Minimum-Impact Mills:
Issues and Challenges

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Abstract

The vision of minimum-impact manufacturing, be it “a completely ecocyclic system for high quality paper production which efficiently utilizes the energy potential of the biomass” or simply “an industry we are so proud of we encourage our grandchildren to join,” has captured the imaginations of the industry’s leaders. There is an opportunity to move public perception from “the pulp and paper industry is the largest water consumer and biggest polluter” to “the pulp and paper industry is ecologically sound, while producing recyclable products from renewable resources.” However, public trust must be earned through addressing local issues such as odor, plumes and other aesthetic issues.

Elimination of ECF or TCF bleaching effluent is not necessary for environmental protection, nor is it necessarily the place to start. Process development toward the minimum-impact mill should begin by concentrating on minimizing releases from the pulping and recovery processes.

Today there are no kraft mills operating full time which completely recover all bleach plant effluent. In other words there are no “zero” effluent kraft mill bleach plants.

The minimum-impact mill does not mean “no bleach plant effluent,” or “zero effluent,” nor is it exclusive to one bleaching technology. It is a much bigger concept. The minimum-impact mill is one which:

- maximizes pulp yield and produces high quality products that are easily recyclable, and/or safely combustible;
- maximizes the energy potential of the biomass;
- minimizes water consumption;
- minimizes wastes - gaseous, liquid and solid - and disposes of them optimally;
- optimizes capital investment; and
- creates sustainable value to shareholders, customers, employees and to local, regional, and national communities.

The industry’s environmental progress over the last 30 years, while maintaining economic viability, bodes well for the next 30 years and provides confidence that the minimum-impact mill of the future will be realized.

Introduction

Throughout the major pulp producing regions of the world, research is focusing on minimizing or eliminating the discharge of process waste waters to the receiving environment.
Some of the strategies that have been proposed are:

- Minimum-Impact Manufacturing -MIM [1];
- The Minimum-Impact Mill - MIM [2];
- Bleach Filtrate Recovery - BFR® [3];
- Closed Loop Bleaching - CLB [4];
- The Eco-Balanced Pulp Mill [5];
- Progressive Systems Closure [6];
- Effluent Free [7];
- Closed Cycle Technology [8];
- Ecocyclic Pulp Mill; and
- Partial Closure [9].

A strong thrust within many of these process technology developments is toward recovery and elimination of bleach plant effluent. However, a direct link between bleaching processes and environmental responses of concern has not been demonstrated. Furthermore, current environmental research is pointing toward other processes within the mill, rather than bleaching, as the sources of substances causing environmental responses.

In light of such information, some have questioned the wisdom of placing virtually exclusive emphasis on reduction or elimination of bleach plant effluent. They ask for example where is the evidence that these technological developments will lead to reduced environmental impact? Will new bleaching sequences complicate process chemistry? Will demand for wood increase due to lower process yields? Will energy consumption increase? Will complicated and expensive control and back-up systems be required?

Finally there is considerable debate as to compatibility and the merits of both ECF and TCF based bleaching strategies within minimum-impact manufacturing processes incorporating recycle and recovery of bleaching effluent.

Given the questions regarding the necessity of eliminating bleaching effluent and the controversy surrounding the compatibility of different bleaching processes, the Alliance for Environmental Technology (AET) convened a scientific workshop to examine and debate the assertions that:

- in the context of the minimum-impact mill, elimination of bleaching effluent is the "right thing to do" to improve the environmental performance of bleached kraft pulp mills with secondary effluent treatment; and
- ECF and TCF-based processes are compatible with minimum effluent process design concepts.

Invited experts were asked to answer a series of questions. The responses and opinions were discussed and debated by the participants, including the experts and those who represented AET member companies. This paper is a summary of the findings of that workshop.

The Environmental Significance of Eliminating Bleaching Effluent

Receiving Water Protection

The invited experts were asked to answer the following questions:

- Under what circumstances is it environmentally important or not important to eliminate bleach plant effluent?

*See listing following references.

• What fraction of toxicologically important loadings can be attributed to bleaching effluents compared to other sources?

• Is elimination of effluents from other sources and/or bleaching necessary for receiving water protection?

Clearly, if treated bleach plant effluent is identified as contributing significantly to negative impacts in the aquatic environment, it would be important to eliminate such effluent. Conversion of mills to ECF and TCF has virtually eliminated production of chlorinated persistent and bioaccumulative compounds. In the case of ECF, the chlorinated organic compounds that are still discharged are chemically similar to naturally occurring chlorinated substances found in many receiving environments. The current consensus is that these are not persistent and bioaccumulative and are broken down naturally through such processes as photodegradation.

Environmental research continues to focus on sub-lethal effects such as altered reproductive systems and induction of the cytochrome P450 mixed function oxygenase (MFO) detoxification systems in fish exposed to treated pulp mill effluent. Reproductive responses have been observed in fish exposed to treated effluent from bleached pulp mills employing a variety of bleaching processes including ECF and TCF, and also effluent from unbleached pulp mills. Therefore, a link to bleaching processes is not supported by current evidence. Natural estrogens like lignans and phytosterols are present in spent cooking liquors as a result of their presence in the so-called wood extractives. Also natural stilbenes may be present in spent cooking liquors and enter the environment through spills and losses. Some stilbenes are known to affect reproductive systems. Stilbenes may also carryover to the bleach plant and may be subsequently chlorinated. Such chlorinated compounds have been tentatively identified in an effluent from a mill using both chlorine and chlorine dioxide in the first stage of bleaching.

Field studies at 5 bleached mills in North America have shown that reproductive responses in fish, such as depressed plasma sex steroid hormone levels and changes in male secondary sexual characteristics, can be eliminated while still discharging treated effluent [10]. This indicates that there may be a "no effect" level attainable by today's bleached pulp mills with secondary effluent treatment.

MFO induction has been observed in both wild fish and laboratory assays with effluent from both bleached and unbleached mills. Suspected sources are inducers present in spent cooking liquor, inducers released or modified during bleaching and inducers produced in secondary treatment systems. Current evidence suggests that minimizing spent cooking liquor inputs to the treatment system may be one effective way to reduce this response. Whether inducers are released during bleaching, are carried into bleaching, or are formed during bleaching, are unanswered questions requiring more research.

Based on current scientific evidence, the best approach to eliminating these environmental responses is to focus on minimizing losses from spent cooking liquors and other liquors containing wood extractives, and improving washing to minimize carryover to the bleach plant, rather than eliminating bleaching effluent.
Reasons for Elimination of Bleaching Effluent

The invited experts were asked to answer the following question:

- Are there compelling reasons other than biological responses for eliminating bleaching effluent?

Elimination of bleaching effluent might be considered in cases where fresh water resources are scarce, when the receiving water or ecosystem is particularly sensitive or where low flow receiving waters are unable to adequately assimilate the increased organic carbon load.

An important aspect of this discussion was the notion of a “pristine” environment. Many richly diverse “pristine” receiving ecosystems are deeply “colored” and are not “crystal” clear and so the residual color from bleaching effluent would not create an unacceptable aesthetic impact. Many “pristine” receiving ecosystems are not very productive. In such cases, the organic carbon emitted in treated mill effluents can have a beneficial effect if it enters the food chain and enhances desirable productivity of the aquatic ecosystem [11]. The high condition factors for fish living downstream of mills results from this carbon utilization. When considering elimination of mill effluent and its associated organic carbon, one must consider which compartment of the environment is best for the carbon’s ultimate destination. It may be more environmentally preferable to discharge the carbon in liquid effluent and have it enter the aquatic food chain than to discharge it as CO₂ in the boiler exit gases or perhaps as precipitated organic material bound for a landfill site.

Elimination, or partial elimination, of bleaching effluent should also be considered in existing mills (with or without secondary treatment) if it is more cost effective, compared to an external treatment option, to reach a desired outcome.

Local and Global Characteristics of a Minimum-Impact Mill

The pulp and paper industry has the opportunity to be a truly ecologically sustainable industrial process. Such an ideal process may be defined as one that:

- uses naturally renewable raw materials in such a manner that local demand stays in balance with sustainable growth;
- does not require thermal or electrical energy from an outside source but satisfies its demand by using its own wastes;
- recovers and regenerates any required chemicals from its own waste streams;
- uses make-up chemicals that are abundantly available in nature and returned to nature in their original form without causing excessive point loading; and
- has waste streams that cause no adverse changes to the local, regional or global environment.

Other considerations in the characteristics and definitions of a minimum-impact mill include the concepts that mills should strive to:

- minimize resource consumption (water, chemicals, wood, energy);
- minimize “pollution” (water, air, noise, solid waste);
- create a safe, productive and attractive working environment;
maximize product quality (brightness, strength, stability);
minimize aesthetic disturbances such as plumes of water vapor and noxious odors; and
maximize profits, employment, taxes paid and returns to shareholders and communities.

Concerns were expressed that the current drive to minimize effluent was increasing the amount of equipment required and increasing energy consumption. In assessing any move in this direction, total energy consumption must be considered. Is it better to evaporate bleach plant effluent, if to generate the additional energy, more fossil fuel must be burned? We must recognize that fossil fuel combustion has its own environmental impacts such as emissions of SO₂, CO₂ and mercury.

A significant portion of the potential energy of a mill is lost in low grade thermal heat. In some cases technologies are being employed that increase energy consumption, such as cooling towers, to remove low grade heat streams, thus wasting useful energy, while at the same time emitting water vapor, a potential aesthetic disturbance. In light of some of these examples, it was suggested that perhaps the most important long term goal for minimum impact manufacturing was to improve energy utilization.

Technology Options for Eliminating Bleaching Effluent

Available Technology

The invited experts were asked to answer the following question:

What processes currently in practice or under commercial development are available to eliminate or partially eliminate bleach plant effluent?

Partial or full bleach plant effluent elimination is in the very early stages of industrial practice. The most popular option is "partial" or alkaline effluent recovery (i.e., recovery of the first extraction stage effluent).

Some mills are just beginning to recover a portion of alkaline effluent and some do so only occasionally. Among those identified were:

- Union Camp, Franklin VA - C-Free® softwood line - ozone/ECF
- Champion International, Canton NC - BFR® softwood line - ECF
- MoDo Cell AB, Husum - hardwood line - ozone/ECF
- Louisiana Pacific, Samoa CA - softwood - TCF
- Aspa Bruk AB, Aspa Sweden - softwood - TCF
- Crestbrook Forest Industries, Skookumchuk, B.C. - softwood - ECF

Even fewer mills attempt to recover acid first stage effluent. Among those mentioned were:

- Union Camp, Franklin VA - C-Free® softwood line - ozone/ECF
- Champion International, Canton NC - BFR® softwood line - ECF

Neither of these mills has fully "closed" the acid stage. The Union Camp mill has reported requiring a purge to control calcium scaling of up to 1.5 m³/ADt with an associated COD discharge of 5-6 kg/ADt. The
Champion BFR® process also requires a metals purge via the Metals Removal Process (MRP®), however, the volume is very low and the associated COD loss is also very low, at less than 0.5 kg/ADt [3,12].

The important finding is that today there are no kraft mills operating full time which have successfully demonstrated sustained, complete bleach plant effluent “closure”. In other words there are no “zero” effluent kraft mill bleach plants. It appears that at a very minimum, a purge will always be required until the non-process metals are no longer brought into the mill.

Compatibility of ECF and TCF Bleaching with Bleach Plant Elimination

The invited experts were asked to answer the following questions:

- Are ECF and TCF based bleaching compatible with processes for partial or complete elimination of bleaching effluent?

- What are the criteria for compatibility?

Both ECF and TCF based bleaching strategies are compatible with a high degree of system closure. Up until just recently, it was believed that TCF was necessary for bleach plant effluent elimination; however, with the development of new technologies and the concept of alkaline recovery, ECF is being seen by some as the more compatible. The main reason is that chlorine dioxide bleaching is less sensitive to the build up of organics and metals in highly closed water recycle circuits compared to ozone and peroxide bleaching.

In both ECF and TCF-based processes, whether partial or full recycle of bleaching effluents, chloride and potassium can build up in the liquor cycle. Purging or leaching precipitator ash or ash recrystallization technology such as the Chloride Removal Process (CRP®) are methods proposed to control the chloride and potassium to levels found in open mills.

The selection of the appropriate method to control chloride and/or potassium to a particular level is constrained by such things as:

- the amount of chlorine dioxide used in the bleach plant;

- the extent of bleaching effluent recovery; and

- the amount of chloride entering the liquor cycle from bleaching or other sources such as wood and make-up chemicals.

For low kappa number, (i.e., 10) ECF and TCF bleaching sequences, precipitator catch purging was proposed to control chloride and potassium levels. However, the yield loss suffered in achieving such low kappa numbers compared to conventional values of 25-30 is significant. Maximizing pulp yield was recognized as a key feature of any minimum-impact mill design. Suggestions for maximizing pulp yield while delignifying to low kappa number included pulping to 25-30 kappa number, followed by two-stage oxygen delignification.

From this discussion emerged another key issue - the minimum-impact mill should maximize yield while maximizing energy production from the recovered organic material. The energy produced would be more than sufficient to run the mill, with excess energy available for export.
Operating Strategies, Training, Monitoring and Control Systems

The invited experts were asked to answer the following question:

- What new operating strategies, training programs, monitoring and control systems are required for elimination of bleaching effluent?

The discussion and presentations concentrated on approach. In particular a step-wise gradual approach for existing mills was advocated. From an environmental impact perspective, concentration on the unbleached part of the mill was emphasized as it represented the largest losses of environmentally significant compounds.

A key issue emerged during the Question and Answer session which followed the panel discussion. Should mills strive to recover all bleaching effluent or simply endeavor to minimize effluent volume and then develop advanced technologies for treatment?

One argument proposed that efforts should initially be directed toward minimizing effluent volume to approach 5 m³/t without increasing interstage carryover and chemical consumption and then develop technologies to treat the remaining volume through evaporation, spray drying, precipitation, etc. Reasons for such an approach were to minimize the risk to an already complex recovery system through corrosion, evaporator scaling and increased loading.

The counter-argument suggested, particularly for those mills practicing some form of chloride removal (either crystallization or purging), that the reduction of chloride and potassium content in the black liquor had provided positive benefits. Furthermore, the oxidized recovered organics did not represent a substantial additional load to the recovery boiler. Constraining the bleach plant to 5 m³/t net volume without subsequent recycle and recovery may unnecessarily increase chemical consumption without providing an environmental improvement other than lower volume.

Economics and Environmental Aspects

Necessary Process Configurations

The invited experts were asked to answer the following questions:

- Are there any necessary process configurations required before contemplation of reduction or elimination of bleach plant effluent i.e., extended and/or oxygen delignification, evaporator, recovery boiler, recasturcizing capacity etc.?

- What incremental technology and equipment and operating strategies are required to manage internal streams to prevent discharges to the environment?

Essentially any mill can start with its existing equipment to move toward elimination of bleach plant effluent. The analogy “what condition do you need to be in before starting an exercise program?” was used to try to capture this notion.

Notwithstanding the above, a desire and need must be present. For new mills, this may be to allow siting in a sensitive area, to obtain financing and to minimize the cost of production. For existing mills, expansion at a site without increasing environmental impact, compliance with new limitations,
access to new markets or the avoidance of capital and operating costs for secondary or tertiary treatment may provide the “need.”

Foundation technologies proposed were:

- High quality chip preparation;
- Extended pulping;
- Oxygen delignification;
- Closure of the unbleached pulp fibre line (closed screen room, black liquor spill control, condensate segregation and cleaning, spill control and recovery, efficient washing, segregation of cooling water, effective warm, cold and hot water distribution)

Incremental Impacts

The invited experts were asked to answer the following questions:

- What is the incremental impact of elimination of bleach plant effluent on solid waste emissions, hazardous air pollutants, waste treatment plant efficiency, energy consumption and sodium-sulfur balance?
- What is the incremental impact of elimination of bleach plant effluent on mill capacity, capital cost, bleaching cost, overall operating cost, energy and wood consumption?

The bottom line was that there is no simple answer. For existing mills, capacity would decrease to permit processing the additional organic and inorganic load. If capacity decrease is to be avoided, a major rebuild would be required thus increasing capital cost. Operating costs would increase to run new processes and additional equipment. Energy consumption on-site would increase depending on the complexity and amount of new equipment and bleaching processes employed (Table 1) [13]. Off-site energy to produce purchased chemicals may decline. The net impact was not established.

Reaching the low kappa numbers (8-10) required for TCF processes and for low chlorine dioxide consuming ECF sequences, using a single oxygen delignification stage, would decrease pulp yield and increase wood consumption by 7-8% compared to a 25 kappa number ECF sequence (see Table 1) [13].

<table>
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<th>Case</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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* Part must be sulfide-free
** Gross energy demand at mill site
Considerable discussion surrounded the notion that low chloride levels in white liquor (5 g/L) was necessary. Designing to such low levels required the unbleached kappa number (in the ECF case) to be as low as 8-10 with its associated yield penalties. It was noted that at least one new boiler is operating at up to 20 g/L without adverse effects on corrosion or plugging and so process designs could accommodate higher kappa number targets and higher chloride input to the recovery cycle [14].

It was agreed that solid waste would increase through: 1) the necessity to remove precipitator dust; and 2) removal of transition metals. Mills with existing waste treatment plants should see efficiency increase through a lower volume to treat which could be traded for lower energy consumption for aeration etc. Energy consumption would likely increase to run new processes and new equipment such as a second oxygen delignification stage. The impact could be mitigated by recovery of some of the waste energy presently leaving the mill.

**Technology and Environmental Issues**

### Dioxin Formation in Recovery Boilers

The invited experts were asked to answer the following question:

- What is the probability of formation of dioxins and furans from incineration of recovered and recycled chlorine (inorganic and organic) in recovery boilers or dedicated incinerators?

The Canadian Council of Ministers of the Environment have set an emission guideline of 0.5 ng/m$^3$ of dioxins and furans expressed as TEQ for municipal waste incineration stack gases. The German government’s more stringent standard was reported as 0.1 ng/m$^3$ expressed as TEQ. Data presented showed that emissions from a recovery boiler burning black liquor with 0.1 to 2% chloride by weight on black liquor solids under two different loadings (65-80% of rated capacity), were well below the guidelines and stringent standards for municipal waste incineration. Emissions of 0.0004 to 0.005 ng/m$^3$ expressed as TEQ were reported [15].

In another mill with 5.4% Cl$^-$ in the black liquor on a dry basis (34 g/L NaCl in white liquor), stack emissions ranged from 0.0022-0.0048 ng/m$^3$ expressed as TEQ [15]. Significantly, 2378-TCDD was not detected. Also 2378-TCDF not detected in one test and in the other test it was found at close to the detection limit.

The discussion noted that boiler burning conditions typically are sufficient to preclude any dioxin formation within the boiler per se. De novo formation, if any, would be occurring in the cooler sections such as the electrostatic precipitator. Mill black liquor systems contain sufficient chloride, even without recycle of bleaching effluent, for some de novo formation to occur. But it is likely inhibited by the sulfur and sodium present. The panelists agreed that, if formed, dioxins and furans would more likely be found in the ash (precipitator catch) than in the gas phase. This could be a concern if precipitator ash was to be purged to the waste treatment plant or directly to the receiving environment for potassium and chloride control.

Significantly, 2378-TCDD was not-detected in analyses of precipitator catch taken from a mill recycling chlorinated organic compounds from colour removal system
sludge to the black liquor with subsequent destruction in the recovery boiler [16]. It was estimated that a 1000 ADt/d mill firing black liquor with chloride content typical of current West Coast Canadian mills, would emit less than 6 mg/year of dioxin expressed as TEQ. Furthermore, 2378-TCDD would not be detected and 2378-TCDF would likely not be detected.

Management of Non Process Elements, Impacts on Product Quality

The invited experts were asked to compare and contrast approaches for elimination of bleaching effluent in regard to:

- management and removal of non-process elements, scaling, metals removal and chelation requirements;
- brightness development, stability, pulp and paper quality and fiber chemistry; and
- bleach plant process control, flexibility and sensitivity.

A key to successful recovery and recycle of bleach plant effluent is management of non-process elements. Controlled purges are required for: chloride, potassium, sulfur, phosphorus, silica, aluminum, calcium, magnesium, manganese and iron. No particular strategy was identified as being a superior approach to management. Clearly any mill contemplating closure must anticipate the negative impacts of build-up of non-process elements and design systems for controlled purges. Examples discussed earlier for chloride and potassium control were removal and disposal of a portion of the precipitator catch, or the Chloride Removal Process - CRP®.

There are many unknowns regarding the impact of bleach plant effluent on pulp and paper quality, and fiber chemistry. When re-

using and recycling filtrates, excellent washing in the bleach plant was identified as a key issue. Carryover of organics and transition metals, particularly in TCF bleaching sequences, may increase chemical consumption and make reaching a desired brightness more difficult. Also the final product may contain organic and inorganic impurities. It will be important for pulp producing companies to work closely with their customers to ensure that their customers final products are not adversely affected.

Conventional drum washers, typical of most existing bleach plants, may not be sufficient in minimum effluent bleach plants. Thus a consequence of eliminating bleach plant effluent may be a need to rebuild the beach plant to maintain product quality and minimize chemical consumption.

Experience in alkaline effluent recovery shows ECF-based sequences would likely be more effective as chlorine dioxide is more selective and is less sensitive to carryover of organics and transition metals.

Regulatory Direction

The invited experts were asked the following question:

- What will be the regulatory climate for future mills?

From a scientific perspective, environmental effects monitoring will become more important as a way of demonstrating "absence of harm". One possible method of demonstrating absence of harm may be through observation of specific cellular responses. An emerging issue which warrants monitoring is endocrine disruption.
Voluntary approaches such as the industry's response to dioxin generation, Canada's Accelerated Reduction and Elimination of Toxics (ARET) program, the Sustainable Forestry Initiative and Europe's EMAS (environmental management program) will become more popular. Ecolabelling and life cycle analysis will also set priorities and drive environmental programs.

Pulp and paper mills have presently the "appearance of a polluting industry" because of residual odor and visual aesthetic disturbances from water vapor. Until some of these very real community impacts are addressed, the industry will continue to have trouble building public credibility in spite of strong technical arguments demonstrating "absence of harm".

Plenary Summary

The vision of minimum-impact manufacturing, be it "a completely ecocyclic system for high quality paper production which efficiently utilizes the energy potential of the biomass" or simply "an industry we are so proud of we encourage our grandchildren to join," has captured the imaginations of the industry's leaders. There is an opportunity to move public perception from "the pulp and paper industry is the largest water consumer and biggest polluter" to "the pulp and paper industry is ecologically sound, while producing recyclable products from renewable resources." However, public trust must be earned through addressing local issues such as odor, plumes of water vapor and other aesthetic issues.

Elimination of ECF or TCF bleaching effluent is not necessary for environmental protection, nor is it necessarily the place to start. Process development toward the minimum-impact mill should begin by concentrating on minimizing releases from the pulping and recovery processes.

Today there are no kraft mills operating full time which completely recover all bleach plant effluent. In other words there are no "zero" effluent kraft mill bleach plants.

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- minimizes water consumption;
- minimizes wastes - gaseous, liquid and solid - and disposes of them optimally;
- optimizes capital investment; while
- creates sustainable value to shareholders, customers, employees and to local, regional, and national communities.

The industry's environmental progress over the last 30 years, while maintaining economic viability, bodes well for the next 30 years and provides confidence that the minimum-impact mill of the future will be realized.

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References


Alliance for Environmental Technology

Mission

The Mission shall be to promote an accurate understanding of the environmental and economic benefits resulting from the use of chlorine dioxide in modern pulp bleaching cycles. In this regard, the Association will marshal sound and objective scientific data and sponsor research where data is inconclusive regarding chlorine dioxide to promote an accurate understanding of its environmental benefits and risks and will work to achieve sound public policy decisions affecting the use of chlorine dioxide in pulp bleaching.

AET Member Companies

Alabama River Pulp
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