

# **Zero Discharge:**

**TECHNOLOGICAL PROGRESS  
TOWARDS ELIMINATING  
KRAFT PULP MILL LIQUID EFFLUENT,  
MINIMISING REMAINING WASTE STREAMS  
AND  
ADVANCING WORKER SAFETY**

**By Jay Ritchlin and Paul Johnston**

**Prepared for *Reach for Unbleached!*  
the Zero Toxics Alliance Pulp Caucus,  
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## EXECUTIVE SUMMARY

**T**he manufacture of wood pulp is the single most important method for chemically converting wood into useful products, and as such is a highly important component of the global manufacturing industry in both economic and environmental terms. In certain regions, pulp and paper manufacture is a dominant industry and is responsible for a large portion of regional economic activity.

At the same time, pulp and paper manufacture can have potentially serious impacts on environmental quality and hence the health of both human and wider ecosystems. In the United States alone, pulp and paper manufacturing is recognised as one of the nation's most highly polluting industries. The US Environmental Protection Agency's 1994 Toxic Release Inventory (TRI) reported that such facilities generate the greatest quantities of polluting substances (measured in pounds per facility) of any industry sector. Each facility was reported as generating an average of 457,457 pounds of reportable toxic substances every year. In addition, these industrial plants discharge an estimated 6.01 billion pounds of other pollutants not covered by the TRI into national waterways and public sewerage systems.

There is, however, great potential for both improving efficiency and moving towards sustainability in this industrial sector. This paper details the state of current research and technological development in the field of ecologically responsible kraft pulp manufacture. Developments designed to mitigate and eliminate human and environmental health impacts are emphasised. Also explored in depth is the potential for operating closed loop pulp mills which discharge no wastewater into our rivers and oceans and minimise the quantity and toxicity of air pollution and solid waste.

While the authors recognise that issues such as sustainable forestry, control of consumer demand and maximising the use of recycled and alternative fibres are critical components in moving the entire pulp and paper industry onto a sustainable footing, these issues are not addressed here.

The concept of a closed loop mill aims to eliminate discharges to the aquatic environment, recycle and reuse all possible solid and liquid process wastes, and reduce air emissions to the lowest possible quantity and toxicity. Ultimately, a mill should be able to produce its primary product, with most or all of its by-products suitable for use as secondary products. To date, much of the by-product in existing mills attempting to go closed loop is burned as a source of energy for the mill. While this may indeed qualify as a "reuse", it is a far from ideal reuse for much of the waste-stream. Future research must continue to develop more sustainable reuse options for kraft pulping solid wastes, as well as pulping methods that result in purified by-products that can serve as feedstock for other manufacturing processes.

Since the discovery of highly toxic dioxin compounds in pulp mill effluent there has been a great deal of work on reducing the toxicity of liquid discharges from pulp mills. There have been efforts at both end-of-the-pipe control, and at eliminating precursors to known toxic compounds. Despite progress on these fronts, a variety of toxic impacts persist. Genetic damage to fish and toxicity to micro-organisms that help to break down waste are still present in secondarily treated effluent from mills employing only chlorine dioxide as a bleaching agent. The presence of resin acids and other unidentified constituents continue to present toxicity problems for all kraft mills, regardless of bleaching chemicals. Ecosystems near pulp mills which meet relatively tough existing environmental regulations continue to experience significantly reduced diversity in the plants and animals able to live near them. These facts emphasize the need to pursue closed loop strategies.

Additionally, the effects of mill process changes on workers and local communities has rarely been factored into the mainstream debate on best routes forward. Exposure to bleaching chemicals, process gasses, emissions from treatment ponds, and bacteria and fungi on wood chips and sludge all directly impact the health and safety of the people working in the mill and the people who live near by. Decisions on how to make an ecologically responsible pulp mill must take these issues into account.

This paper reviews the literature on a wide variety of factors that will influence the overall impact of a pulp mill on its total environment. An attempt is made to draw conclusions about which pathways the research and practical experience indicate are the best ways forward to a kraft pulp industry with the lowest possible negative influence on its surroundings. Areas addressed include: effluent toxicity, air emissions, sludge and solid waste, raw material utilisation (i.e. energy usage, chemical consumption, wood yield and paper quality), bleaching methods, capital, conversion and operating costs, and worker and community health and safety. Current progress on closed loop mills is reviewed and evaluated with a particular look at non-bleach plant improvements, non-process element control to manage the build-up of recycled chemicals that can harm mill equipment and product quality, bleaching chemical choices and effects on mill equipment. Finally, looking to future improvements in the industry, emerging work on alternative pulping methods is discussed and a summary of next steps and gaps in existing research is presented.

A different quality and quantity of information is available for each area reviewed. Effluent toxicity has been, and continues to be, extensively researched. While the most advanced mills in the world may have similar final effluent toxicity, those employing only oxygen based bleaching chemicals continue to have the lowest toxicity on a full spectrum of toxicity parameters. As important as this area of study is under existing circumstances, closed loop operations will eliminate all toxicity to aquatic environments by eliminating all discharge into them.

**The characteristics of air emissions, on the other hand, have not been well documented, nor have there been adequate comparison studies between various mill types. The current regulatory standards are inadequate. Existing data suggest that oxygen based closed loop operations will have either no difference in air emission impacts, or an improved one. However, this conclusion warrants further testing, especially as emissions to air will continue as a major output of closed loop mills.**

**The production of waste fibre sludge should end with a closed loop pulp mill. Until that time, some sludge will continue to be produced as mills increase the degree of effluent recycling they are able to accommodate. An increasing push towards land-spreading of this material is being seen throughout many jurisdictions with intensive pulp production. This method of sludge disposal is an area of concern, as sludge constituents are not well identified, the sludge in any given mill is highly variable, and the fate of the sludge on land is not thoroughly researched. Well designed, independently monitored pilot projects of significant duration are necessary before this practise becomes widespread. The closed loop process will likely increase the amount of solid waste being generated in the dregs, grit, and ash of pulp mills as these waste streams become the only remaining options for the purge of chemicals and elements that can upset the process or damage equipment. While the quantity of dregs, grit, and ash in a closed loop mill will increase over current mill designs, total solid waste will be significantly reduced. Recovery of process chemicals from these purge points should be maximised. Remaining wastes will likely be committed to secure landfills. Therefore, more work on the composition and reprocessing of these waste streams is needed.**

**The review of total energy consumption is a critical element of evaluating an ecologically responsible pulp mill. A major factor in this calculation is the energy balance inherent in the various bleaching chemicals. Almost without exception, the literature indicates that oxygen based bleaching sequences have a superior efficiency over chlorine dioxide based sequences in this area. Even when combined with potential increased energy consumption in some oxygen based configurations, these mill designs are the most energy efficient available.**

**Wood yield and paper quality are two areas that have been frequently used by the North American pulp industry, in particular, to suggest that oxygen based bleaching sequences are neither ecologically, nor economically preferable. Many of these comparisons cite reductions in wood yield based on how the wood fibre is turned into pulp. This type of comparison is spurious and has no bearing on yield variations due to the type of bleaching used in a mill. Setting aside the yield effects of pulping processes, assertions made about yield loss due to oxygen based bleaching have been based on measurements of carbohydrate content in effluent and the resulting Chemical Oxygen Demand (COD), a standard regulatory measurement. These have suggested that there is between 0-1% increase in wood consumption for oxygen based production. These estimates, based on secondary measurements, have not been substantiated on a practical basis. The widely reported fall in**

**yield of 6% at the Wisaforest TCF mill in Finland is thought to be due to the fact that the mill switches between ECF and TCF pulp production and as a result is not optimised for TCF production methods. Södra Cell has not seen a change in wood consumption since full conversion to TCF bleaching, in common with reports from the Louisiana Pacific mill in Samoa California after conversion to TCF. While there is undoubtedly a need to evaluate the yield aspect in greater detail, on the basis of the available evidence, yield loss does not appear to be a significant factor detracting from the overall benefits of using oxygen based bleach processes.**

**Similarly, claims made about inferior pulp quality from oxygen based sequences, while touching on an area of real concern for a small portion of the market pulp produced world-wide, seem to have been exaggerated, presented as representative of the full spectrum of bleach kraft pulp, and continually based on outdated information. As a general observation it appears that oxygen based kraft pulps show no appreciable shortcomings in quality relative to chlorine dioxide bleached products and that the unhelpful debate which has surrounded the product quality issue is of rapidly diminishing relevance both to pulp users and wider consumer markets.**

**The costs of converting an existing mill to closed loop operations are one area where there is extensive and often contradictory information in the public realm. Finding estimates that consider all relevant aspects of mill conversion and have access to enough detailed, mill-specific information is nearly impossible. In general, it appears that costs for converting an existing mill to a closed loop mill are similar regardless the type of bleaching chemicals used. The authors acknowledge that the actual cost of any conversion will be highly influenced by the state of the mill in question and we encourage the industry to open the evaluation process to public scrutiny. New, or “greenfield”, mills appear to be most financially efficient when designed to optimise oxygen based bleaching and a closed-loop design.**

**As mentioned earlier, the health and welfare of the workers and surrounding communities has not been a regular feature of the debate over how to achieve an ecologically responsible pulp industry. This is most unfortunate because workers, especially, have often had to suffer increased workplace concentrations of hazardous chemicals as laws preventing those substances from entering the environment have been tightened. While no bleaching chemical is benign, the conclusion based on extensive available literature is that the oxygen based bleaching chemicals present the least immediate and long term hazards for workers and the general public. Additionally, the upgrades inherent in designing a closed loop mill should include other improvements, such as light gas strippers and, non-condensable gas collection systems which will remove hazardous and foul smelling pollution from the air and increase workplace safety.**

**Finally, we look at the current state of efforts to build and run an actual industrial scale closed loop mill. Efforts continue with both chlorine dioxide- and oxygen-based systems.**



**Progress has been made on both fronts, with non-process element control (i.e., managing the build-up of chemicals which are recycled through the system), being the greatest barrier to final effluent circuit closure. For oxygen based sequences, the control of metals in the process liquor is the greatest challenge, while systems employing chlorine dioxide must have as a primary concern equipment damage from the recirculation of highly corrosive chlorides. A final solution has not been achieved for either approach. However, mills attempting to run chlorine dioxide based recycling have not been able to run at a high degree of effluent closure for extended periods. Oxygen based sequences have reached the lowest effluent flow levels and been able to run for longer periods between system purges.**

**The conclusion, given the best research in all of these areas, is that oxygen based, closed loop kraft pulp mills are the best route forward to a successful and ecologically responsible kraft pulp industry.**

## INTRODUCTION

**T**he goal of this paper is to examine the potential for ecologically and economically sustainable kraft pulp mills. This paper reviews technical and scientific literature on a wide range of factors that will influence the overall impact of a pulp mill on its total environment. The emphasis is on efforts to achieve "closed-loop," or Totally Effluent Free (TEF) mills which eliminate all liquid effluent and minimise the quantity and environmental impact of air and land discharges. An attempt is made to draw conclusions about which areas of research and practical experience indicate the best pathways to move towards a kraft pulp industry with the lowest possible negative influence on its surroundings. Areas addressed include: effluent toxicity, air emissions, sludge and solid waste, raw material utilization (i.e., energy usage, chemical consumption, wood yield and paper quality), bleaching methods, capital, conversion and operating costs, and worker and community health and safety. Current progress on closed loop mills is reviewed and evaluated with a particular focus on non-bleach plant improvements, non-process element control, bleaching chemical choices and effects on mill equipment. Finally, looking to future improvements in the industry, emerging work on alternative pulping methods is discussed and a summary of next steps and research gaps is presented. Each area reviewed has a different quality and quantity of information available and some effort is made to indicate where this is a significant factor in coming to useful conclusions, although this paper in no way attempts to critique all the research referred to in the text.

This issue is relevant because the manufacture of wood pulp is the single most important method for chemically converting wood, and as such is a highly important component of the global chemical manufacturing industry in both economic and environmental terms. World consumption of paper products continues to rise, and is expected to do so for some time (Myreen 1994). This trend obviously has potential negative impacts on the environment and must be addressed through education and public policy at the same time as efforts proceed towards technological solutions to pollution caused by the industry.

Pulp manufacturing accounts for one percent of the worlds' total economic output (Johnston, *et al* 1996), and in some regions is a highly significant factor in the local economy. At the same time, pulp and paper manufacture has the potential to seriously impact environmental quality and hence the health of both human and wider ecosystems. For example, in the United States, pulp and paper manufacturing is recognized as one of the nation's most highly polluting industries. The US Environmental Protection Agency's 1994 Toxic Release Inventory (TRI) reported that such facilities generate the greatest quantities of polluting substances (recorded in pounds per facility) of any industry sector.

Each facility was reported as generating an average of 457,457 pounds of reportable toxic substances every year. In addition, these industrial plants discharge an estimated 6.01 billion pounds of other pollutants not covered by the TRI into national waterways and public sewerage systems (USEPA 1993). These figures emphasise the importance of minimising the environmental impacts of pulp manufacturing.

There are several major methods for producing pulp from wood fibre: mechanical pulping, sulphite pulping, and sulphate (kraft pulping). Each method has several variations, and produces pulps of different quality. The dominant method, by far, is kraft pulping followed by some form of bleaching. The top pulp producing nations clearly show this trend. Bleach kraft pulp production alone accounted for 48% of the US total, 44% in Canada, 46% in Sweden, 66% in Japan, and 69% in Brazil during 1994 (Pulp & Paper International 1994).

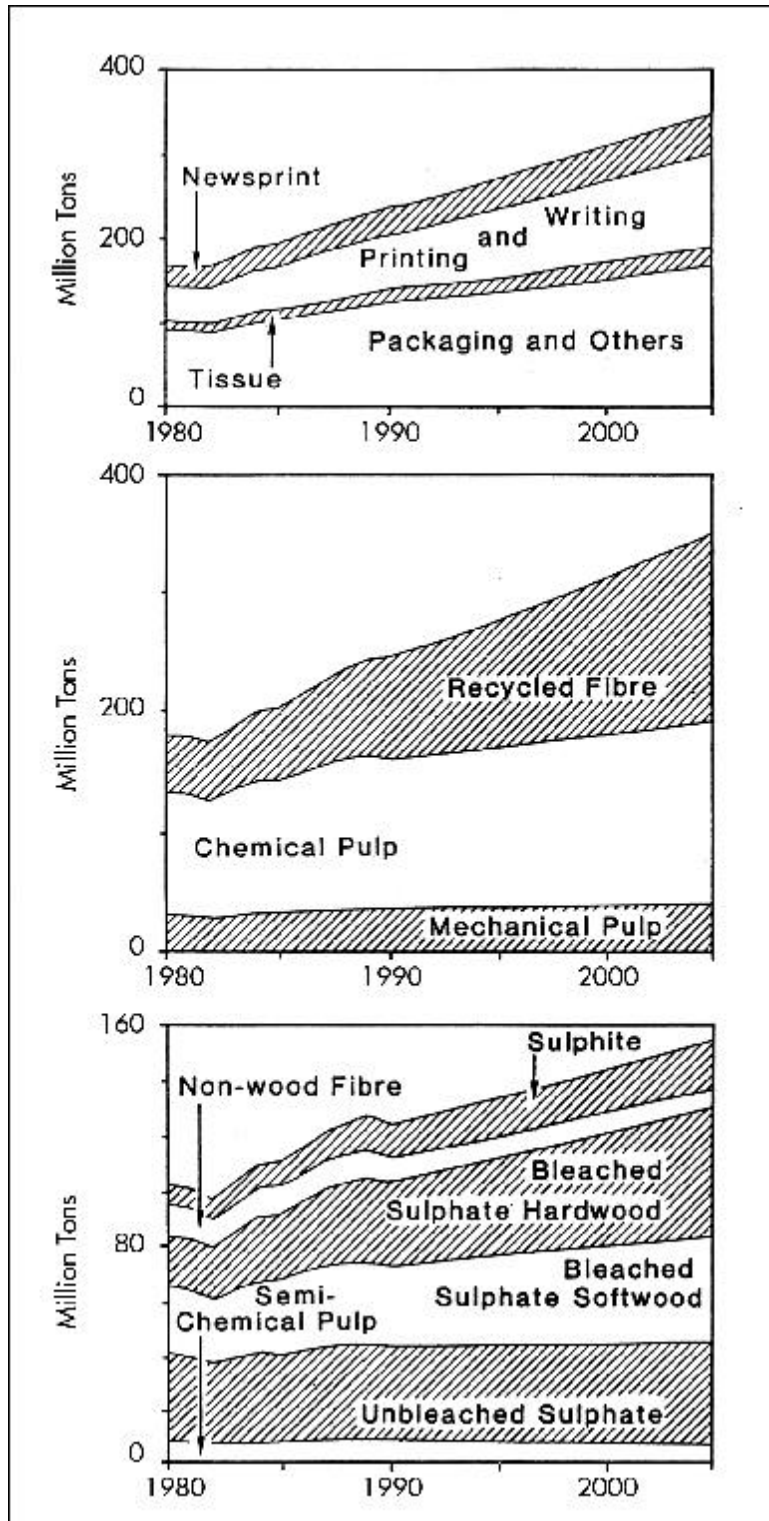


Table 1: Productio (x1000t)						
	Sulphate		Sulphite		Mechanical	
	B	U	B	U	M	S
USA	28249	19870	1334	0	5338	3719
Canada	10958	1474	313	512	10851	440
China*	Total 893		Total 89		Total 473	
Sweden	4990	2048	639	82	2858	250
Japan	6928	1638	9	0	1636	214
Finland	5157	687	0	0	4181	-
Brazil	3606	1247	17	-	333	37
CIS	1140	866	194	316	Total 915	
France	1025	494	262	0	886	119
Norway	346	162	189	41	1516	90

**Designing and operating pulping processes to acceptable and sustainable standards necessitates the consideration of all aspects of the pulp production cycle. These include, *inter alia*, the source of the pulp mills' raw material (furnish), the quality of the produced pulp, the quality of the liquid effluent and solid wastes produced, and process economics, including energy efficiency. In some cases, for example, concerning liquid effluent quality, a good body of data exists. In the case of issues such as atmospheric pollution, worker safety and current sludge disposal practices, the data are far less comprehensive. The standard suite of air pollution parameters: nitrogen oxides (NO<sub>x</sub>), total reduced sulphur (TRS), particulate matter (PM), and carbon dioxide (CO<sub>2</sub>) are insufficient and are only slowly being augmented by measurements of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) in some jurisdictions. Improvements in these and other measurements are still necessary. The composition of precipitator ash generated from recovery boilers, particularly in closed cycle mills, has received relatively little attention despite being a major component of the waste stream. Sludge generated by mill effluent treatment plants are sometimes spread on forest and agricultural land, yet remain poorly characterised in chemical and toxicological terms. Much of the debate surrounding the environmental impact of pulp mill operations has centred around the production of the chlorinated dioxins and dibenzofurans in chlorine-based bleaching processes together with other toxic chemicals present in the liquid effluent. Although this is an extremely important aspect of the environmental impacts associated with the industry, and has generated extensive and widely reviewed literature, (see: e.g. Johnston *et al* 1996) this focus has tended to obscure other important environmental aspects. Accordingly, the imperative for improvements in these areas has also remained less extensively discussed.**

**Paper products are an extremely important part of modern society. They are aggressively marketed and consumer demand continues to grow. Inevitably, therefore, pulp and paper manufacture has both significant economic and environmental impacts. Nonetheless, it is also true that there is a great potential for improving efficiency and for moving towards**

**sustainability in this industrial sector. While sustainable forestry, control of consumer demand and maximising the use of recycled and alternative fibres are critical components in moving the industry as a whole onto a sustainable footing, they are not considered in this document. This paper is restricted to consideration of the state of current research and technological development in the field of primary pulp manufacture. It emphasises developments designed to minimise and eliminate human and environmental health impacts and concentrates upon the potential for operating pulp mills in a closed configuration.**

## **MODERN BLEACH KRAFT MILL TYPES**

**T**he processes used in pulp and paper production are a significant determinant of the environmental impacts associated with these operations. In particular, effluent quality is contingent upon the bleaching process. Much research has focused upon the bleaching technology employed because this component of the production process has historically been associated with the formation of chlorinated dioxins and other environmentally significant chlorinated organic chemicals. Bleaching technology is also a key determinant of the potential for the closure of mill process circuits to achieve zero effluent operation.

**In this context, a certain confusion exists with respect to the terminology commonly in use. Accordingly, it must be stressed that where this paper indicates similarities in the environmental performances of Elemental Chlorine Free (ECF) and Totally Chlorine Free (TCF) mills, only the most advanced, state-of-the-art ECF mills (see “Advanced ECF”, below) approach the standards achievable in the TCF mills. Currently, most North American mills do not meet these state-of-the-art criteria. They have not, in the main, invested in oxygen delignification or extended cooking systems, regarded as key contributors to improved environmental performance (Södra-Cell 1996) and a key prerequisite of TCF bleaching. Moreover, it should be recognised that the newly proposed Cluster Rule in the USA does little to drive mills towards the highest achievable standards. By contrast, the regulations adopted in British Columbia and Ontario, Canada which require the elimination of adsorbable organic halogens (AOX) are having the effect of moving mills in these jurisdictions toward the lowest possible environmental impact. With the above in mind, several approaches can be identified which are being taken in order to reduce the environmental effects of bleached kraft pulp mills. The three major process pathways being explored, developed and implemented are:**

**TCF low-flow**, mills using extended cooking/oxygen delignification, and bleaching with ozone, hydrogen peroxide and peracetic acid, either alone or in various combinations. Enzymes may also be used in bleaching. The majority of these mills are in Scandinavia and either have been, or are conducting trials with high degrees of effluent recycling (e.g. Sodra-Varo, MoDo-Hussum, and SCA-Östrand in Sweden, and Metsä-Rauma and Wisaforest in Finland).

**Advanced ECF low-flow**, including oxygen delignification, 100% chlorine dioxide substitution, possibly some ozone or peroxide in the sequence and some bleach plant effluent recycling (Champion's BFR mill and Union Camp's ozone+ECF mills in the USA, MoDo and Södra-Mörrum in Sweden and SAPPI-Ngondwana in the Republic of South Africa).

**Traditional ECF**, 100%  $\text{ClO}_2$  substitution only. No extended cooking or oxygen delignification (Most mills in N. America that are described as ECF).

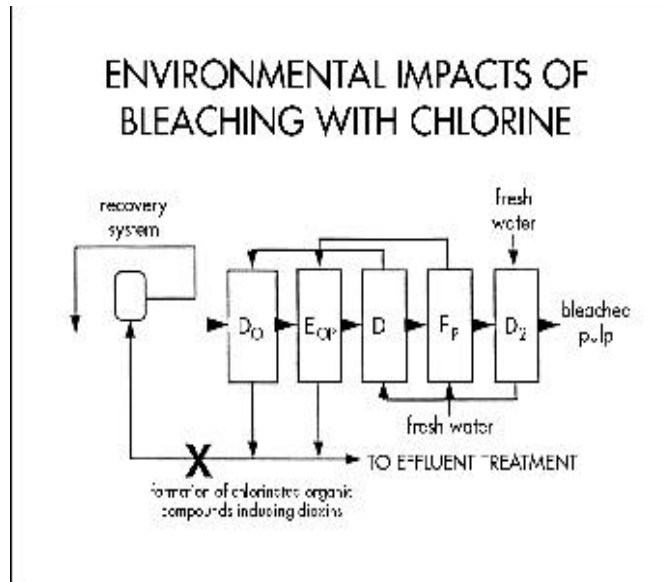
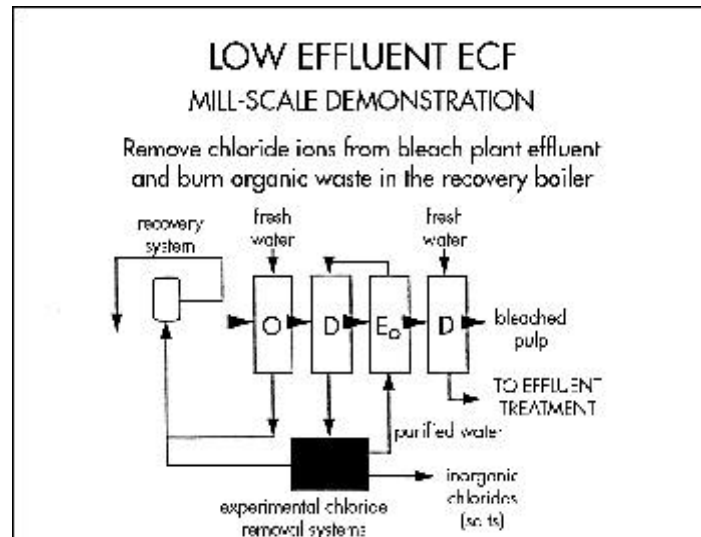
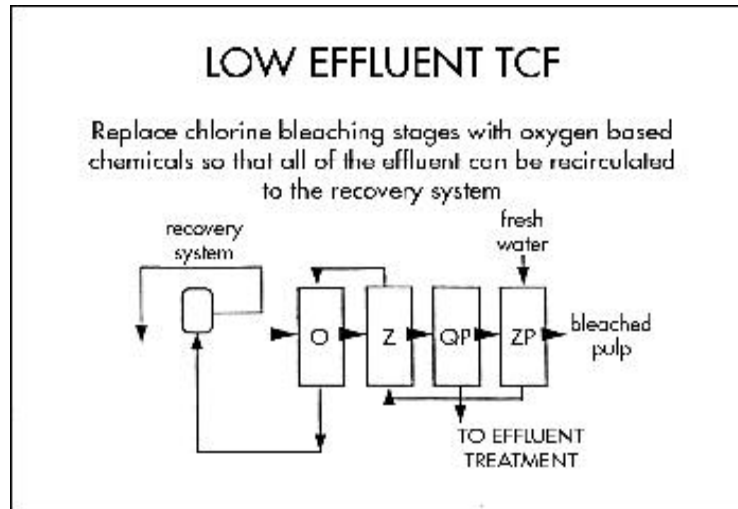


Figure 2: Three major process pathways. Adapted from Blum 1997

As a result of the various process systems under which chlorine dioxide is used, ECF can technically describe a range of processes with widely differing environmental performance (Södra-Cell 1996). Mills and process configurations that have not moved to at least 100%  $\text{Cl}_2$  substitution are not considered in this paper. These mills, which do not meet even the minimum requirements of the US Cluster Rules, cannot be regarded as adequately positioned to evolve into environmentally acceptable and sustainable kraft pulp mills.

## EFFLUENT TOXICITY

**L**iquid effluent discharged to adjacent aquatic systems has traditionally comprised the bulk of material discharged as waste from pulping and bleaching operations, as well as a significant proportion of the known environmental toxicity. The environmental impacts of these effluents have been widely reported in the literature, which has been regularly reviewed (see: Johnston *et al.* 1996). Accordingly, reducing the toxicity of discharged effluent through various treatment regimes and process modification has been a major focus of research. Some recent data suggest that the toxicity of treated effluent from advanced ECF mills can be similar to treated TCF effluent (Verta *et al.* 1996) but the data have been derived from processes using different mill furnishes and specific process sequences. The most advanced TCF effluents generally show the lowest toxic effects for effluents tested using standardised techniques. Moreover, many studies continue to suggest that even the most advanced ECF mills produce effluent with a higher toxicity than TCF mills. (Vida *et al.* 1997; Cates *et al.* 1995; Kovacs *et al.* 1995; Rappe & Wagman 1995; Rosenber *et al.* 1994; Tana *et al.* 1994). Some of these studies also suggest that formation of bioaccumulative dioxins and furans, while indeed greatly reduced in mills using ECF processes, continues to occur (Environment Canada, 1998). This is most probably due to the partial dissociation of chlorine dioxide to produce elemental chlorine, throwing some doubt on the accuracy of the term ECF (Johnston *et al.* 1996). Research has recently been conducted on ecosystem integrity and biodiversity in waters which receive treated effluent from ECF mills in British Columbia, Canada. These mills meet some of the strictest existing standards in the world. The data continue to show a strong correlation between exposure to the effluent and severe ecosystem disturbance (Bard 1998).

An interesting example is the Fletcher Challenge owned Tasman Mill in Kawerau, New Zealand, which introduced a 100% ECF bleaching system in 1998 alongside its existing oxygen delignification, enzyme pre-bleaching and secondary treatment systems. The mill discharges 150,000 cubic metres of effluent into the Tarawera River per day. Evidence presented by the Department of Conservation (DOC) at consent hearings in November 1997, when the mill was still 50% ECF and 50% chlorine gas, describes how mill effluent appeared to act as a barrier to the upstream migration of juvenile indigenous fish species. DOC also cited evidence of disease in fish and raised concerns over the absence of certain

**indigenous fish in the polluted lower river. DOC described how adult whitebait (*Inanga*) are completely absent in the main stem of the lower river. It remains to be seen how far these adverse effects are reduced, if at all, as a result of introducing a 100% ECF system given the existence of oxygen delignification, enzyme pre-bleaching and secondary treatment systems prior to the change (NZ DOC 1997).**

**In general, treatment of effluent reduces toxicity in the case of all effluents (Verta/ 1996), although toxicity of the effluent can itself influence the effectiveness of biological treatment processes. There are indications that TCF effluents may be simpler to treat. For example, reduction of AOX and chlorate, which are only generated in ECF, but not TCF, bleaching (Germgard *et al* 1981), requires anaerobic conditions, while COD and BOD, produced in both ECF and TCF mills, are most effectively removed in aerobic conditions (Duncan *et al* 1995). Because TCF mills do not produce AOX and chlorate, the treatment systems needed are, therefore, likely to be less complex. A recent study, which contradicts assertions that ECF and TCF effluents have a similar toxicity, demonstrates that ECF effluents are more toxic to methanogenic organisms than TCF effluents. A greater potential for anaerobic biodegradation was also demonstrated for TCF effluent (Vidal *al* 1997) as might have been expected from these results. Nonetheless, certain types of chronic toxicity do appear in both the treated ECF and TCF effluents (Stauber *al* 1996).**

**Despite the general reductions in toxicity which have been achieved for pulp effluents, certain biologically active chemicals present in the wood furnish can pass through treatment plants without being degraded. Hence, impacts on fish populations have been detected following exposure to a wide variety of mill effluents employing various bleaching processes (see: Johnston *et al* 1996). Recent research from British Columbia has shown that dilute concentrations as low as 2% of treated bleach effluent from kraft mills with 100% ClO<sub>2</sub> substitution can cause actual, physical genetic damage to salmon (Easton *al* 1997). This research needs to be replicated for the effluents of the most advanced ECF mills, as well as TCF mills. Indeed, these observations have provided a compelling argument for developing Totally Effluent Free mills.**

**In addition to the identified problems of chemicals in the wood furnish, alternative bleaching processes require changes in process chemicals. One group of chemicals which has given rise to concerns are the chelating agents (EDTA and DTPA are examples). Such agents are used to remove metallic contaminants in the pulp before bleaching with peroxide and are employed in most currently operating TCF mills as well as in some ECF mills with peroxide stages. Metallic contaminants would otherwise reduce the efficiency of the peroxide (Södra-Cell 1996). These chelating agents are currently discharged to effluent treatment and appear to be relatively resistant to degradation. At present, there does not appear to be an efficient decomposition pathway for the chelants EDTA and DTPA and their presence may initially inhibit the efficiency of activated sludge secondary treatment (Larisch and Duff 1997). However, treatment with aluminum sulphate can result in a 65%**



EDTA reduction in treated effluent, and photochemical degradation is known to be a possibility (Saunamaki 1995). While most toxicity studies seem to support the claim that any chelants and metals coming through to treatment and/or the final effluent are not a significant environmental problem (Saunamaki 1995), this issue needs to be more specifically studied in relation to aspects other than direct toxicity. In particular, the ability of chelating agents to mobilise metals after discharge, and the potential consequences of this for natural systems requires comprehensive evaluation.

Some studies suggest that efficient acid washing of the pulp before bleaching can eliminate the need for chelating agents (Bouchard *et al* 1995), but this may be very dependant on furnish. Moreover, acid wash strategies that can fully eliminate the need for chelants may cause unacceptable viscosity loss in the pulp. Metal removal treatments using acid washing need to be further developed into processes which avoid degradation of the final product quality (Lapierre *et al* 1997). Alternative chelants are being investigated. Hydroxycarbolates (glycolate and galactarate) have been shown to act as effective complexing agents in closed TCF process simulations (Gevert *et al* 1997a). Moreover, commercial research has led to the identification of chelants that may be used to control process metals and which appear to be readily biodegradable (Lockie 1996). While these initiatives show promise, the usefulness, degradability and toxicity of such alternative chelating compounds requires exhaustive evaluation. It is inevitable that some of these chemicals will be purged from pulp production systems as a result of the need to control the build up of non-process elements, particularly in the bleach lines. The purging of non-process elements from pulp production systems is, therefore, an issue of some importance in relation to the potential for full mill closure and zero-effluent operation in both TCF and ECF systems and is reviewed below.

## AIR EMISSIONS

**W**hile the advantages of in-mill process changes with respect to the use of water resources and concomitant impacts upon receiving aquatic systems are well documented, the implications for changes in air emissions (principally from recovery boiler systems) as a result of closed-loop operation have been less well explored. Analysis has been somewhat subjective. For example, Champion International has declared an intention to investigate changes in recovery boiler emissions as a result of the BFR process, but have stated prior to testing that they do not expect these to be of significance (Caron & Delaney 1998). Accordingly, relatively few data have been published in the literature on this subject.

Södra Cell has reported occasional increases in  $\text{NO}_x$  emissions at its low-flow TCF plants located at Värö and Mörrum, but these have been reduced and attributed to the numerous mill start ups and shutdowns as the various processes were refined (Södra Cell 1996;

Lovblad 1997b). It is likely that data collected over several years of operation will be required to confirm operational standards and trends. In the meantime, the company is considering additional technological controls to reduce NO<sub>x</sub> emissions to 1 kg/tonne of pulp or less (Södra Cell 1996). The increased quantity of organic matter reaching the recovery boiler from recycling of effluent has increased the amount of electricity the mill is capable of generating for itself. As a source of energy from combustion, recovery boilers are regarded as preferable to hog fuel boilers in terms of the relative amount of air pollutants generated (Lutheet *al* 1997). Information contained in the annual environmental reports from mills in Scandinavia producing both advanced ECF and TCF pulp suggest that overall releases of NO<sub>x</sub>, TRS, SO<sub>2</sub> and particulate matter are similar for both production processes (Södra Cell 1996; MöDö 1997). This includes comparisons between mills with and without effluent recycle. This data gives a somewhat incomplete picture, however, since the standard air emission parameters measured for pulp mills do not capture the full range of contaminants of concern which can potentially be emitted. While NO<sub>x</sub> (nitrous oxides), CO<sub>2</sub> (carbon dioxide), TRS/SO<sub>2</sub> (total reduced sulphur/ sulphur dioxide), and PM (particulate matter) continue to be important, there are other emissions which must be considered.

The potential for products of incomplete combustion (PICs) and other hazardous compounds, including chemicals such as the chlorinated dioxins, from ECF mills is an obvious area of concern (Environment Canada 1992). PCBs, dioxins and furans have been found in fly ash from the burning of sludge from kraft mills (Kopponen 1994) raising concerns that substantial quantities may be emitted to atmosphere. One study from British Columbia, Canada suggests that the flue gas from recovery boilers with high chloride loading due to salt-laden wood does not represent a major source of dioxin/furan emission to air, however, levels of these persistent organic pollutants have been observed in other recovery boiler emissions (Lutheet *al* 1997).

In addition, some of the hazardous air pollutants (HAPs), or trace air contaminants and total reduced sulphur (TRS) compounds such as methyl mercaptan, chlorine dioxide, formaldehyde and chloroform are a priority for individual regulation and control, particularly with respect to their potential to compromise mill worker health and safety. Accordingly, Södra Cell has installed a "light stripper" for cleaning the less polluted condensates in the evaporator stage. The aim is to eliminate emissions of polluted condensates and reuse them in the process. This company has also installed the first weak gas system in Sweden (Södra Cell 1996). The weak gas system is able to collect malodorous gases and combust them in the recovery boiler. This limits malodorous discharges and aerial emissions of process sulphur (Södra Cell 1996). Both of these systems were added at the Värö Bruk mill. This mill already used TCF bleaching, and generates bleach plant effluent of between 10-15 m<sup>3</sup>/ADT.

Hydrogen chloride (HCl) and methanol are other major air pollutants of concern produced in recovery boilers (Andrews *et al* 1996). Older, direct contact evaporator recovery boilers emit greater quantities of these pollutants, as well as generating significant sulphur emissions. Accordingly, upgrading of mills to closed loop operation should ideally include installation of non-direct contact, low odour recovery boilers (Simons 1994). This type of recovery boiler should be fitted at newly constructed mills. In addition to reducing environmentally significant air emissions these recovery boilers also allow the firing of black liquor solids (BLS) at greater concentrations (up to 80% BLS) than direct contact units. In turn, this increases recovery boiler capacity and generally reduces emissions of TRS and  $\text{SO}_2$  (McCubbin 1996).

Methanol and a wide range of other HAPs (hazardous air pollutants) and VOCs (volatile organic compounds) are also generated in the process lines and vented from oxygen delignification (OD) systems and white liquor oxidation systems (Crawford *et al* 1995; NCASI 1994). Methanol, especially, may be generated in large quantities. Reducing the methanol content of the final post-oxygen washer shower water is likely to have a significant positive impact on emissions of methanol from oxygen delignification systems (Crawford *et al* 1995). It is not clear from the literature if this measure will also lower the concentrations of the other HAP and VOC compounds present. Hence, the USEPA Cluster Rules outline techniques for these gaseous streams to be collected and introduced into the fire zone of the recovery boiler (USEPA 1998). It has also been pointed out (Crawford *et al* 1995) that there is a need to routinely monitor the areas around the OD system for HAPs and VOCs.

The question of precisely what to monitor in the way of air emissions from pulping operations is an important one. The USEPA suggests that methanol is an acceptable surrogate target compound for monitoring and regulation of gas phase HAP compounds. This assertion is, however, somewhat difficult to verify. A wide range of HAPs and VOCs have been detected in studies of pulp mill air emissions (NCASI 1994). Moreover, it appears that no direct correlation exists between reduction in emissions of methanol and reduced emissions of other pollutants such as methyl mercaptan and chlorobenzene among the variety found in actual working mill environments. Phenols, as well, do not appear to be reduced proportionally to methanol (Simons 1994). This is of significance in terms of potential long term, low level worker and community exposure to the other compounds. It implies that monitoring needs to be extended in scope and should encompass not only recovery and power boiler stacks but also cooling towers, process vents from oxygen delignification, washers and chemical generation processes. Additionally, internal mill working areas need to be subjected to monitoring as well as external environments. In bleaching operations, TCF mills emit no chlorinated compounds, which are generated in ECF mills by bleaching or chlorine dioxide manufacture (EKONO 1997). Chloroform, dichloroacetic acid methyl ester, 2,5-dichlorothiophane and other volatile organochlorine compounds have been found in the vent gases of mills using 100% chlorine dioxide

substitution. These compounds have also been found to volatilise from the treatment ponds of these mills, but were almost non-existent when investigated in a TCF mill (Juuti/ 1996). Side reactions during chlorine dioxide bleaching lead to the formation of chloroform, chlorinated phenolics and other chlorinated organics, as well as phenol and methanol (Simons 1994). The precursors for the chlorinated organic chemicals are not present in TCF bleach plants. While the concentrations of chlorinated compounds have decreased markedly from levels generated by mills employing elemental chlorine as a bleaching agent, they have not been eliminated by the use of chlorine dioxide. These chemicals are of environmental significance because they are released into the local environment and may also be transported over large distances from the mill (Juuti/ 1996; Calamari *et al* 1994). Chlorine dioxide itself is an air pollutant of great concern, especially in relation to the possibility of leaks and fugitive emissions in the plant (Simons 1994; Henton personal communication 1998).

The USEPA has recognised the major benefit that TCF systems are not expected to produce HAPs in the bleach plant. Thus, the Air section of the recently promulgated Cluster Rules states that:

*§ 63.445 Standards for the bleaching system.*

*(a) Each bleaching system that does not use any chlorine or chlorinated compounds for bleaching is exempt from the requirements of this section. Owners or operators of the following bleaching systems shall meet all the provisions of this section:*

The Rules go on to describe extensive collection, enclosure, reduction, and monitoring equipment and processes that must be in place for any bleach plant using "chlorine or chlorinated compounds." (USEPA 1998).

It appears, therefore, that for the most part there are overall positive environmental benefits in relation to air emissions from the use of modern mill technology and additional benefits for non-chlorine chemical bleach sequences. Nonetheless, the implications of technology and process change upon this aspect of pulp mill operations have not been exhaustively explored. There is a need to generate comparative information from advanced mill operations in order to assess the nature and scale of likely atmospheric emissions under closed loop mill operations in order to establish, as a minimum, that improvement in effluent quality is not at the expense of air quality.

## SLUDGE AND SOLID WASTE

**T**he goal of a closed loop mill is to eliminate discharges to water, while minimising land and air emissions. As such, solid waste disposal issues should significantly decrease in a perfect closed loop mill. However, the need to control the non-process elements will necessitate purge points to prevent upsets in bleaching and recovery chemistry, and minimise corrosion of mill equipment (Glead~~ow~~al 1997). Given that there will continue to be some sludge and solid waste produced, the quality of these wastes becomes of considerable concern. This is particularly the case since, increasingly, land spreading is being promoted as a means of disposing of these wastes. Uncontaminated sludge could prove to be a beneficial resource. Composting of properly treated sludge could facilitate the reuse of otherwise un-recyclable wastes. Use of pulping and bleaching wastes as raw materials for other processes may also be a desirable goal.

However, long-term studies on the feasibility and safety of composting and re-using waste solids from either ECF or TCF mills need to be carried out (Kookana and Rogers 1995). In practice, sludge is increasingly being fed into mill recovery boilers. While current evidence suggests that both ECF and TCF mills increasing their burn volume in the recovery boiler are maintaining compliance with air quality regulations, this must be continuously monitored as the move to full effluent loop closure proceeds. As noted above, current air monitoring obligations are demonstrably deficient. Increased combustion of sludge provides a further imperative for developing the scale and scope of air monitoring programmes.

Sludge from bleach kraft pulp mills contains a wide variety of chemicals, of both natural origin and originating *de novo* from pulping and bleaching activities. The commonly tested regulatory chemical parameters include chlorinated dioxin congeners and heavy metals, together with agriculturally orientated parameters such as carbon:nitrogen ratio and salt content (O'Connor 1995; Rabert & Zeeman 1992; ME DEP Chapter 567). While all of these parameters continue to be important, improvements to secondary treatment and the move towards complete chlorine dioxide substitution have revealed new compounds that need to be addressed. Plant sterols, resin acids, phthalates, chlorinated and non-chlorinated alcohols (phenols, guiacols, catechols), terpenes and benzene have been detected in ECF kraft mill secondary sludge (Martin *et al* 1995; Fitzsimmonset *al* 1991; O'Connor and Voss 1992; Breznyet *al* 1993; Kookana & Rogers 1995). These studies primarily address sludge from mills at, or approaching 100% chlorine dioxide substitution. The concentrations of chlorinated, bioaccumulative compounds found in these studies vary. Some debate has taken place concerning the best sampling and testing methods for low levels of these compounds, as well as on their origin: from the breakdown of chlorolignin or through a sorption - desorption pathway (Martin *et al* 1995; O'Connor & Voss 1992).

**Table 2:** The distribution and mass balance of chlorophenolics (ug/L) during treatment of BKME. Adapted from Martin 1995.

Chlorophenolic	Primary treated effluent			Secondary treated effluent			Mass balance <sup>a</sup>
	Free	Bound	Total	Free	Bound	Total	
2,4-DCP	2.3	ND	2.3	0.8	ND	0.8	- 1.5
2,4,6-TCP	8.5	1.1	9.6	1.0	1.0	2.0	- 7.5
2,3,4,6-TeCP	0.8	1.0	1.8	0.2	1.1	1.3	- 0.6
PCP	0.2	2.0	2.2	0.1	ND	0.1	- 2.1
3,4-DCG	1.6	5.7	7.3	0.9	5.5	6.4	- 0.1
4,6-DCG	1.1	ND	1.1	1.0	ND	1.0	- 0.8
4,5-DCG	11.5	41.6	53.1	1.0	34.0	35.0	- 18.1
3,4,5-TCG	6.7	29.0	35.7	4.0	33.1	37.1	+ 1.4
4,5,6-TCG	4.7	7.7	12.4	1.7	6.7	8.4	- 4.1
TeCG	4.0	11.0	15.0	2.4	12.8	15.2	+ 0.2
6-CVa	16.9	157.3	174.2	1.7	226.9	228.6	+ 54.4
5,6-DVCa	13.7	43.0	56.7	0.7	80.0	80.7	+ 24.0
2-CSAId	ND	ND	-	ND	25.2	25.2	+ 25.2
2,4,6-TCA	0.2	ND	0.2	<0.1	ND	<0.1	+ >0.1
2,4,5-TCVe	0.1	ND	0.1	0.6	ND	0.6	0.5

<sup>a</sup> Removal of chlorophenolic by secondary treatment

Regardless of the origin of such substances in mill sludge, it is clear that long-term studies under realistic conditions, backed by comprehensive chemical analysis are necessary before large scale land-spreading of kraft mill sludge can be justified (Kookana & Rogers 1995; ME DEP 1991). Additionally, the extreme variability in sludge indicates a need for continuous testing at each mill before sludge can be spread on land (Aitken *et al* 1995). This has been emphasised by the New Hampshire Department of Environmental Services following recent experiences in New Hampshire, USA. This body consider that the inherent variability in sludge composition necessitates extensive testing and monitoring prior to spreading on land (NH DES 1998). This followed the discovery of VOCs during post application testing in landfill groundwater where short paper fibre sludge had been used for remediation purposes. The potential for this problem was not identified through pre-application tests.

The process changes adopted by the industry are known to have resulted in qualitative changes in the sludge. For ECF sludge, closing the loop is resulting in increased disposal of sulphur chemicals from the ClO<sub>2</sub> generator (Paleologou *et al* 1997) due to the fact that sulphate compounds are by-products of ClO<sub>2</sub> generation and often used as make-up chemicals in bleaching and pulping. Increased chlorine dioxide production for ECF, and increased filtrate recycling heighten concentration of sulphur chemicals in process circuits. Because increased sulphur becomes a concern for non-process element control in closed loop designs (see section on NPE's below) this increase necessitates disposal of excess sulphates. These eventually end up in effluent treatment in many current mills. Under anaerobic conditions, certain bacteria can reduce sulphate, leading to increased bacterial growth, corrosion problems, and increase in treated effluent toxicity (Hanel 1988; Walski *et al* 1994; Islander 1991; Chevalier 1973; Prasad 1980; Goth & Konar 1980). TCF sludge has not been commonly tested. Also, in Scandinavia, secondary treatment has not been

commonly applied until relatively recently. Hence, few data have been generated from the area where most of the existing, full scale TCF mills are located. Because many of the TCF mills in the world are in the forefront of effluent recycling technology, it is likely that issue of waste fibre sludge disposal will progressively diminish in importance. As mentioned elsewhere, the impacts of burning this material must be continuously evaluated, and opportunities for more beneficial re-use sought out.

Assertions that increased effluent recycling will lead to an eventual doubling of lime muds, dregs, precipitator ash and other purge streams must be viewed with some concern (Ryynänen and Nelson 1996). One industry consultant estimated that, on average, grits, dregs and ash currently comprise about 3% of the dissolved material resulting from pulping and bleaching operations (Liebergott personal communication 1998). While closed loop operations may double that figure to 6%, this must be weighed against the complete elimination of liquid effluent discharge and of dissolved waste fibre and spent liquors going to aquatic or land-based discharge. For example, a MacMillan Bloedel (MB) mill in Powell River, Canada applied to land spread their sludge in 1995. MB Powell River produced over 190 million litres of liquid effluent (BC MOELP 1995), about 25,000 dry tonnes per year (dt/y) of primary sludge and 7500 dt/y of secondary sludge (PGL Organics 1995).

Assuming the mill runs 365 days per year, this gives 89 tonnes of sludge per day. Using reported daily production of 1,430 tonnes of pulp/day (Ochman 1997), the mill currently produces approximately 62 kg of solids requiring disposal per tonne of pulp. Using the estimated percentages above, approximately 2 kg of the current solid waste would be grits, dregs and ash. Under closed loop operations 4 kg of grits, dregs and ash are generated per tonne of pulp that would require disposal or treatment. The remaining solids would go to the recovery boiler and be used as fuel to supply additional energy to the mill. While this is a vast improvement, there would still be approximately 2.09 million kg/year of material requiring some sort of treatment and or disposal as well as the incineration of a vast amount of organic material. The composition, potential for re-use, and requirements for safe disposal of this material requires more study. Ultimately, processes that allow for a maximum of non-polluting and worker-safe re-use of pulping and bleaching by-products are needed.

## RAW MATERIAL UTILISATION

**W**hen considered in a comprehensive way, the environmental impact of kraft mill pulping operations can be indexed using a variety of parameters. Overall chemical usage and chemical cycling together with overall mill energy balances are among the most important operational parameters to consider. For example, the chemicals and enzymes consumed in the manufacture of bleached kraft pulp both consume energy in their production and comprise the greater part of the overall burden of chemical contamination emitted to the wider environment in the form of gaseous, liquid and solid wastes. The wood furnish can also be regarded as a chemical input in so far as pulping is essentially a chemical based processing of the wood furnish, and hence the efficiency of the chemical conversion process is germane to the analysis. A full analysis of environmental impacts would necessarily include consideration of the wood supply and its production methods and issues concerned with transportation of the mill furnish as well as the generation of wastes (in particular, sludge). Indeed it must be recognized that the former two aspects will have a great influence on the overall environmental impact of a given mill (Ryynänen & Nelson 1996). While these issues are considered to be beyond the scope of the current document they are of great importance to the actualisation of sustainable, ecologically responsible pulp mills and demand further study. As far as impacts

on the furnish acquisition and transport cycle as a result of changes in bleaching methods and operational changes are concerned, these could only arise if bleaching changes led to less efficient conversion of wood furnish and greater furnish consumption.

#### **a) Energy Usage & Chemical Consumption**

In terms of raw energy generated and consumed in pulp manufacture, estimates in the technical literature vary widely. Such estimates tend to be constrained by a number of implicit assumptions and are also affected on a site specific basis by differences in mill design and relative base efficiencies. Variation in pricing structures for local electricity supply can also affect these estimates. Issues of these kinds, however, although commonly raised to differentiate between ECF and TCF mill operation in economic terms, generally become less significant as mill closure becomes a factor in the analysis.

Cooking to lower kappa numbers requires more energy, but this is offset by increased recycling of effluents to the recovery boiler which in turn increases steam and in-mill electricity generation. The gain for TCF mills may be slightly greater here: the lowest kappa numbers are generally desired for effective TCF bleaching. In practice, however, this difference is not likely to be large in the most advanced mills. Steam generation for the pressurized peroxide stage is regarded as increasing steam demands for TCF, but many ECF mills attempting to move towards closure also employ this stage. Higher electricity costs for ozone generation are also commonly cited as a disadvantage, but several mitigating factors are becoming increasingly relevant in this case. Among these are new processes which reportedly reduce the energy consumption and cost for ozone production by as much as half as well as producing recoverable and marketable by-products (Chang 1997; Lawrence Berkeley Laboratories 1994). In general, it is expected that ozone generation will become more efficient as the demand increases (Laxen 1996) and certain industrial gas providers are beginning to develop leasing and gas delivery pipeline schemes that will help reduce the costs to any given mill (Albert 1997).

Several studies have investigated the overall consumption of energy in bleaching chemicals. The goal has been to determine the energy, in kilowatt hours/tonne (kWh) of pulp produced, consumed by the various chemicals from their manufacture to their end-use in bleaching processes. Some of the different variables used that can alter the outcome of a given analysis include: inclusion/exclusion of the energy costs of base chemical manufacture (e.g. sodium chlorate to produce chlorine dioxide); in the case of peroxide manufacture the availability of several production methods with differing energy demands (e.g. steam reforming, methanol cracking, water electrolysis); inclusion/exclusion of the energy required to mix the chemicals with the pulp in the bleaching tower. Regardless of the assumptions made, ECF sequences are found to consume more kWh/t than TCF sequences (Laxen 1996; Folke 1996; Henricson 1992).

In addition to relative energy efficient production, the by-production of oxygen in ozone generation processes can be used to advantage elsewhere in the mill. Mills requiring over 30 tonnes oxygen/day may find separate oxygen supply systems economical. On site oxygen generation can allow for the use of oxygen to improve other mill processes including: enrichment of lime kiln and recovery boiler air, introduction into waste water treatment processes, liquor oxidation for reuse in closed processes, injection into cooling water returns. Nitrogen similarly produced as a by-product can also be used in a number of mill processes (Ehtonen 1994).



## **b) Wood Yield**

**Yield differences between TCF and ECF bleaching processes are an issue that has received considerable attention in recent years. Given the importance of properly and sustainably managing forest resources, this is without doubt a highly important issue. Kraft pulping in general, is weak in terms of efficient wood utilization. Maximising the efficiency of fibre resource use can, therefore, be regarded as a central focus of a sustainable and environmentally acceptable primary pulp and paper production cycle. This can potentially be affected by both pulping and bleaching methods.**

## **i) Alternative pulping methods**

**This document has largely focused upon the prospects for circuit closure in a bleached kraft mill operation and the degree to which closure is facilitated by adoption of non-chlorine chemical bleaching processes. Kraft pulp is of great importance to the industry on account of its high strength and its ability to bleach to high brightness with very low brightness reversion or loss of strength. Many of the pollution problems associated with kraft mills, particularly sulphur emissions, are linked directly to the kraft method of producing pulp. Kraft pulping efficiency is relatively low (between 41-50%). This is unlikely to be the most efficient use of a valuable resource. Moreover, it results in the high levels of waste that must be disposed of through combustion, land-filling or land-spreading.**

**Most alternative pulping methods are currently at various stages of intensive research and development. Much attention is currently focused on methods based on the use of organic solvents. Alkaline Sulphite Anthraquinone Methanol (ASAM), minisulphide sulphite anthraquinone (MSSAQ), Alcell and neutral alkali earth metal (NAEM) salt alcohol catalysed pulping are examples of such methods which are being progressively refined and taken towards the market place.**

**Alcell® was originally developed by Repap Enterprises Inc. (Pye and Lora 1991) and much of the experimental work performed at the Limerick Pulp and Paper Research and Education Centre at the University of New Brunswick in Canada. The process claims several advantages over conventional kraft pulping. The environmental performance is improved in part because there is no longer a need for sodium sulphide and sodium hydroxide, thus eliminating the generation of malodorous sulphur compounds and the need for a capital intensive recovery furnace (Nät *al* 1997). This also confers on the Alcell process the advantages listed earlier for general reduction of caustic use. Reports also indicate that Alcell-derived pulp is easier to bleach than comparable kraft pulp (Pye and Lora 1991). TCF bleaching sequences which produce strength and brightness properties comparable to ODED bleached kraft pulp have been developed for Alcell pulps (Ooi 1995; Ni & van Heiningen 1997). One potential drawback of the Alcell process is that recovery of pulping chemicals has not been demonstrated and this may ultimately mean it is not viable economically (Paszner personal communication 1998). In future research, the environmental benefits of Alcell also need to be weighed against the need to constantly buy new pulping chemicals.**

**The ASAM process was developed at the University of Hamburg, Germany (Patt and Kordsachia 1986) and has been tested at a pilot plant in Germany for several years (Schubert *et al* 1991; Schubert *et al* 1993). The ASAM process has two chemical recovery loops, one for alkaline sulphite and alkali and another for the methanol used as a solvent. Numerous papers report the high bleachability and strength properties achievable by**

bleaching ASAM hardwood, softwood, and non-wood pulps (Kordsachia *et al* 1995; Glasenapp *et al* 1996; Teder & Sjodstrom 1996; Puthson *et al* 1997; Patt & Kordsachia 1997). It has been suggested that the ASAM process is, in fact, the process most likely to meet the environmental and paper quality needs of the future. It increases pulp yields, improves strength, and bleaches more easily with TCF processes than traditional kraft pulp (Patt & Kordsachia 1997). Separation of the sodium and sulphite components in the green liquor should also allow very efficient removal of undesired inorganics from the chemical loop. Combined with the potential to include required alkali in the loop, these are good precursors to a closed mill (Patt & Kordsachia 1997). Increased strength results were initially not anticipated from pulp viscosity measurements in ASAM pulps. This led to the exploration of viscosity-strength relationships in pulped and bleached fibres. It was found that the fibre weakening suggested by decreased viscosity is compensated for by improved bonding ability of TCF bleached fibres (Puthson *et al* 1997).

The MSSAQ process was developed in Sweden. It is a two stage process and includes sulphite and sulphide, for improved delignification (Dahlborn *et al* 1990). Sulphide inclusion should not be a problem for chemical recovery because it is achieved by allowing a minor flow of green liquor to by-pass the sulphite generation process (Teder and Sjodstrom 1996). While MSSAQ produces pulps of acceptable quality, ASAM pulps appear to give better brightness characteristics (Teder and Sjodstrom 1996) and this may lead to ASAM being the preferred of these two similar processes.

NAEM and other organosolv processes are still in the earlier experimental stages. Many of these focus their pulping effectiveness on non-wood pulps (Yawalata 1998). The ultimate goal of these processes is to produce high quality pulps with low emissions and purified, saleable by-products such as xylanose for sweetener production and lignin for polymer production (Paszner personal communication 1998).

The debate over efficient use of trees cannot take place in isolation but must involve an extensive consideration of the use of non-wood fibres. This issue is likely to be of critical importance to the future development of the pulp and paper industry. An exhaustive review of the current work in this field would be welcomed. It is noteworthy that several closed-loop, TCF non-wood fibre mills already exist. The technology for producing high quality pulps from these resources is rapidly improving, and this realm deserves continued attention in the development of sustainable and acceptable pulp production methods.

## ii) Bleaching Methods and Pulping Yield

In view of the considerable environmental importance of using wood resources efficiently and the economic significance of maximising yield, the choice of which technological pathway to follow towards closed loop operation will be contingent upon the yield variable to some degree. Against these dual backgrounds, claims of a 5-10% yield loss in TCF bleach-based systems need to be taken seriously. In fact, it seems that these estimates have been made on the basis of yield losses in rarely used extended delignification practices coupled with assumed losses for TCF bleaching. These have then been compared with high kappa ECF bleach processes. It is important to differentiate between pulping yields and actual bleaching yields (McCubbin 1996; Fleming and Sloan 1995; Moldenius 1997). These estimates ignore the fact that pulping to kappa 30-40, followed by oxygen delignification is now common at TCF and ECF mills attempting effluent closure, and that this pulping process actually increases yield (McCubbin 1996; Parsad *et al* 1993).

Setting aside the yield effects due to variation in pulping processes, statements about yield loss due to TCF bleaching have been based on effluent chemical oxygen demand (COD) and carbohydrate content. These have suggested that there is between 0-1% increase in wood consumption for TCF production (Suss 1997). These surrogate estimates have not been substantiated on a practical basis (Gleadow *et al* 1997a). The widely reported fall in yield of 6% at the Wisaforest mill using TCF is thought to be due to the fact that the mill switches between ECF and TCF pulp production and as a result is not optimised for TCF production methods (Boudreau 1996). Södra Cell has not seen a change in wood consumption since full conversion to TCF bleaching (Moldenius 1997), and the same was reported by Louisiana Pacific mill in Samoa California after conversion to TCF (Jaegel personal communication 1997). While there is undoubtedly a need to evaluate the yield aspect in greater detail, on the basis of the available evidence, yield loss does not appear to be a significant factor detracting from the use of TCF bleach processes.

## PROGRESS ON CLOSED LOOP MILLS

**T**he considerable research currently directed at alternative bleach processes and associated chemicals is being conducted as part of a general goal to develop mills capable of operating without discharging liquid effluent. A key component of this is within-mill recycling of process liquors from bleach plants. The lowest effluent flows have been achieved in the bleach plants of TCF mills. Metsä-Rauma, Södra's Mörrum, and SCA Östrand have been able to achieve the effluent flows from the bleach plant in the order of 4-5 m<sup>3</sup>/ADT (air dried ton) of pulp. This compares with an average of 7-10 m<sup>3</sup>/ADT for the best efforts made with ECF installations (Annergren and Sandstrom 1996; Ferguson and Finchem 1997). Mills which have been specifically designed for TCF bleaching and low flow operation (exemplified by SCA Östrand, Sweden), have the best current operational performances and record fewer upsets in pulp quality and mill mass balances (Annergren and Sandstrom 1996). The Södra-Cell Mörrum mill is designed to operate with an entirely closed bleach line (Södra-Cell 1996). By contrast, the most effective closure of ECF mills generally only includes the first Cl<sub>2</sub> stage and the oxygen extraction stage (Ferguson and Finchem 1997) in order to avoid the build-up of chloride in the process. The effluents from subsequent chlorine dioxide bleaching stages are still discharged to sewer, or at best recycled only intermittently. Under these circumstances, experimental pilot mills, such as the Champion BFR mill in Canton, North Carolina, USA have only been able to run for continuous periods of less than 4 months with approximately 80% recycling (Ferguson and Finchem 1997; Caron & Delaney 1998).

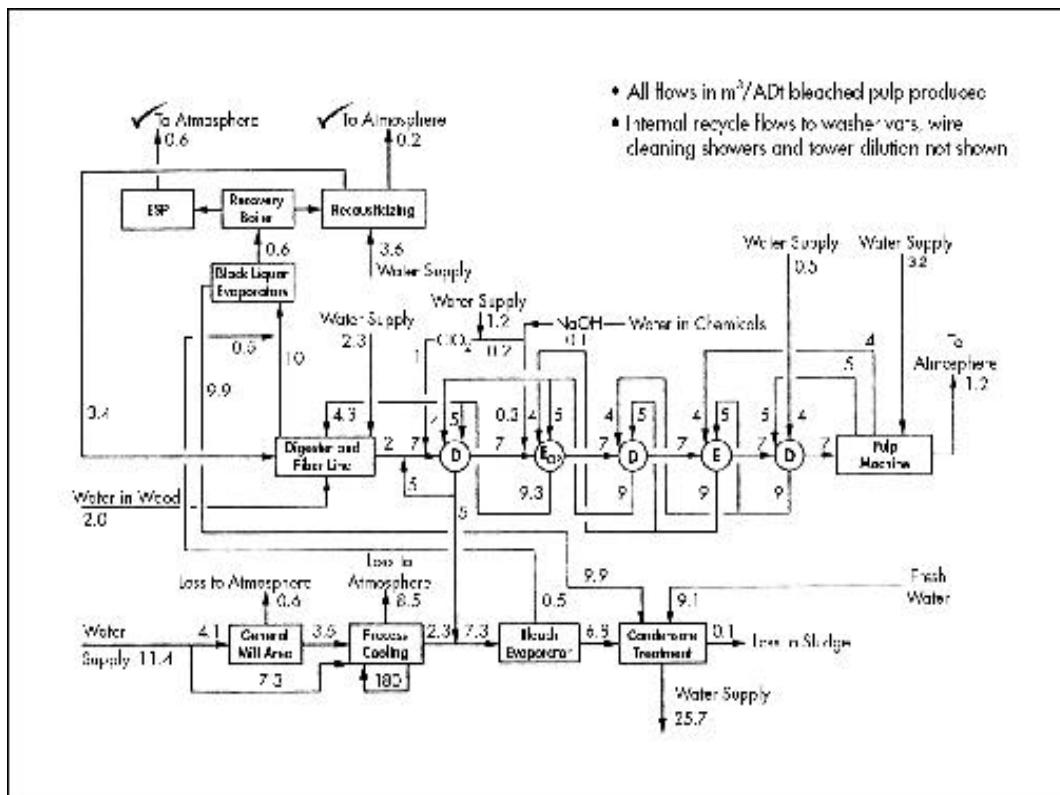


Figure 3: Closed-cycle mill water balance. Adapted from Gleadow 1997.

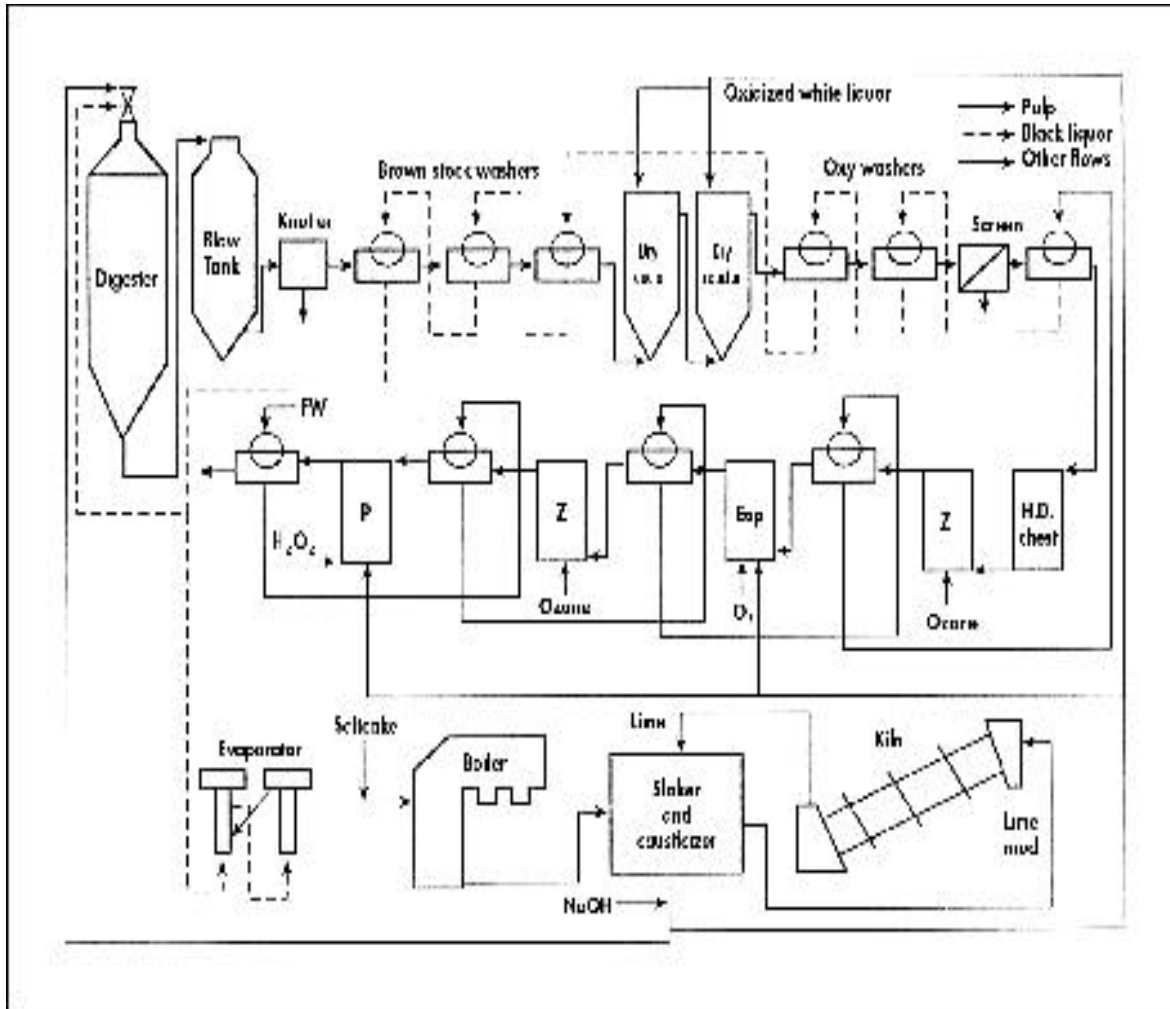
## NON BLEACH PLANT IMPROVEMENTS

### A) Furnish Handling, Pulping, Spill & Chemical Recovery

While the potential for closure of the bleach plant circuits is critical to the achievement of a zero-effluent mill and arguably the most difficult to close in existing kraft mills (Albert 1997), non-bleach circuits can be closed with less difficulty and can provide an effective focus to reduce effluent generation. The brown line can be closed (pressurized screen room and counter-current washing), liquor, chemical cycle, filtrate, and fibre spill recovery and reuse systems can be installed, and fresh water showers can be replaced with showers using machine white water or bleach filtrates. Other prerequisites for a modern, low-flow or closed loop kraft mill involve process changes and capital investment. These include increased delignification before bleaching (oxygen and/or extended delignification), wash presses after brown stock, and the use of filtrates for post press dilution and wire cleaning purposes (Gleadow *et al* 1997; Parthasarathy 1997). All of these changes will reduce effluent from the mill, and can also result in higher on-site energy efficiency.

Another important benefit of using bleaching filtrates for wire cleaning and oxidised white liquor (OWL) for extraction is the reduced need for fresh caustic. Caustic is a by-product of chlorine manufacture and given that the price of caustic will increase as demand for chlorine falls, more efficient use of alkali will result in significant economic savings. Substituting filtrates and OWL can reduce chemical cost (Parthasarathy 1997) and free mills from the need to buy sodium hydroxide manufactured by the suppliers of chlorine and chlorine based chemicals. Techniques such as bipolar membrane electro dialysis can also be used to recover caustic from kraft process liquors and in addition to reducing demand for

caustic also have the potential to further reduce the loading to the effluent treatment plant. (Paleologou *et al* 1997).



**Figure 4:** Example of a possible effluent-free fibre line and recovery with two-stage oxygen and TCF bleaching sequence. Adapted from Parsad 1996.

## B) Non-Process Element Control

As noted in the discussion of effluent toxicity above, both ECF and TCF recycle systems must be capable of controlling the build-up of chlorides and other non-process elements (NPEs) such as sodium, calcium, sulphur, potassium, magnesium, manganese, silica, iron and aluminum in the various process liquors. The build-up of these elements has the potential to cause process upsets and to impair product quality. Most approaches to this problem focus on collecting the waste streams where NPEs accumulate, evaporating the liquid and combusting the remaining waste. Energy and steam generated from the burning can fuel or serve a variety of mill processes. The electrostatic precipitator ash, containing the elements of concern, is collected and is disposed of in a variety of ways. This is commonly referred to in the industry as the "concentrate and burn" approach. Mill closure will result in a loss of the traditional purge points for non-process elements. Strategies for controlling the build-up of all of these will need to be implemented to prevent detrimental effects on pulp quality, as well as to control equipment corrosion and scaling. More studies are required to understand the environmental implications of various NPE control options.

EFFLUENT-FREE BKPM (Pounds Per Ton of Pulp)

**Table 3:** General description of non-process elements in - out, with sample quantities and routes.

Non-Process Elements	Source			Total In	Principal Discharge Point		
	Wood	Process Chemical	Water		Precip.	Dregs	Grits
Ca	2.36	T	0.08	2.44			X
Mg	0.70	1.0	0.01	1.71		X	
K	1.66	-	0.01	1.67	X		X
Cl	T	1.09	0.17	1.26	X		
C	0.63	0.04	T	0.67		X	
P	0.24	-	T	0.24		X	
Mn	0.23	T	0.23			X	
Al	0.20	-	T	0.20			X
Si	0.10	-	0.07	0.17			X
Fe	0.07	T	T	0.07		X	
*Other	0.17	1.65	0.17	1.99		X	X
Total	6.36	3.78	0.51	10.65			

*Adapted from Albert 1997.*

NPEs can also negatively affect the processes in which concentrated liquors are combusted. Chloride and potassium, for example, can result in sticky ash and plugging, increased corrosion, and ring formation in the lime kiln (Singh and Singh 1995; De Pihno 1996; Sharp 1996). Because chlorides can accumulate at 20-200 times their initial concentrations (Gleadow *et al* 1997a), the issue is of greater significance in relation to liquors generated by ECF mills due to the initial high chloride levels resulting from chlorine dioxide use (Singh and Singh 1995). Several processes exist which are designed to remove chlorides (Ferguson and Fincham 1997), but generally speaking, they are removed together with potassium from electrostatic precipitators on recovery boiler stacks (De Pihno *al* 1996).

The composition and fate of this ash is not well documented for either TCF or ECF mills. A study from British Columbia, Canada suggesting that the flue gas from recovery boilers with high chloride loading does not represent a major source of dioxin/furan air emissions (Luthe *et al* 1997) does not present data on the composition of the electrostatic precipitator ash itself. Regardless, the effect of bleach effluent recycling on recovery boiler behaviour due to high chloride concentration is only inferred from this study. Further, chlorinated dioxins, while still an important parameter to monitor and control with a view to their elimination, are not the only compounds of concern which can potentially be deposited in the ash.

For chlorine dioxide mills, the efforts to control NPEs through the use of ESP purges from the recovery boiler stack will mean lower operating temperatures, increased wash frequency in most cases, and quite possibly new high-grade materials, such as titanium, to tolerate increased chloride levels (Gleadow *et al* 1997a; Annergren and Sandstrom 1996). Modern recovery boilers designed for use on the west coast of Canada, where chloride levels are high due to salt water storage of mill furnish, may be adaptable to closed-cycle operation (Luthe *et al* 1997). There is not sufficient information in the literature to conclude what effect lowering recovery boiler temperatures to prevent plugging would have *an novo* synthesis of and destruction efficiency of contaminants in the boilers.

Reduced process sodium losses as a result of mill circuit closure mean that sodium input needs to be minimised. The use of oxidised white liquor instead of fresh caustic in oxygen delignification and in extraction stages is an option currently being employed in both ECF and TCF mills attempting to close the loop. Because spent chemicals from chlorine dioxide generation are a source of sodium, the elimination of  $ClO_2$  from the mill is another way to reduce sodium balance difficulties. (Gleadow *et al* 1997a; Annergren and Sandstrom 1996; Ferguson and Finchem 1997; Gleadow *et al* 1997b).

Sulphur also can also arise from  $ClO_2$  generator spent chemicals, and likewise, needs to be reduced as purge points are lost through closure strategies. Sulphur balances are important for product quality in the kraft pulping process, and because the needs for sulphur are very mill specific, reduction strategies need to be formulated on a site specific basis. Calcium, a NPE when not in the lime and recausticizing areas of the mill, enters with the furnish and can cause serious scale build-up. Counter-current recycling must be designed to prevent direct acid to alkaline transfer in order to prevent calcium precipitation (Gleadow/ 1997a).

Magnesium, manganese, silica, iron and aluminium all also enter with the furnish and can cause either glassy scale deposit, calcium cycle problems, or interference with the bleaching chemistry. Interference with bleach processes by NPEs is a particular problem with hydrogen peroxide based bleach sequences as noted above. There is evidence, however, that managing magnesium to manganese ratios in TCF bleaching can actually improve selectivity (viscosity). Using this approach, the recycling of spent bleach liquor actually improves the properties of the final pulp (Gevert *et al* 1997 a & b). This suggests that, if the various influential parameters are adequately regulated, closing the loop may actually be beneficial to TCF bleaching in terms of final product quality. Other technical approaches in addition to the use of chelation stages include improved debarking of the wood furnish and improving the management of the lime mud discard. However, using the lime cycle as a means of purging non process elements from ECF bleach effluent and filtrates may have undesirable environmental impacts due to poor control over the combustion of chlorinated organics (Gleadow *et al* 1997b).

In general, while the removal of non process elements can be achieved to some extent through the purging and leaching of the recovery boiler precipitator ash and while there may be opportunities to recover caustic or other chemicals from the ash, this control method enriches the concentrations of a variety of chemicals in the ash (Gleadow *et al* 1997a) and carries with it a commitment to disposal of the residual ash in a hazardous waste landfill. The transfer of pollutants from one medium (liquid effluent) to another (ash residue) must be seen as undesirable in the longer term. Processes which replace the "concentrate and burn" approach are under development and hold the prospect of greatly improved performance. An example is the SAPPI Bleach Chemicals Recovery Process. This would allow the recovery of a variety of waste streams at the same time keeping those elements capable of compromising the pulping process under control and out of the recovery cycle. The system depends on a separate treatment of the acidic and alkaline components of the waste stream arising from the bleach plant. This requires the construction of an entirely new and separate recovery system, and to date, although demonstrably more efficient than traditional effluent treatment, the plant is not regarded as generating adequate return on capital investment under current regulatory regimes (Gleadow *et al* 1997a; Bohmer *et al* 1991). Trials with ECF bleaching were abandoned by SAPPI but may be resumed if TCF bleaching is installed at the mill (Albert 1997).

Overall, a combination of measures designed to reduce process water demands and eliminate polluted water discharge to the environment are the primary aims of closed loop mill operations. Even fairly modern mills which implement improvements in bleaching and chemical recovery processes can expect to reduce effluent flows from 70 m<sup>3</sup>/ADT or more, to less than 15 m<sup>3</sup>/ADT (Gleadow *et al* 1997a; Annergren and Sandstrom 1996; Ferguson and Finchem 1997; Gleadow *et al* 1997b). Much of the remaining water loss is likely to be through evaporative losses from process water cooling. In addition to the environmental benefits which accrue from the elimination of toxic effluents and the large volumes of water used to dilute them, there are some significant commercial advantages also. These include improved energy efficiency and reduced demand for process chemicals as well as the possibility of siting new mills closer to the source of the mill furnish.

### CAPITAL, CONVERSION AND OPERATING COST

**T**CF bleach processes compare highly favourably with ECF processes in relation to energy consumption, and chemical usage is either equivalent or demonstrably

	Cl	K	Ca	Fe	Mg	Mn	Zn
Average for 4 Mills	2.69	.68	0.25	0.79	0.22	0.54	2.44
Std Deviation	0.38	0.26	0.16	0.28	0.13	0.29	0.29
Average for Interior Mills	3.02	1.68	0.14	0.98	0.34	0.84	2.11
Average for Coastal Mills	2.36	1.68	0.30	0.59	0.16	0.40	2.60

**Table 4:** Average enrichment factors of precipitator dust / heavy black liquor, with reference to sodium (all on a dry basis) for four kraft mills. Adapted from Gleadow *et al* 1997b.



superior. The comparative costs of building TCF mills or converting existing mills have also been examined using a number of approaches and assumptions. Complete analysis of these case studies is difficult, but some generalised conclusions are possible for closed loop and low flow mills. It is widely agreed that TCF, closed cycle greenfield mills will show some important savings in capital cost as opposed to an ECF mill. This is attributable to the lack of a chlorine dioxide generator and the use of less expensive metals in the bleach plant of TCF mills (Albert 1995 & 1997; Grant 1996). Cost estimates for operating closed cycle TCF & ECF greenfield mills vary widely. In addition to energy considerations and chemical costs, however, analyses also need to take into account the fiscal impacts of eliminating pollution controls for hazardous substances created by the use and generation of chlorinated compounds, and reduced safety procedures which apply when chlorine dioxide is not stored on site (Jaegel & Girard 1995). Because no ECF mills regularly achieve the same flow reductions as current TCF mills, it is difficult to compare the fiscal impacts associated with flow reduction.

The estimated conversion costs for current mills also vary widely and in part are determined by both perceived and technological difficulties on a mill specific basis. In some cases the estimates provided are difficult to confirm by independent scrutiny because much of the relevant information is considered proprietary in nature. In the USA, in particular, conversion to either advanced ECF or TCF closed cycle operations could have higher capital costs than elsewhere. This is largely due to the fact that a relatively small percentage of the mills in the USA have oxygen delignification, which is generally considered a prerequisite for low-flow or closed loop ECF and TCF. At least one study suggests that a conversion to high kappa (30) TCF is possible without extended or oxygen delignification and with pulp properties equivalent to conventional bleach sequences (Ni and Ooi 1996). It is not clear, however, what effect this route to TCF would have on eventual closure of the effluent loop. What does seem clear, especially in the North American context, is that conversion from the average current mill to either advanced ECF, low-flow, or TCF closed loop will involve similar levels of investment (EKONO 1997). One economic conversion study done recently in Canada showed conversion to TCF to be a fully competitive option for closing the loop. Three scenarios were presented:

- conversion from a 100% chlorine dioxide mill designed in the 1980's to TCF, closed-cycle involved initial investment of CND\$76.1 million (discounted cash flow CND\$22/ADT over 15 yrs at 8% capital charges), and the operating cost was estimated at an additional CDN\$38/ADT,
- conversion from a 1965 ECF mill to ECF, closed cycle (BFR-style) was estimated at CND\$90 million (discounted cash flow of CND\$45/ADT, over 15 yrs at 8%) with incremental operating costs of +CND\$36/ADT, and
- conversion from a 1965 D<sub>0</sub>C<sub>30</sub> substituted mill to ECF, closed-cycle (SAPPI BPRP) mill cost CND\$79.6 million (CND \$34.40/ADT over 15yrs at 8%) with operating cost increase CND\$34/ADT (Gleadow *et al* 1997b).

**These estimates generally represent developments up to 1993/94 and many advances in acceptable technology have been made since. Various authors state, moreover, that closure**

Operating Cost Estimation (\$/ADT)	1965 ECF kraft to theoretical ECF closed cycle		1990 ECF kraft to TCF closed cycle		1965 70% ClO <sub>2</sub> to ECF closed cycle	
	Base Case	Closed Cycle	Base Case	Closed Cycle	Base Case	Closed Cycle
Wood	209	209	217	217	190	190
Chemicals	55	40	53	62	63	54
Energy	30	30	3	3	30	30
Work Force	121	121	90	90	121	122
Maintenance	55	61	50	56	55	61
Delivery	60	60	60	60	130	130
Capital	---	45	---	23	---	36
Total	530	566	473	511	589	623

**Table 5:** *Sample Costs of Conversion for three existing mill types. Includes incremental capital charges only. Adapted from Gleadow et al 1997b.*

**of mill bleach circuits appears to be easier with TCF technologies (Gleadow al 1997a; Rautonen et al 1996).**

## PAPER QUALITY

**I**n addition to comparisons of the economic and environmental performance and the various technological options for mill circuit closure, the issue of product quality is highly important. Indeed, the quality of TCF papers as compared to ECF papers is currently the subject of intense debate. It should be recognized that debate about relative strength and brightness characteristics should only apply to softwood kraft pulps. Hardwood TCF kraft pulp now has comparable properties to ECF hardwood kraft. Hence TCF bleach sequences are regarded as very promising for the processing of plantation eucalyptus wood in S.E. Asia and for plantation hardwood elsewhere (Sussal 1997; Ryyänen, et al 1995). The attempts by some organizations to paint all TCF paper with the same brush has made discussion of the issues highly polarised and largely unproductive (AET 1997).

Reduced tear strength at a given tensile strength (70Nm) is the most commonly cited drawback to the use of TCF pulps. Indeed, tear strength does seem to be, on average, slightly lower for some TCF softwood pulps. Nonetheless, this difference has not had any apparent detrimental effect on most commercial uses, with the properties of the pulp deemed to be adequate for the intended uses (Ryyänen al 1995). Brightness properties of TCF pulps have also come under scrutiny, and this is another controversial area where claims have been made that TCF brightness is inferior to that of ECF paper. Nonetheless, full brightness TCF pulp is currently being produced and there is a general high level of satisfaction on the part of producers of paper and paper products with the brightness achieved through using TCF pulps (Karker & Mitchell 1997).

Recent refinements in TCF bleaching processes have significantly improved the strength and brightness differentials relative to ECF kraft pulps (Heijnesson-Hultén *et al* 1997). A number of recent studies have demonstrated optimised TCF sequences to achieve both high brightness and tear strengths equivalent to ECF pulps. Metal removal, borohydride reducing stages, and magnesium sulphate additions can allow 90% ISO softwood kraft to be produced with strength comparable to ECF pulps (Chirat & Lachenal 1997). Reductions in cooking temperature improve TCF pulp bleachability and viscosity, again allowing for 90% ISO brightness to be developed together with good strength (Fuhrmann *et al* 1996; Bäckström *et al* 1996). One relevant aspect to the whole debate which requires evaluation is the need for 90% ISO pulp as opposed to lower brightness grades. Many end uses simply do not require full brightness pulp. In wood containing papers, the addition of between 20% and 50% mechanical pulp is common. Adding chemical pulp with a brightness between 86% ISO and 90% ISO increases final brightness by one point at most for 20% mechanical pulp mix, and not at all for mixes in the 50% mechanical pulp range. TCF pulps are unquestionably currently capable of achieving 86% ISO with no loss in strength properties (Chirat and Lachenal 1996 & 1998) and can therefore easily meet the requirements for these uses even with the most pessimistic assumptions about brightness and strength levels.

Medium consistency bleaching and mixing rates are being refined to optimum levels (Mielisch *et al* 1995) for TCF pulps. The removal of surface materials, even if they are subsequently allowed to stay in the pulp suspension, improves brightness stability and final viscosity (Lumialnen 1997). It has also been shown that TCF pulps can actually have better brightness stability than ECF pulps (Fuhrmann *et al* 1996). Peroxyacetic acid and Caro's acid, together with other chemicals coming into use in TCF production are also improving TCF bleaching processes (Bäckström *et al* 1996; Fuhrmann *et al* 1997; Lapiere *et al* 1997). Distillation technology improvements have helped make peroxyacetic acid more economically attractive, and its superior selectivity over ozone is increasing its use (Ni & Ooi 1996). Finally, the use of enzymes, like xylanase, is breaking new ground for increased brightness and reduced chemical use in both TCF and ECF bleaching (Pham *et al* 1995; Suurnakki *et al* 1996).

These extensive research efforts have led to the important discovery that TCF and ECF pulps do not necessarily develop strength characteristics in the same way (Laine & Stenius 1997). In particular, conclusions drawn about final paper making characteristics from pulp viscosity values may be misleading. The viscosity of TCF pulp is often lower than ECF pulp, yet the final strengths can be the same (Ryynänen *et al* 1995; Laine & Stenius 1997). Improved bonding characteristics of TCF bleached fibres are one suggested explanation for this observation (Puthson *et al* 1997).

As a general observation it appears that any actual variations in TCF kraft pulp result in no appreciable shortcomings in final product quality relative to ECF products throughout the vast spectrum of pulp uses and that the somewhat unhelpful debate which has surrounded the product quality issue is of rapidly diminishing relevance both to pulp users and wider consumer markets.

## WORKER AND COMMUNITY HEALTH AND SAFETY

**T**he potential health and safety impacts of pulp mill processes upon workers and local communities is a largely ignored component in most comparative analyses of pulp mill improvements. As technology progresses towards minimising the impacts of pulp mill operations on the environment, great care must be taken to ensure that these advances are not at the expense of worker or public health and safety. Increased in-mill recycling carries with it the risk of exposure to potentially more concentrated waste streams. Hence efforts need to be directed at reducing and eliminating the toxicity of these waste streams, and at reducing the likelihood of human exposure. These considerations become particularly important during operational upsets of mill processes (Andrews/ 1996).

There are hazards associated with every stage of pulp manufacture, from wood handling through pulping and bleaching to effluent treatment processes. Kraft pulping and recovery operations present numerous exposure opportunities to a variety of chemicals including reduced sulphur compounds (e.g. methyl mercaptan), terpenes, acids, alkalis and wood dust, including explosive chemicals. High temperature steam and thermal processes also present hazards (Teschke *et al* 1983). In general, process related hazards can be expected to diminish as old recovery boilers are replaced and as condensate recovery systems are fitted. These will reduce or eliminate the hazards associated with materials released from process vents (Simons 1994; Södra Cell 1996). Process changes which concentrate black liquor sent to the recovery boiler reduce the chances of moisture causing events such as "puffing" or "going positive" (McCubbin 1996). This event occurs when the boiler fuel stream is not uniform and causes intermittent, rapid expulsion of hot, toxic gasses into working areas. Boilers "going positive" are a major source of exposure to toxic gasses for workers in the recovery area (Henton personal communication 1998; PPWC 1998)

#### **BLEACH CHEMICAL HAZARDS**

All bleaching chemicals are potent oxidisers and thus present a hazard to workers. When compared over a full range of characteristics, oxygen-based chemicals are less dangerous overall than chlorine dioxide (Jamieson 1997).

##### **A) Chlorine Dioxide**

Chlorine dioxide is highly unstable and explosive and must be manufactured on-site. Concentrations of greater than 10% in air are associated with explosion hazards resulting from decomposition (CCOHS 1996). Chlorine dioxide is produced from sodium chlorate. This chemical can cause fires when it contacts organic materials after drying (Teschke/ 1983). Worker exposure during the unloading of tank cars bringing sodium chlorate to the mill can be fatal (Penner 1997). To produce chlorine dioxide, the sodium chlorate is reacted with a strong acid and a reducing agent. The reducing agent will vary depending on the type of generator used, but hazardous by-products can include chlorine gas, formic acid, and some un-reacted methanol as well as chlorine dioxide. Moreover, formic acid can linger and produce additional ClO<sub>2</sub>, creating a risk of explosion minutes or hours after the generator has been shut down. Numerous examples of this problem have been documented (Cowley 1995).

Both chronic and acute toxic effects can result from ClO<sub>2</sub> exposure including irritation of the eyes, nose, and throat, coughing, wheezing and breathing difficulties (possibly delayed), pulmonary edema, possible chronic bronchitis and asthma (Kennedy *et al* 1991; Salisbury *et*

al 1991; NJ DoH 1992). The decomposition products of chlorine dioxide are also toxic. Effects of acute exposures are also linked to chemical sensitivities and respiratory diseases that may not show up for years. According to researchers at New York University,

*Five years after a chemical exposure incident involving chlorine dioxide in the workplace, increased upper airway inflammation and other nasal biopsy abnormalities were still found in 13 patients who developed MCS and RUDs [Reactive Upper airway Disease] after the exposure...some...also developed RADS [Reactive Airway Disease]. (Meggs et al 1996).*

Chlorine dioxide is a 10 times more powerful oxidising agent than chlorine gas. This is an advantage in bleaching applications, but increases the hazards associated with repeated low-level exposures. These may occur due to process upsets, leaks, and improper plant operation. While obviously undesirable, such occurrences appear to be frequent. Workers frequently report the tell-tale sensation of seeing halos around lights after time spent in bleach plant areas (Teschke *et al* 1983; PPWC 1998). One of the more dangerous aspects of chlorine dioxide exposure is that its odour threshold is near to or higher than the level at which it begins to do harm. While some agencies list the odour threshold as 0.1 ppm (OSHA/NIOSH 1981), the Canadian Centre for Occupational Health and Safety considers a more realistic threshold to be 9.4 ppm (CCOHS 1996), well above the Permissible Threshold Limit (0.1 ppm) and close to the level considered immediately dangerous to life and health (10 ppm) (ACGIH 1991; NJ DoH 1989). Some workers report a diminishing ability to smell chlorine dioxide at all as exposure time increases (PPWC 1998).

In addition to the on-site work hazards, chlorine dioxide can present a great danger to communities living near mills. One well documented example is an accident at the MacMillan Bloedel pulp mill in Powell River, BC, Canada. An explosion from a pulp tank caused debris to rupture a Cl<sub>2</sub> storage tank, in turn causing 600,000 litres of dilute Cl<sub>2</sub> spill. Only favourable winds prevented the resulting gas cloud from traveling over the nearby town-site and/or the Sliammon Reserve (Hamilton 1994). The International Agency for Research on Cancer (IARC) has also published data that chlorine dioxide can create the powerful mutagen MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2(5h)-furanone), which, if only present as 0.0001% of pulp mill effluent, can be responsible for 30-50% of the mutagenicity of those waters (Holmborn 1992). This, along with the chloroform and other VOCs produced from ECF bleaching (Juuti *et al* 1996; Simons 1994) contribute to the hazard profile of this chemical.

## B) Hydrogen Peroxide

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) used in TCF bleaching is generally delivered in liquid form via rail cars to pulp mills, although it is also possible to generate it on-site (Pulp & Paper Canada 1997; Laxen 1996). Hydrogen peroxide is created by water electrolysis, methanol cracking, or re-condensation. Unused methanol is the main hazard of production when the cracking method is used. Unloading and handling present the greatest hazards, but the fact that H<sub>2</sub>O<sub>2</sub> is applied in the bleach process in aqueous solution significantly reduces workplace and community hazards. Nonetheless exposure to hydrogen peroxide can cause mild respiratory tract irritation or in more severe exposures, bronchitis. Severe nose and throat irritation and pulmonary edema can also result from exposure. Skin contact can result in burns and eye contact can lead to severe eye injury and blindness. There are no chronic exposure data for H<sub>2</sub>O<sub>2</sub>. Decomposition products are air and water, and high concentrations are only stable when cool and pure (CCOHS 1996). Hydrogen peroxide has no odour threshold, so its warning properties are very poor. The Threshold Limit Value (TLV) is 1 ppm, and

Immediately Dangerous to Life and Health (IDLH) is 75 ppm (ACGIH 1991; NJ DoH 1989).

Industry experience with hydrogen peroxide has been very good and data have been reported which suggest that TCF bleaching processes improve worker safety. Södra Cell reported at least one incident a year with chlorine dioxide exposure resulting in hospitalisation. None have occurred at the Värö Bruk mill since conversion to full TCF bleaching with  $H_2O_2$  (Lovblad 1997a). At Louisiana Pacific's Samoa mill, perhaps the most notable and tangible benefit reported from converting the mill to TCF has been the elimination of the worker safety hazards and risks to the surrounding community associated with the production of chlorine dioxide (Jaegel & Girard 1995).

### C) Ozone

Ozone ( $O_3$ ) is generated onsite by passing electricity through oxygen, resulting in low concentrations of  $O_3$  in a carrier medium of oxygen (Ehtonen 1994). The regulatory exposure limits set are similar to those for chlorine dioxide (0.1 ppm TLV, 10 ppm IDLH). Ozone has a higher oxidative potential (Laxen 1996). The odour threshold for ozone is 0.076 ppm which gives it excellent warning properties. As with exposure to other bleaching agents, ozone can cause chest pain, coughing and wheezing, congestion, labored or faster breathing, sore or dry throat, dyspnea, and eye and nose irritation. Lung edema symptoms are often delayed. Headache and nausea are non-respiratory effects, and skin contact can cause frostbite. Eye contact can cause redness, swelling and loss of vision. There is little information about long term exposure impacts. Ozone decomposes rapidly to oxygen gas, creating no hazardous polymers in the process. Oxidation with combustible and reducible materials can be violent. Ozone is not combustible, but can enhance combustion of other substances (ACGIH 1991; NJ DoH 1989; CCOHS 1996). One important benefit of ozone based processes is that the gas is produced and fed directly into the process, leaving very little as residual in the generators at any time. Leaks that do occur can be readily detected and flushed with oxygen. Pressurized ozone systems, however, may be more prone to leaks than ones that operate at atmospheric pressure (Griggs personal communicatio 1997).

Clearly, all bleaching chemicals are hazardous. In terms of persistence, odour threshold, breakdown products, and potential for exposure through explosion, chlorine dioxide appears to present the greatest risks. Studies of pulp mill worker cancer incidence and mortality are have not yet generated enough data to be useful in the determination of the best technical pathway towards closed loop operation from a worker health viewpoint. Studies from Finland and Canada show increased risk to kraft mill workers for several cancer types but there are as yet no firm conclusions about specific workplace exposures that could be linked to these observed increased disease rates (Bandt *al* 1997). A study is currently underway to determine if certain mill jobs and/or types of exposure can be associated with specific health risks (Astrakianakis 1998).

## NEXT STEPS/MISSING RESEARCH

**E**fforts to achieve a mill capable of operating in a closed loop configuration, thereby minimising impacts on the environment, have accelerated in recent years and continue to gather pace. From being regarded as a utopian goal some ten years ago, it is now widely recognized within the industry that mill circuit closure is a vital

**component of sustainable pulp production. Nonetheless, as the research and development moves forward, there are several potentially problematic areas that need to be addressed and resolved.**

**Ambient air at TCF and ECF mills needs to be monitored using compatible protocols. In this regard it is important that debates include not only environmental and cost considerations, but also the health and safety of workers and communities likely to be exposed to routine emissions from the mills. Internal air quality at ECF and TCF mills needs to be well characterised for the same reasons. Some studies already suggest that VOCCs are present at significant levels in ECF mills, and the health and safety implications of these need to be researched.**

**Full spectrum analyses of TCF and ECF sludge are needed so that the process generating the highest quality sludge can be identified. The potential for eliminating this waste arising through mill circuit closure must be a factor considered in this evaluation. There is likely to be some time lag before closed loop mills become commonplace, and until then sludge will exist and pose potential disposal problems. With this issue in mind, the potential for composting TCF and ECF sludge needs to be researched so there will be a good understanding of whether or not the possibility exists for beneficial reuse of pulp mill sludge. As well as considering the chlorinated chemical content of ECF sludge, a greater knowledge of the fate and effects of chelating agents from metals removal processes in TCF and ECF systems is highly desirable.**

**The ash content from electrostatic precipitators at ECF and TCF mills needs to be fully characterized, and plans need to be developed for the interim safe disposal of these materials, as well as process modifications which will ultimately eliminate hazards. This is also the case for other purge points used in closed loop mills to control process integrity. Early indications are that volume, worker hazards and environmental impact will certainly be far less than currently seen in open cycle mills, but this needs to be very clearly established.**

**The debate concerning fibre resource use efficiency and product quality of TCF pulps relative to ECF pulps needs to be resolved. In both cases there is a need for empirical data to be generated and reported together with suitable market based analysis of feasible pulp end uses. In connection with efficient fibre use, alternative pulping processes also need to be evaluated. This will need to include studies on the pollution potential, chemical consumption, potential residual reuse as product, and energy issues associated with new pulping technologies. Indeed, if these, or other, non-kraft processes can deliver high quality pulp that is simpler to bleach with oxygen based chemicals, adapt readily to wood or non-wood fibre and leave residuals that are useful as feed-stock for other important manufacturing processes, they may signal a whole new direction for the pulp mills of the future.**

**One common problem exists for much of the research data generated in North America. Working mill and laboratory data are often compiled and compared for ECF mills. By contrast, conclusions about TCF processes are often based on lab data alone, with no parallel mill testing to establish the reliability of the assumptions made in experimental design. Some authors acknowledge this to be the case. Many do not and this considerably complicates comparative process assessments. An allied problem is the spurious use of the achievements of the most advanced ECF mills to characterise environmental performance of the high kappa, no-recycle, no oxygen delignification ECF characteristic of the pulping industry in the US and some of Canada.**

## CONCLUSIONS

**D**evelopment of pulp mills to reduce their impact on the environment has advanced rapidly in the past ten years. Closed loop, and minimum impact concepts continue to be intensively researched and implementation of process improvements is ongoing. While some analyses from the industry downplay any difference between the overall performance of the most advanced ECF and TCF mills, when all aspects are considered, TCF has significant advantages in the development of closed loop processes. Other factors must be kept in mind when evaluating comparative literature.

First, it must be recognised that only a small percentage of mills in Canada or the United States of America can perform to the optimum ECF standards reported in the literature. In the USA, oxygen delignification, which is a prerequisite for low-flow and potential effluent recycling as well as reduced bleaching chemical demand, is not common, and the industry as a whole has been demonstrably reluctant to accept OD as a standard operating component. Bringing most of these mills to closed loop operation in either ECF or TCF configurations will incur similar costs.

Second, mills which are optimised for running TCF processes actually encounter far fewer of the operational and product quality problems commonly cited by pro-ECF industry sources as reasons to avoid TCF. Process scaling problems are real, but are encountered by both ECF and TCF mills attempting to close the loop. Brightness, strength, and wood consumption associated with TCF systems are well within industry standards and adequately meet consumer needs. Concomitant with this point is the fact that the brightness provision, in particular, is an arbitrary demand made by advertisers, and not truly a quality necessary for the efficient production of high quality pulp and paper.

Finally, the impact of bleaching technology choices on workers and local communities is often ignored by the industry, and must be taken into account in the future. The elimination of chlorine chemicals improves hazard profiles in the work environment and reduces the danger of chemical spills when they do occur. The production of oxygen based bleaching chemicals requires less toxic precursors than does chlorine dioxide, and is more energy efficient overall.

There is close competition in terms of some standard environmental factors between the most advanced TCF mills (which still hold an advantage overall) and the most advanced ECF mills. Outstanding factors which favour the TCF approach include: worker and community safety, bleaching chemical life-cycle energy, generation of persistent organic pollutants from bleaching with chlorine-based chemicals and burning of wastes containing chlorine-based chemicals, and the fact that numerous researchers still conclude that closing the loop will be simpler and safer without chlorinated chemicals. Given these concerns, eliminating chlorine-based chemicals is still a desirable goal and the right step towards an ecologically responsible pulp and paper industry.

Accordingly, there is a need to place the ECF/TCF debate onto a more robust footing so that realistic comparisons can be made and zero emission systems developed as rapidly as possible. The debate should be objective and not held hostage to poor previous investment and development decisions made by certain sectors of the industry in the past.



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