of calcium and magnesium ions in water and is frequently expressed as mg/L calcium carbonate equivalent
Hardwood	Group of wood species including the following pulpwoods: aspen, beech, birch and eucalypt
Hemicelluloses	Short-chain polysaccharides having a DP (degree of polymerisation) of 15 or less, mainly polymers of sugars other than glucose. Principal hemicelluloses are xylan in hardwoods and glucomannan in softwoods
Hexenuronic acids	Approximately 75% of the hemicelluloses in hardwoods consists of <i>xylan (4-O-methyl-glucuronoarabinoxylan)</i> . Under the kraft pulping conditions, xylan generates hexenuronic (4-deoxy-β-L-threo-4-enopyranosyluronic) acid groups (HexA) which form a considerable part of the residual oxidisable material after pulping (measured by the kappa number). Hardwood kraft pulps, and especially eucalypt kraft pulps, may contain high amounts of hexenuronic acids (HexA), contrary to softwood kraft pulps. HexA have adverse effects in bleaching. The most important ones are: increased consumption of bleaching agents such as chlorine dioxide (ClO ₂) and ozone (O ₃) to reach target brightness, increased brightness reversion and contribution to formation and scaling of oxalates in bleaching equipment
Holdout	Extent to which a paper or board surface resists penetration by

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	liquids
Humic substances	Organic substances only partially broken down that occur in water mainly in a colloidal state. Humic acids are large-molecule organic acids that dissolve in water
Hydrolysis	1. The formation of an acid and a base from a salt by the ionic dissociation of water 2. The decomposition of organic compounds by interaction with water
Hydrophilic Hydrophobic	Having an affinity for water, readily absorbs water Having little or no affinity for water, repels or does not absorb water
Industrial smog	Air pollution in which the principal pollutants are SO ₂ (g), SO ₃ (g), H ₂ SO ₄ mist and smoke
Ion	Electrically charged species consisting of a single atom or a group of atoms. It is formed when a neutral atom or group of atoms either gains or loses electrons
Ion exchange	A process in which ions in solution are exchanged for corresponding ions held on the surface of an ion exchange material. For example, Ca ²⁺ and Mg ²⁺ may be exchanged for Na ⁺ ; or SO ₄ ²⁻ for OH ⁻
Kappa factor	Ratio between 1 st -stage bleaching chemical charge and kappa number. If the 1 st bleaching stage is D, the kappa factor is usually expressed as active chlorine
Kappa number	A measure of residual oxidisable material content in pulp. It is the volume (in mL) of 0.1N potassium permanganate (KMnO ₄) solution consumed by one gram of moisture-free pulp under the conditions specified in TAPPI Test Method T 236 cm-85
Leachate	Water that has passed through a soil and that contains soluble material removed from that soil
Leaching	A hydrometallurgical process in which a metal is dissolved in aqueous solution and then deposited from it after purification
Levels associated with AMT/BPEM	Emission (and consumption) levels that represent the environmental performance that could be anticipated as a result of the application of AMT/ BPEM, bearing in mind the balance of costs and advantages inherent within in the definition of AMT
Ligand	A molecule, ion or atom that is attached to the central atom of a co-ordination compound, a chelate or other complex. May also be called complexing agent.
Lignin	Natural binding constituent of the cells of wood and plant stalks, a complex 3-dimensional polymer of phenylpropane or propylbenzene structure. The chemistry of lignin is characterised by having hydroxyl (OH ⁻) or methoxyl (CH ₃ O ⁻) groups attached to the benzene carbon atoms
Limit of detection	The limit of detection (LOD) for an analytical procedure is the lowest amount of an analyte in a sample that can be detected, but not necessarily quantitated as an exact value. The LOD may be determined by the analysis of samples with known concentrations of analyte and by establishing the minimum level (lowest calibration standard) at which the analyte can be reliably detected. The lowest calibration standard which produces a peak response corresponding to the analyte should be measured n times (normally 6- 10). The average response (X) and the standard deviation (SD) calculated. The LOD is X + (3 x SD)

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Limit of quantitation	The limit of quantitation (LOQ) for an analytical procedure is the lowest amount of the analyte in the sample that can be quantitatively determined with defined precision under the stated experimental conditions. The LOQ is a parameter of quantitative assays for low levels of compounds in sample matrices and is used particularly for the determination of impurities and/or degradation products or low levels of active constituent in a product. The LOQ may be determined by preparing standard solutions at estimated LOQ concentration (based on preliminary studies). The solution should be injected and analysed n times (normally 6-10). The average response and the standard deviation (SD) of the n results should be calculated and the SD should be less than 20%. If the SD exceeds 20%, a new standard solution of higher concentration should be prepared and the above procedure repeated. The LOQ is $X + (10 \times SD)$
Lipids	Several naturally occurring substances (e.g. fats and oils) sharing the property of solubility in solvents of low polarity (such as $CHCl_3$, CCl_4 , C_6H_6 and $(C_2H_5)_2O$)
Lipophilic	Hydrophobic
Littoral zone	Nearshore. Area out from the shore to the depth of the euphotic zone
Loft	Refers to the bulk of pulp fibres and its ability to absorb moisture
Market pulp	Pulp produced for sale to the open market and not used for the manufacture of paper and/or board at the same site
Mass spectrometer	A device used to separate and measure the quantities and masses of different ions in a beam of positively charge gaseous ions
Mesotrophic	Moderately productive (in terms of its algal biomass) body of fresh water with moderate nutrient concentration (11 to 20 $\mu g/L$ of phosphorus)
Microtox®	The Microtox® system is a bioassay to test the acute toxicity on environmental samples and pure compounds based on the natural bioluminescence of the marine bacteria <i>Vibrio fischeri</i> ; in presence of pollutant agents, the natural bioluminescence of <i>V. fischeri</i> is reduced and the toxicity is expressed as the agent concentration which produces a 50% reduction of the initial luminescence (EC_{50}). Nowadays Microtox® is a widespread screening toxicity test for its characteristics of sensitivity, discriminant power, reproducibility and easy application for organic and inorganic pollutants
Minimum level	Defined by USEPA as the level at which the analytical system gives recognisable signals and an acceptable calibration point. The ML for Method 1613 is 10 ppq for 2,3,7,8-TCDD/F, 50 ppq for penta- through hepta-substituted CDD and CDF congeners, and 100 ppq for octa-substituted congeners
Mixing zone	A three-dimensional area of the receiving waters around a point of discharge of pollutants within which it is recognised that the water quality objectives for the receiving waters may not be achieved [SPWQM, 1997]
Monosaccharides	The simplest repeating units of carbohydrates. Also known as sugars or saccharides (glucose and fructose are monosaccharides)
Not detectable	Below the limit of detection of a specified method of analysis

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Oils	Triglycerides in which unsaturated fatty acid components predominate
Oligosaccharides	Carbohydrates that hydrolyse to yield 2-10 molecules of a monosaccharide (maltose and sucrose are disaccharides)
Oligotrophic	Very unproductive (in terms of its algal biomass) body of fresh water with low nutrient concentration (<10 µg/L of phosphorus). Oligotrophic fresh water bodies are usually photosynthesis - limited, very transparent and oxygen rich
Organochlorines	Group name for organic compounds containing chlorine, both those occurring naturally and those formed during bleaching with chlorinated compounds
Osmosis	Diffusion of a solvent through a semi-permeable membrane into a more concentrated solution, tending to equalise the concentrations on both sides of the membrane
Oxidation	The combination of oxygen with a substance, or the removal of hydrogen from it or, more generally, any reaction in which an atom loses electrons
Oxidation/ reduction	The process in which electrons are "lost" or "gained" and the oxidation state (valence) of some atoms increases or decreases. The substance containing atoms whose oxidation states <i>increase</i> is oxidised. The substance containing atoms whose oxidation states <i>decrease</i> is reduced.
Oxidising agent	An agent that makes possible an oxidation process by itself becoming <i>reduced</i>
Paper	Sheet of fibres with a number of added chemicals. According to the basic weight it can be distinguished as follows: Paper <150 g/m ² <paper-board (or board) <250 g/m ² <cardboard
Para (p-)	An isomer with 2 substituents located opposite to each other on a benzene ring
Pelagic	The pelagic zone is the part of the open sea or ocean comprising the water column, i.e. all of the sea other than that near the coast or the sea floor. In contrast, the demersal zone comprises the water that is near to (and thus is significantly affected by) the coast or the sea floor. The name is derived from the Greek <i>pélagos</i> , which is roughly translated as "sea" but is more accurately translated as "open sea"
Phenols	Phenol is a benzene ring with one -OH radical replacing hydrogen. Phenols are compounds which contain additional chemical groups bound to this basic structure (each replacing hydrogen)
Photodegradation	Breakdown of a substance by exposure to light; the process whereby ultra-violet radiation in sunlight attacks a chemical bond or link in a chemical structure
Photolysis	The decomposition of a compound into simpler units as a result of the absorption of one or more quanta of radiation
Photosynthesis	The process by which green plants convert carbon dioxide (CO ₂) dissolved in water to sugars and oxygen in the presence of chlorophyll using sunlight for energy. Photosynthesis is essential in producing a lake's food base and is an important source of oxygen
Phytoplankton	Microscopic free floating aquatic plants, mainly unicellular algae, that live suspended in bodies of water and drift about because they cannot move themselves or because they are too small to swim
Pitch	Resinous material in virgin pulps

Glossary of terms	
Polysaccharides	Carbohydrates that hydrolyse to yield more than 10 molecules of a monosaccharide (cellulose and starch are glucose polymers)
Primary treatment	Physical treatment of wastewater to reduce settleable and floatable solids
Protocol	A formally agreed method and procedure for measuring an indicator; it defines the sampling, sample handling procedures and sample analysis
Pulping	The process of converting raw fibre (e.g. wood) or recycled fibre to a pulp useable in papermaking
Reactivity	Reactivity may be defined in terms of the fraction of the residual oxidisable material that a bleaching agent is capable of removing (i.e. $\Delta \kappa / \Delta$ bleaching agent)
Redox potential	An expression of the oxidising or reducing power of a solution relative to a reference potential. This potential is dependent on the nature of the substances dissolved in the water, as well as on the proportion of their oxidised and reduced components
Reducing agent	An agent that makes possible an reduction process by itself becoming <i>oxidised</i>
Refinability	The ease with which paper or pulp can be treated in a refiner as measured in kWh/ODt or MJ/kg
Salinity	The presence of soluble salts in or on soils or in water
Saponification	The hydrolysis of a triglyceride by a strong base. The products are glycerol and a soap
Schopper Riegler value	Refining pulp is one of the most important stages in the paper production process and influences strongly the sheet forming and its physical properties. The Schopper Riegler value ($^{\circ}$ SR) is a measurement of the rate at which a diluted pulp suspension may be de-watered and is specified according to the Zellcheming Merkblatt V/7/61 (Germany)
Secondary treatment	Biological treatment of wastewater to reduce BOD and toxicity; it normally reduces TSS also
Sediment	Unconsolidated mineral and organic particulate material that settles to the bottom of aquatic environment
Selectivity	Selectivity is the degree to which a pulping or bleaching agent can lower the kappa number without dissolving or damaging the other components of the fibre, cellulose and hemicellulose (i.e. $\Delta \kappa / \Delta$ viscosity). Selectivity can be loosely defined as the ratio of attack on lignin to attack on carbohydrate
Soaps	The salts of fatty acids, e.g. $\text{RCOO}^{-}\text{Na}^{+}$, where the R group is a hydrocarbon chain containing from 3 to 21 C atoms
Softwood	Group of wood species including the following pulpwoods: pine and spruce
Sootblowing	Blowing of soot carried over from the furnace section of a boiler. This carry-over, along with the high temperatures in the heat transfer section of the boiler, causes continuous deposition and fouling on the outside of heat transfer tubes. Sootblowing is usually done with steam
Specific water consumption	The amount of fresh water consumed during production (surface water, ground water) which is taken out from external resources. This fresh water demand is related to air dry net production and is expressed as m^3/t . Fresh water that is only used for cooling purposes (i.e. water that had no contact with fibres and additives) and that is directly discharged into the environment is

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	not included. Wastewater generated in steam and power plants on site is also not included
Stakeholder	A person or group (e.g. an industry, a government jurisdiction, a community group, the public, etc.) who have an interest or concern in something
Stock	The mixed suspension of fibre and other materials used to form paper
Stripper Stripping (desorption)	Equipment used to carry out stripping (desorption) A unit operation in which a volatile component of a liquid mixture is transferred into a gas
Strong acid	An acid that is completely ionised in aqueous solution
Strong base	A base that is completely ionised in aqueous solution
Sub-lethal	Involving a stimulus below the level that causes death
Sulfidity (on AA)	The ratio of sodium sulfide to AA or $\text{Na}_2\text{S}/(\text{NaOH} + \text{Na}_2\text{S})$, as g/L Na_2O
Sulfidity (on TTA)	The ratio of sodium sulfide to TTA or $\text{Na}_2\text{S}/(\text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3)$, as g/L Na_2O
Total nitrate (NO_3)	Nitrates are a form of nitrogen found in aquatic ecosystems and an essential plant nutrient. In excess amounts nitrate can cause significant water quality problems. Together with phosphorus, nitrates in excess amounts can accelerate eutrophication, causing dramatic increases in aquatic plant growth and changes in the types of plants and animals that live in the stream. This, in turn, affects dissolved oxygen, temperature, and other indicators. Excess nitrates can cause hypoxia (low levels of dissolved oxygen) and can become toxic to warm-blooded animals at higher concentrations (10 mg/L or higher) under certain conditions. The natural level of ammonia or nitrate in surface water is typically low (less than 1 mg/L) but the level of ammonia or nitrate in the effluent of wastewater treatment plants can be up to 30 mg/L. Sources of nitrates include wastewater treatment plants, runoff from fertilised lawns and cropland, failing on-site septic systems, runoff from animal manure storage areas, and industrial discharges that contain corrosion inhibitors
Total phosphorus	Phosphorus is an essential plant nutrient and the one that most often controls aquatic plant (algae and rooted plant) growth. Total phosphorus includes both soluble and particulate forms of phosphorus and is measured in milligrams per litre (mg/L). Elevated levels of total phosphorus increase plant growth producing increased plant/algae decomposition, which depletes dissolved oxygen concentrations. The water quality problems that result from phosphorus overload are collectively known as eutrophication. Phosphorus enters aquatic systems: as organic material like dead organisms or yard waste, attached to soil particles, with fertilisers, with industrial by-products and via resuspension from lake bottom sediments
Toxicant	A chemical capable of producing an adverse response (effect) in a biological system at concentrations that might be encountered in the environment, seriously injuring structure or function or producing death
Toxicity	The inherent potential or capacity of a material to cause adverse effects in a living organism
Transition metals	Consist of the 38 elements in groups 3 through 12 of the periodic

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	table of the elements. As with all metals, the transition elements are both ductile and malleable, and conduct electricity and heat. One interesting aspect of transition metals is that their valence electrons, or the electrons they use to combine with other elements, are present in more than one shell. Consequently, they often exhibit several common oxidation states. A partial list of transition metals includes: titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), molybdenum (Mo), silver (Ag), cadmium (Cd), tantalum (Ta), tungsten (W), platinum (Pt), gold (Au) and mercury (Hg). Transition metals of interest in chemical pulp bleaching are Mn, Fe and Cu because they catalyse the decomposition of hydrogen peroxide. Transition metals of interest for their environmental impact are Cd and Hg because of their poisoning effect
Trigger values	These are the concentrations (or loads) of the key performance indicators measured for the ecosystem, below which there exists a low risk that adverse biological (ecological) effects will occur. They indicate a risk of impact if exceeded and should 'trigger' some action, either further ecosystem specific investigations or implementation of management/remedial actions
Triglycerides	Esters of glycerol (1,2,3 propanetriol) with long-chain monocarboxylic (fatty) acids
Trophic status	Trophic means nutrition or growth. Trophic status is a means of classifying lakes and describing lakes' processes in terms of productivity: <i>oligotrophic</i> lakes have low nutrients and plant growth, <i>eutrophic</i> lakes are well nourished with high nutrients and plant growth and <i>mesotrophic</i> lakes fall somewhere in between oligotrophic and eutrophic
Turpentine	A mixture of terpenes, principally pinene, obtained by the steam distillation of pine gum recovered from the condensation of digester relief gases from the cooking of softwoods by the kraft pulping process
Uptake	A process by which materials are absorbed and incorporated into a living organism
Viscosity	Measured by dissolving pulp fibres in CED and observing the time taken for the solution to pass through a standard capillary (TAPPI Test Method T230 om-94). Viscosity is expressed in centipoises (cP) or milliPascal-seconds (mPa s), which are numerically the same. It is related to cellulose molar mass (degree of polymerisation) and indirectly to fibre strength
Volatile	Having a low boiling or subliming pressure (a high vapour pressure)
Water quality objective	A numerical concentration limit or narrative statement that has been established to support and protect the designated uses of water at a specified site. It is based on scientific criteria or water quality guidelines but may be modified by other inputs such as social or political constraints
Watershed	All land and water areas that drain towards a receiving body (river or lake). Also called drainage basin or water basin
Weak acid	An acid that is only partially ionised in aqueous solution
Weak base	A base that is only partially ionised in aqueous solution
Whole effluent toxicity testing	The use of toxicity tests to determine the acute and/or chronic toxicity of effluents

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Whole mill effluent	All of the process effluent generated by the mill excluding uncontaminated cooling water and surface run-off as it enters the aquatic environment
Woodfree paper and/or board	Paper and board having in principle only chemical pulp in its fibre composition; in practice however it may contain a small amount of other fibres or pulps (less than 5% non-cellulosic compounds)
Yield	The amount of useful fibre after pulping and/or bleaching expressed as a percentage of the raw fibre on an oven dry basis
Zooplankton	The animal portion of the living particles in water that freely float in open water. They eat bacteria, algae, detritus and sometimes other zooplankton and are in turn eaten by other planktivorous fish

APPENDIX A

SYNOPSIS OF THE TEAM

APPENDIX B

**CHEMISTRY
OF
CHLORINE DIOXIDE BLEACHING**

APPENDIX C

ARTICLE 5 AND ANNEX C OF THE STOCKHOLM CONVENTION

APPENDIX D

VERIFICATION MATRIX