INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
Atlanta, Georgia

OVERVIEW OF CLOSED-CYCLE TECHNOLOGY FOR KRAFT PULPING AND BLEACHING

Project F017
Report 1

A Progress Report
to the
MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

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November 21, 1994
EXECUTIVE SUMMARY

Environmental concern, and particularly the proposed EPA Cluster Rule, has recently heightened interest in Closed-Cycle Mill Technologies. The proposed Cluster Rule covers only a portion of the environmental regulations for pulp and paper operations. It ignores discharges to the air from combustion sources and solid waste discharges. Closed-cycle schemes primarily deal with effluent discharge and often ignore the impacts on air and land discharge. Mill closure may adversely affect these other two environmental areas, VOC's and metals concentration in dregs and ash are examples.

The purpose of this report is to present a broad overview of Closed-Cycle Mill Technologies, and to provide access to the extensive literature on this subject. The report first defines what is meant by the terms "Closed-Cycle," "Zero Discharge," and "Environmentally Friendly/Low Impact Mill." This is followed by discussion of the three implementations of closed-cycle technologies and identification of the common features of this technology for pulping and bleaching operations. There is limited industrial experience with the impact of closed-cycle operation on equipment and processes, but there are many proposed schemes for mill closure and some clearly identifiable common features in these schemes.

Key to the success of closed-cycle technology is control of non-process elements (NPE's), particularly chlorine. Purges of the NPE's must be designed into the overall mill closure arrangement. NPE's can be either inorganic or organic in nature. For the inorganic, removing them from the process streams and disposing of them at suitably low concentration is needed. Organic NPE disposal usually involves oxidation of organic carbon to CO$_2$, whether by combustion, biotreatment, supercritical water oxidation, or some other process. The means of controlling these two types of NPE's often conflict because destruction of the organic NPE's concentrates the inorganic NPE's. Both overall destruction efficiency and total environmental impact must be taken into account in any scheme for
NPE's control. Work is needed in the areas of assessing the closed-cycle schemes for total environmental impact and identification of technologies which address this total impact.
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OVERVIEW OF CLOSED-CYCLE TECHNOLOGY
FOR KRAFT PULPING AND BLEACHING

INTRODUCTION
For several decades the pulp and paper industry has worked to reduce the discharge of undesirable materials from mill operations. This effort has been driven both by the need for water conservation and the need for environmental protection. Changes in individual equipment design and operation have contributed to the dramatic improvements in mill discharges to the air, water, and land. Increasingly, these efforts have included the recycle of effluents either within a piece of equipment or to other equipment elsewhere in the mill. These schemes for recycle are referred to as “mill closed-cycle technologies.” The recently proposed EPA Cluster Rule has heightened interest in these technologies for environmental protection.

The broad elements of closed-cycle technologies and a few specific schemes will be presented and discussed in this report. What is not usually immediately obvious about these technologies is that they generally apply only to recycle of liquid effluent discharges, not to solid or gas recycle. Closed-cycle technologies reduce the discharge to receiving water but may, and in some cases must, increase the discharge to air and land.

Closed-cycle technology always involves recycle of a process discharges back to an earlier stage in the pulp and paper manufacturing process. This recycle may be either with or without intermediate treatment. The recycle stream usually replaces a fresh water input so it brings contaminants into these processes which were not introduced with fresh water. It is these contaminants which are the cause of most of the problems and limitations of closed-cycle technologies. Recycle loops cause the build up of organic and inorganic materials generally referred to as “Non-Process Elements” (NPE’s).
NPE's affect the pulping and bleaching process in many ways. They may be responsible for deposition and scaling, foaming, corrosion, and direct interference in the chemical process of pulp manufacture. In the case of organic NPE's, air discharges may become worse as liquid effluent discharge is reduced. For example, recycle loops may decrease effluent discharges but increases organic concentrations in process fluids elsewhere in the mill. This can result in increased emission of volatile organic compounds (VOC's) to the air.

Closed-cycle technologies have the potential to adversely affect the mill operation in other ways. Operating load at a given pulp production can increase for individual units. An example of this is the additional organic and inorganic load on the evaporators and recovery boiler with bleach plant filtrate recycle. The higher concentrations of non-process materials increases maintenance and operating costs. Safety can be compromised by accelerated corrosion rates or build up of organic vapors.

The most difficult aspect of closed-cycle technologies is the increased interdependence of mill departments. With recycle, individual departments are dependent on departments both up and down stream. The optimum trade off between interdepartmental cooperation and buffer storage between departments must be worked out for each mill and closed-cycle scheme.

There have been a few implementations of closed-cycle schemes for zero or near-zero effluent discharge, as well as many partial implementations of such schemes. These have provided some information about mill impacts. This report is broken into sections which deal with: 1) basic limitations on closed-cycle operations, 2) a review of recent pulping and bleaching technologies which facilitate closed-cycle operations, 3) presentation and discussion of industry experience with closed-cycle technologies, 4) presentation and discussion of the elements common to all closed-cycle schemes, 5) discussion of the non-process elements, and 6) a discussion of the proposed EPA Cluster Rule, COD, and organic
destruction. In this report, only the technologies associated with pulp manufacture will be addressed.

LIMITATIONS ON CLOSED-CYCLE OPERATIONS

The phrase "closed-cycle technologies" conjures the image that there will no longer be discharges from mill operations and that this will take care of all environmental issues. Figures 1-3 help to define the meaning of closed-cycle technologies and attach meaning to the phrases "zero-discharge" and of the "environmentally friendly or low impact mill."

**Figure 1** shows a global view of an entire pulp and paper mill. This slide shows the inputs and outputs from the mill. The inputs are wood, water, makeup chemicals, and fuel, and there is also an input of air. What comes out is fiber product, lignin, water, steam, non-process elements, and combustion products. Shown in Figure 1 is a very coarse breakdown for the wood, just fiber product and lignin. Of course, the lignin is not going to leave the system as lignin, but rather as combustion products or byproducts. Nevertheless, the material which is lignin in the original wood must leave the mill; in fact, all the things listed as inputs must leave the plant in one form or another.
The input materials all contain non-process elements such as silicon, aluminum, magnesium, manganese, iron, and other materials which do not participate in the pulping and bleaching process. They enter as contaminants and must leave the mill at some point. This is the basic situation irrespective of how the mill is configured.

The term "zero-discharge" particularly conjures the image that there will be no discharge from the mill at all. The actual situation is shown in Figure 2. The inputs are the same as before, and the outputs have been given slightly different names, but still, what goes in must come out. The only real difference shown here is that the liquid water is internally recycled so that there is no liquid effluent. Some of the "benign salts" may also be recycled to reduce the need for makeup chemicals. However, all the non-process elements must still be discharged from the mill in a benign form if the environmental regulations are to be met.

![Diagram of a closed-cycle mill with zero discharge]

*Figure 2—Closed-cycle mill with "zero" discharge.*

Because of the need to discharge materials in an environmentally friendly way, the zero-discharge, closed-cycle mill may not be the best option. Shown in Figure 3 is a depiction of
the Environmentally Friendly/Low Impact Mill. There are many variations to this title. The implication is that the system is not entirely closed as far as water is concerned. Some water is discharged as effluent in order to discharge the non-process elements and other materials in the most environmentally sound way. The fiber product is still the most important discharge from the mill, and there is still a steam discharge.

![Diagram of Pulp and Paper Mill]

Figure 3—Environmentally friendly/low impact mill.

For the environmentally friendly/low impact mill the effluent stream contains controlled levels of AOX (Absorbable Organic Halide), color, and COD (Chemical Oxygen Demand). As well, the primary combustion products, CO₂ and H₂O, leave along with control amounts of such species as carbon monoxide, VOC’s, sulfur dioxide, NOx, methanol, and other gaseous materials.
The makeup chemicals and the non-process elements must leave the mill or they will eventually fill up every tank and line. Discharging them as solids is often not a good means of waste management and disposal. The more environmentally friendly way is for them to be dissolved in water for dilute discharge to receiving waters and eventual return to the sea.

PULPING AND BLEACHING TECHNOLOGIES
Before presenting specific technologies developed for closing up the mill, a very brief overview of pulping and bleaching changes which can lead to alternative means of reducing water use and reducing effluent discharge will be presented. These pulping and bleaching technologies are described in references [104–231]. Figure 4 is a very coarse breakdown of the pulping and bleaching process for a kraft mill. Single blocks are shown for pulping, bleaching, biotreatment, evaporation, recovery, and recausticizing. The important properties of the fiber product and the ultimate effluent discharge parameters are also shown. It is evident here that part of the pulping process is already "closed." The recovery cycle already constitute about 90% closure of the mill. Closed-cycle technologies really deal with closure of approximately the last 10% of the process.

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**Figure 4—Kraft pulping and bleaching**

- Brightness
- Strength
- Yield

- AOX
- COD
- Color
**Figure 5** shows a number of improvements in the pulping process which increase the degree of closure of the existing recovery process. These improvements cut down the amount of material going to bleaching and direct more material to recovery. These improvements including the use of anthraquinone (AQ), or polysulfide pulping, to improve yield at lower kappa numbers, extended delignification, and oxygen delignification. The techniques referred to as Super Batch, Rapid Displacement Heating (RDH), Modified Continuous Cooking (MCC), Extended Modified Continuous Cooking (EMCC), and IsoThermal Cooking (ITC) all are means to extend delignification within the context of kraft pulping. Oxygen delignification also continues delignification in a more specific way. All of these pulping modifications remove more organic material from the wood and direct it to the recovery department, thus, reducing the organic to bleaching and reducing the required use of bleaching chemicals.

- Extended delignification
- Super batch
- RDH
- AQ
- MCC/EMCC/ITC
- Polysulfide

![Diagram of pulping process]

*Figure 5—Improvements in pulping.*
**Figure 6** shows some proposed and implemented improvements in bleaching. Enzymes can improve the performance of the other bleaching chemicals that follow in the bleaching sequence. EDTA is an agent needed in conjunction with peroxide bleaching. Peroxide can be used in separate bleaching stages or within an extraction stage either with or without oxygen to “reinforce” the extraction. Ozone is another of the bleaching agents that has been implemented in bleaching processes to replace chlorine and chlorine dioxide. Chlorine dioxide itself has now been widely used to substitute for chlorine in the initial bleaching stage. All of these and other modifications reduce the use of chlorine, thus improving the effluent quality and allowing some or all of the bleach plant effluent to be recycled back to the recovery department.
EXPERIENCE WITH CLOSED-CYCLE TECHNOLOGIES

One of the early attempts to close the kraft pulping cycle is a scheme proposed in the 1970’s and implemented at one mill in the late 1970’s and early 1980’s, the Rapson-Reeve process [66, 72, 73, 75, 77, 79, 80, 84, 85, 86, 88, 93, 102, 216, 220, 225]. A very elementary schematic of this process is shown in Figure 7. This process used a bleaching sequence involving 70% substitution of ClO₂ for Cl₂ and a complete recycle of the bleach plant effluents to the pulping and recovery processes. The relatively large amount of chlorine brought back to recovery with the bleach plant effluent was to be purged in a salt recovery process set up in the recausticizing department. This implementation of a closed-cycle scheme was carried out at the Great Lakes Forest Products mill in Thunder Bay, Ontario. The mill was not operated 100% closed, but averaged about 50% closed compared to similar mills of the same vintage. Some of the problems that were identified from this effort included pitch deposits, scale deposits, and foam, as well as corrosion due to high chlorine contents of all liquor streams, and particularly corrosion and pluggage of the recovery boiler.

![Figure 7-The Rapson-Reeve closed-cycle process.](image)

*Figure 7—The Rapson-Reeve closed-cycle process.*
Recently there has been implementation of another closed-cycle technology in two mills [8, 13, 15, 16, 19, 26, 27, 29, 30, 34, 38, 39, 41]. The two installations are not kraft pulp mills, but are bleached chemithermomechanical pulping (BCTMP) operations. There is no recovery operation in the standard configuration of a BCTMP mill. The closed-cycle scheme used at these two mills is shown schematically in Figure 8. A mechanical vapor recompression evaporator is first used to concentrate the bleach plant effluent. The condensate is returned to the process, while the concentrated effluent is sent to a small recovery boiler for organic “destruction.” Finally, the inorganic product from the recovery boiler is sent to a storage area. So far, the inorganic has only been stored and may either be recovered or disposed of at a later date. This arrangement is a working system today at two BCTMP mills, but it has not been tried at a kraft mill.

![Diagram of closed-cycle process for a BCTMP mill.](image)

*Figure 8—Closed-cycle process for a BCTMP mill.*
COMMON ELEMENTS OF CLOSED-CYCLE TECHNOLOGIES

Figure 9 shows the general arrangement for closed-cycle mill technology at a kraft mill. There are many specific schemes proposed for this application [1–103]. They all contain some common elements shown in the slide. There is usually a recycle directly from the bleach plant to the recovery process, along with equipment to concentrate the bleach plant effluent, separate the organic from the inorganic, and, finally, recover the chemicals. The concentration step always results in recycle of process water, and some arrangement for purge of chloride and non-process elements is always provided.

Figure 9—Common features of closed-cycle schemes.
Mechanical vapor recompression is the technique used to concentrate bleach plant effluent at the two BCTMP mills where closed-cycle schemes have been implemented. These evaporators require power for their operation. Multiple-effect evaporators have also been proposed for this service and may be more suitable for a kraft mill steam balance. Both of these evaporator-types are familiar to pulp and paper operations. A freeze crystallization process has been tried at a commercial scale for concentration of bleach plant effluent [36]. Though the specific application was ultimately not successful, a good deal was learned about this process for this application which may allow its use in the future, and there are significant potential advantages in power and energy use. Ultrafiltration and reverse osmosis have been proposed and tested in mill service for this application, but have not yet been proven commercially viable [28, 47, 49, 54, 58, 236, 298, 303, 305, 311]. The same is true of absorption techniques. The filtration and absorption processes would represent significant advantages if fouling and other problems could be overcome.

There are several methods for organic/inorganic separation. Combustion is, of course, the most familiar method used in mills today to separate organic from inorganic. The recovery boiler does this for black liquor. Either an incinerator or a small recovery boiler has been proposed for separation of bleach plant concentrate. A recovery boiler is what is used in the BCTMP closed-cycle mill. Gasifiers could also be applied to this service, and two units are under development for black liquor. Both the CHEMREC [244, 247] and the MTCD [245, 246] gasifiers are being demonstrated for black liquor, and other gasifiers are being tested for this service. Bleach plant concentrate is similar to black liquor in many ways, so use in such a gasifier would be a natural extension, though no demonstration has been discussed or reported. Gasification would have the advantages of producing a clean fuel gas and having lower corrosion sensitivity. Both wet-air and supercritical oxidation [6, 7] have also been proposed.
Three methods proposed for inorganic chemical recovery. An evaporator-crystallizer was the process used in the Rapson-Reeve process. Differential solubility has been used in a few applications to recovery boiler precipitator dust with some success [1, 98]. Acidification of the concentrate prior to combustion has also been tested for bleach plant concentrates.

The diagrams and descriptions above focused on bleached Kraft pulp production, but the basic elements of the closed-cycle schemes for unbleached pulp production are the same. Effluent concentration, organic/inorganic separation, and inorganic separation are steps that apply to closed-cycle for all pulp production.

**NON-PROCESS ELEMENTS (NPE'S)**
Recycle of effluents back into the mill always has the potential to increase NPE concentrations, and recycle always eliminates one discharge stream for NPE's. Research has focused on how much of each NPE enters the mill and with what material, how high the concentration of each NPE can become, what the impact of each NPE is on various pieces of mill equipment, and how to purge the NPE's from the mill stream.

**Organic and Inorganic NPE's**
Simple conservation concepts indicate that all inorganic NPE's and all organic materials will be discharged from the mill. Only the form and concentration of the discharges can be affected by the specific closed-cycle scheme. The proposed EPA Cluster Rule focuses on the organic portion of the discharges with limitations on AOX, COD, color, BOD, suspended solids, target chlorinated organic compounds, and VOC's from non-combustion sources. Many of the closed-cycle schemes also concentrate on the organics. They may include means to control the concentration of NPE's in process streams, but may not pay attention to environmental impact of the discharge of inorganic NPE's.

There is a fundamental difference between the organic and inorganic discharges. Aside from the obvious chemical differences, there is a difference in how their discharge
limitations are specified. Organic discharges are generally limited on total mass per tonne of pulp production, whereas, inorganics are limited on concentration. Conservation of species principles dictate that all inorganic NPE's that enter the mill must leave. Limiting the discharge of these inorganics could only be achieved by limiting the input rather than any closed-cycle scheme. As well, at the low concentration and in the form they enter, inorganic NPE's are benign. Adverse environmental impact can only result from their being concentrated, or, to a lesser extent, by changing their oxidation state.

Wood or an alternative fiber source is, by far, the largest organic input to the mill. All chemical pulping processes break the wood down into a fiber product and byproduct organic materials which must be disposed of in an environmentally sound way. In Kraft pulping only about 45% to 55% of the wood becomes the fiber product, 45% to 55% becomes byproduct. Most of this non-fiber material becomes the organic in black liquor, which is burned in the recovery boiler. For a bleached Kraft mill, about 4% of the organic in wood is normally discharged in the bleach plant effluent, and subsequently partially destroyed in a biological treatment facility. A small portion of the non-fiber organic may be converted to a product such as tall oil or turpentine which can be sold.

The common feature of the current means of "destroying" the byproduct organic either by combustion or biotreatment is oxidation to \( \text{CO}_2 \) and water. \( \text{CO}_2 \) is the only broadly acceptable way of discharging organic carbon from the mill other than as the fiber product.

An initial comparison of combustion and biotreatment would favor combustion as a means of treating byproduct organics. The conversion efficiency of organic carbon to \( \text{CO}_2 \) in a recovery boiler or hog fuel boiler is about 99.9%. The corresponding figure for biotreatment for total organic carbon conversion to \( \text{CO}_2 \) is only about 50% (though BOD conversion efficiency is considerable higher than this).
The comparison does not reflect the full environmental impact of these methods. First, combustion drives off all water and gasifies almost all the organic. The remaining solids (dregs, bottom ash, and fly ash) now contain very high concentrations of the inorganic NPE's which will complicate their environmentally sound land disposal. As well, destruction of chlorinated organics may not be adequate in existing equipment.

Chloride has gotten the most extensive treatment and study. Its effect on corrosion rates under acidic conditions and its effect on corrosion and plugging in recovery boilers is well known. Several studies have identified the ways chloride enters the mills from sources other than the bleach plant. As well, strategies and equipment to remove chloride have been studied and implemented in mill practice.

**Chloride in the Pulping and Recovery Cycle**

Chloride in various pulp mill liquors has always been a concern. At its most benign, chloride is simply a deadload in the liquors which increases the hydraulic and evaporative load. However, it is also a well known cause of corrosion in many areas, particularly the recovery boiler. As well, chloride lowers the melting point of recovery boiler deposits and substantially aggravates fouling and plugging in the tube banks. Current efforts to reduce the impact of mills on the environment may increase the input of chloride to the pulping and recovery cycle or reduce the means of purging chloride from the cycle.

Chloride enters and leaves the mill in a variety of ways as depicted in Figure 10 [52, 96–98]. The inputs of chloride are with the wood, water, makeup chemicals, and potentially with recycled bleach plant filtrates. The losses are with the pulp leaving the pulp mill, dust, and HCl out the recovery boiler stack, and through spills and other discharges. Table I summarizes the typical values and ranges of chloride inputs and losses. Some of these are very small, such as the typical chloride input with wood and chloride loss with recovery boiler stack dust. In comparison the potential input of chloride with the recycle of some or all of the bleach plant filtrate is truly huge. The loss of chloride with the HCl that leaves the
recovery boiler stack can be a very substantial term, and it is not well known for most mills. An estimate of the importance of the HCl loss can be made using a simple calculation of total mill chloride input and loss. The results of this calculation are clear enough to draw some important conclusions.
Figure 10—Chloride inputs and losses.

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<td>STREAM</td>
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<td>Inputs</td>
</tr>
<tr>
<td>Wood</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Makeup</td>
</tr>
<tr>
<td>• purchased</td>
</tr>
<tr>
<td>• ClO₂ gen.</td>
</tr>
<tr>
<td>BP filtrates</td>
</tr>
<tr>
<td>Losses</td>
</tr>
<tr>
<td>With pulp</td>
</tr>
<tr>
<td>RB stack</td>
</tr>
<tr>
<td>• dust</td>
</tr>
<tr>
<td>• HCl</td>
</tr>
<tr>
<td>Spills etc.</td>
</tr>
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</table>
At steady state the loss of chloride from the pulping and recovery cycle must equal the input. When chloride input increases, the chloride level in the mill liquors will increase until the loss with liquor discharges and pulp losses, along with the loss through the recovery boiler stack, equals the input. This means that the chloride-to-sodium ratio in the mill liquors will increase or decrease as the chloride input increases and decreases. All the liquors, green, white, and black have almost the same Cl-to-Na ratio, and it is the same for the pulp washing losses and the weak wash. The Cl-to-Na ratio is typically about 3% by mass, but ranges from 1% to 35%. In many mills this can be calculated from the analysis of strong black liquor which is often tested for both sodium and chloride content. The Na content is usually about 19% and the chloride content is often near 0.6% making the Cl-to-Na ratio about 3%. Because all the spills and pulp losses have this level of Cl-to-Na, one element of the chloride balance can be calculated by multiplying the Cl-to-Na ratio in the mill liquors by the sodium makeup for the mill. This along with the HCl loss constitutes the vast majority of the chloride losses so that:

$$\text{Cl loss} = \text{(sodium makeup)} \times \text{(liquor Cl-to-Na ratio)} + \text{(fraction of black liquor Cl lost as HCl)} \times \text{(liquor Cl-to-Na ratio)} \times \text{(sodium content of black liquor solids)} \times \text{(black liquor solids per tonne of pulp)}$$

$$\text{Cl loss} = \text{Cl input} \approx \text{Na}_{\text{mu}} \times (\text{Cl}/\text{Na}) + \text{HCl} \times (\text{Cl}/\text{Na}) \times \text{Na}_{\text{buls}} \times \text{BLS}_{\text{pulp}}$$

Typical values for some of the parameters needed in the above expression are given in Table II.
As an example, a mill with sodium makeup of 10 kg Na/odt pulp, a chloride-to-sodium ratio in the strong black liquor of 3%, a 5% black liquor chloride loss as HCl, a sodium content in the black liquor solids of 19%, and 1600 kg BLS/odt pulp would have a loss of 0.3 kg Cl/odt with spills and pulp losses, and 0.46 kg Cl/odt loss with the HCl loss. The total chloride input and loss would then be 0.76 kg Cl/odt.

If only a quarter of the bleach plant filtrate was recycled to brownstock washing or directly to the weak black liquor, the chloride input would increase by about 2.5 kg Cl/odt to 3.26 kg Cl/odt. With no other changes in the purge of chloride from pulping and recovery, the Cl-to-Na ratio would increase to 13%, i.e., the chloride content of the black liquor would increase to 2.5% from an initial value of 0.6%, a factor of four increase.

Several important conclusions can be drawn from the above simple examples. First, it is relatively easy for a mill to make an estimate of current chloride input. Second, almost any estimate will show that HCl is currently an important purge for chloride. Any reduction in the HCl purge will significantly increase the chloride levels in all liquor streams. Third, any

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<th>TYPICAL</th>
<th>RANGE</th>
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<td>Black liquor solids</td>
<td>BLS&lt;sub&gt;pulp&lt;/sub&gt;</td>
<td>1600 kg/odt pulp</td>
<td>1400-1800</td>
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<td>Sodium in BLS</td>
<td>Na&lt;sub&gt;bls&lt;/sub&gt;</td>
<td>19%</td>
<td>18-20</td>
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<tr>
<td>Na volatilized to fume/dust in RB</td>
<td></td>
<td>10% of Na in BLS</td>
<td>8-12</td>
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<tr>
<td>Total Na makeup to mill</td>
<td>Na&lt;sub&gt;mu&lt;/sub&gt;</td>
<td>10 kg/odt pulp</td>
<td>5-20</td>
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<td>Cl/Na in BLS</td>
<td>Cl/Na</td>
<td>3%</td>
<td>1-35</td>
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<tr>
<td>HCl loss</td>
<td>HCl</td>
<td>5% of Cl in BLS</td>
<td>0-25</td>
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<tr>
<td>Cl in BLS</td>
<td>Cl&lt;sub&gt;bls&lt;/sub&gt;</td>
<td>0.6% of BLS</td>
<td>0.2-7</td>
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<td>Cl/Na enrichment in fume/dust</td>
<td>2.5 x Cl/Na in BLS</td>
<td>2-3</td>
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recycle of bleach plant filtrate will substantially increase chloride levels in the liquors if alternative chloride purges are not provided.

The information in Table II can be used to estimate the total quantity of dust going to the recovery boiler precipitator and the quantity of chloride carried with it. The total quantity of Na in the dust is about 30.4 kg Na/odt pulp. The chloride in this dust is enriched by a factor of about 2.5 above the typical level of 3% Cl/Na mass ratio in black liquor solids. The total quantity of chloride that could be purged by discharging the dust or leaching chloride from the dust would then be about 2.3 kg Cl/odt pulp. This is approximately equal to the increase in chloride input in the example above with one-quarter of the bleach plant filtrate recycle.

The enrichment of chloride in recovery boiler precipitator dust and the large quantity of dust make it a good candidate stream to work on for a new chloride purge. This purge will only be sufficient if the increase in chloride input doesn't exceed the chloride purge potential of the dust within a liquor Cl-to-Na ratio that avoids recovery boiler corrosion and pluggage.

**Chloride Inputs and Purges**

The individual inputs and losses of chloride from pulping and recovery are described below.

**Wood** - Pulp wood contains small amounts of chloride, usually less than 0.05 kg Cl/odt pulp. Logs may have substantially higher chloride contents if they are in contact with salt or brackish water during transportation or storage. Chloride input with the wood from these logs can range from 0.1 to 15 kg Cl/odt.

**Water** - The water used in such mill operations as pulp washing and lime mud vat dilution, showers, and scrubbers always contains some level of chloride. The typical range of chloride in water is from about 1 ppm to 1000 ppm. The higher values are usually associated with well water. The impact of this chloride depends on the quantity of water that actually enters the liquor cycle. An approximate conversion for a kraft pulp mill would
be that water containing 20 ppm would add between 0.15 and 0.4 kg Cl/odt pulp to the liquor cycle.

Makeup Chemicals - Sodium and sulfur losses are made up with saltcake, caustic, NaSH, or sulfur purchased from outside suppliers. As well, saltcake in spent acid from ClO₂ generation is often used as a makeup chemical. The chloride-to-sodium mass ratio for purchased saltcake is typically less than 2%. It ranges substantially for the spent acid, but is typically less than 4%. The sodium makeup for a typical kraft mill including all forms of purchased and internally generated sources ranges from 5 to 20 kg Na/odt pulp (15-45 kg saltcake/odt or about 30-90 lb saltcake/odt). This means that the chloride input will be from about 0.1 to 0.8 kg Cl/odt with the makeup chemicals.

Sodium Losses with the Pulp - Some sodium and chloride remains in the pulp that leaves the pulp mill. Depending on washing efficiency, sodium losses can range from about 5 to 15 kg Na/odt. The chloride-to-sodium ratio is the same in the pulp as for the liquors, typically between 1.5% and 6%, but with some mills using saltwater-floated logs it can be as high as 35%. This makes the chloride loss with the pulp typically between 0.07 and 0.9 kg Cl/odt.

Bleach Plant Filtrate - Chlorine and chlorine dioxide used in the bleach plant eventually find their way into the bleach plant filtrates except for very small fractions which remain with the bleached pulp product. The amount of chloride (and other chlorine forms) in the filtrates varies substantially with the pulping and bleaching sequence. The chloride generated when pulping softwood to a kappa number of 30 and bleaching with chlorine in the first stage would be about 70 kg Cl/odt pulp. Pulping hardwood with oxygen delignification to a kappa number of 11 and bleaching with 100% substitution of ClO₂ (Elemental Chlorine Free, ECF, bleaching) could result in filtrate chloride as low as 4 kg Cl/odt pulp in the filtrates.
Recovery Boiler Stack Losses - Sodium fume is generated during black liquor combustion. Approximately 10% of the sodium is volatilized and forms precipitator dust. About 1500 kg to 1700 kg of black liquor solids (BLS) are formed per ton of pulp, and Na constitutes between 18% and 20% of the BLS. This means that about 30.4 kg Na/odt is carried by the flue gas to the precipitator as dust, mostly in the form of Na₂SO₄. Electrostatic precipitators are typically 99% efficient in capturing this dust, so only 0.3 kg Na/odt escapes out the stack. Chloride in the black liquor volatilizes more readily than the other sodium compounds so chloride is enriched in the dust. Typically this enrichment is by a factor of 2 or 3. Using a typical Cl-to-Na ratio in black liquor of 3%, an enrichment factor of 2.5, the loss of chloride with the recovery boiler stack dust is about 0.02 kg Cl/odt pulp. In addition to the chloride-enriched dust that escapes the precipitator, some chloride is converted to HCl through reactions of the dust with SO₂. Measurement of HCl in recovery boiler stacks have shown wide variation from practically zero to 120 ppm. The level seems to correlate with stack SO₂ and O₂ concentrations, but with a great deal of scatter. The average of the fraction of chloride as HCl in the stack compared to the chloride in the black liquor for one group of recovery boiler tests was 4.7%. Using the chloride-to-sodium ratio in the liquor of 3% along with an HCl chloride loss of 5% results in a chloride loss as HCl of 0.46 kg Cl/odt pulp.

Spills and Other Losses - Some liquor leaves the pulping and recovery cycle with grits and dregs or as spills of liquor or weak wash. These losses are very hard to quantify.

What this general description makes clear is that HCl emission limitation promulgated by the EPA for combustion source will place increased pressure on chloride concentration in the pulping and recovery cycle, even without recycle of bleach plant filtrate.

Other than as a bleaching agent, chlorine compounds do not play a useful role in pulp manufacture. Removal of chlorine compounds from mill inputs of water, wood, and make
up chemicals, or removal from mill process streams is mandatory for chloride control in liquor streams. Some of the literature listed under "Bleaching Technology" in the reference section below deals with non-chlorine bleaching which reduces chlorinated organics in bleach plant effluent and allows recycle of BP filtrate back to pulping and recovery. Research has also been carried out in concentration crystallization, differential solubility, and freeze crystallization for removal of chlorine salts. All of these techniques would apply to inorganic liquor in the mill or to the input streams. Less effort has been made with membrane technology and electro-dialysis. These technologies offer significant savings in energy for solid separation compared to evaporation.

Other NPE's
The other NPE's have received less attention than chlorine. Because of their effect on peroxide bleaching, the transition metals have received most of the research effort [2]. Silicon and aluminum have been studied because high concentrations of these in white liquor can cause scaling of the evaporators [62, 63, 249, 251]. The effects of magnesium on aluminum concentrations have also been researched [52]. The solubility of these and the other NPE's is less well known and can be strongly influenced by pH. Some are also affected by the presence of fibers. These complications make the level of current knowledge about concentration buildup difficult to determine, and likely purge points difficult to identify. Research on solubility characteristics of the individual NPE's in the complex, concentrated liquors of pulping operations would find immediate application. Likewise, mill liquor sampling or mill process simulation would be key to understanding NPE build up on closed-cycle operations.

THE PROPOSED EPA CLUSTER RULE, COD, AND ORGANIC DESTRUCTION

The Proposed EPA Cluster Rule
The proposed EPA Cluster Rule covers the mill effluent, the bleach plant effluent, and non-combustion sources of air emissions. Combustion sources of air emissions are covered by
other regulations. Most discussions of the proposed Cluster Rule have focused generally on the mill effluent and more specifically on AOX. The proposed limit on AOX is 0.156 kg/tonne of pulp. Less emphasis is usually placed on COD and color though at 25.4 kg/tonne pulp COD is as limiting as AOX. Very extensive research has shown that ECF bleaching is effective in controlling targeted organochlorine compounds in the bleach plant effluent, but changes in pulping or delignification are required to control AOX.

**Chemical Oxygen Demand (COD)**

Kraft pulping dissolves most of the lignin and some of the hemicellulose and cellulose from wood. The residual liquor in the wood must be removed or bleached to produce bright pulp that does not yellow. The early stages of bleaching primarily remove lignin while the latter stages brighten the pulp. Most of the lignin in unbleached pulp is removed in the early bleaching stages so the organic compounds in the bleach plant effluent will be approximately equal to the lignin in the unbleached pulp. Residual lignin is most often indicated by the kappa number or, alternatively, k-number. A kappa number of 30 corresponds to a residual lignin of about 4.5% in the pulp. In other words, a pulp with a kappa number of 30 would discharge about 45 kg/tonne of pulp from the bleach plant.

The chemical oxygen demand is essentially the stoichiometric amount of oxygen required to convert organic to \( \text{CO}_2 \) and \( \text{H}_2\text{O} \). A value near 1:1 is approximately correct for bleach plant effluent organic. Black liquor is similar to bleach plant effluent concentrate. Black liquor solids have a stoichiometric air requirement of about 4.5 kg air/kg BLS. The black liquor stoichiometric oxygen requirement is then 1.06 kg oxygen/kg BLS. This means that a kappa number of 30 corresponds to a COD from the bleach plant of about 45 kg/tonne pulp.

A kappa number of 30 is a conventional level for unbleached softwood pulp intended for bleached pulp production. The COD from the bleach plant alone exceeds the proposed Cluster Rule COD limitation. Other sources of dissolved organics such as open washing stages and black liquor spills also contribute to COD in the mill effluent. It is clear that the
pulp entering bleaching must have a far lower kappa number than 30 if the COD limit is to be met. All the pulp processing liquors up to the stage where the kappa number is less than about 10 must be recycled back through the recovery department or treated in a separate closed-cycle system in order to destroy the organics and provide purges for the NPE’s from the mill.

Both extended delignification and oxygen delignification produce lower kappa number pulps for bleaching, and allow the lignin to be processed through the conventional recovery system. The load on the evaporators, recovery, and recausticizing increases. Non-chlorine bleaching agents such as ozone or peroxide allow uncomplicated recycle of bleach plant filtrates to the recovery process. The filtrates from chlorine and chlorine dioxide are less compatible chemically, but their biggest impact on recovery is the very substantial increase in chloride input to pulping and recovery.

**Organic Destruction**

The ideal circumstances for oxidation of organics is the same as for most chemical reactions: premixed reactants, homogenous medium, stoichiometrically correct mixture, sufficient temperature, and sufficient time for reaction completion. Very complete destruction of most hydrocarbons, organics, chlorinated organics, and CO occurs in a few hundred milliseconds at 800°C under perfectly mixed and homogeneous conditions. Most recovery boilers operate above 1000°C and have average gas residence times of 5 to 7 seconds. The fact that the fuel and air are introduced separately, the gas mixing is poor, and the combustion is heterogeneous, prevents really good conversion efficiencies of organic to CO₂. Mixing is a key element of proper combustion and the huge combustion boxes and separate fuel/air introduction in recovery boilers hinders rapid and complete mixing.

The complex chemistry of recovery boilers may either simplify or complicate the destruction of organics from the bleach plant. First, black liquor contains a large fraction of sodium. Much of the chloride in bleach plant filtrate will be captured as NaCl in the smelt
when bleach plant filtrate is fired with black liquor. This traps chloride in the recovery loop and causes buildup of chloride in the liquor, with all the attendant corrosion and plugging problems in the boiler. Some chloride will not be captured in the smelt but will travel with the combustion gases. This chloride can either react with the sodium fume to form NaCl which is caught in the precipitator or not react with fume and form HCl. The HCl passes through the precipitator and, unless taken out with a scrubber, becomes an air pollutant.

One proposed alternative to either combustion or biotreatment for bleach plant filtrate is Supercritical Water Oxidation (SCWO) [6, 7]. This process concentrates bleach plant filtrate to about 5% organic, injects oxygen into the concentrate, and then processes this mixture at supercritical conditions. For water, critical conditions are 219 atmospheres pressure and 374°C (3,200 psi and 705°F). Under these conditions water becomes a very powerful solvent, dissolving essentially everything in the bleach plant concentrate, and the oxygen as well. This means the organic is oxidized under homogeneous, premixed conditions. Stoichiometry and reaction time are controlled by design and operation so that very complete destruction of organics and organochlorine compounds can be achieved.

SCWO has two advantages as a closed-cycle mill technology aside from homogeneous, premixed reaction. The advantages are that only modest concentration is required, and that the treated effluent provides a purge for NPE’s. Bleach plant filtrate is usually about 0.5% solids. Concentration to about 5-8% solids removes 90% of the water for reuse within the mill. This concentration is far lower than the 50-70% concentration required for combustion. The lower concentration requirement lends itself to more modest energy and equipment requirements for concentration. The remaining water provides a diluent for the NPE discharge.

CONCLUSIONS
Environmental concern, particularly the proposed EPA Cluster Rule, has heightened interest in Closed-Cycle Mill Technologies. There is some industrial experience on the impact of
closed-cycle operation on equipment and processes from three implementations, one for a bleached Kraft mill and two for BCTMP mills. There are also many proposed schemes for mill closure and some clearly identifiable common features of these schemes. The currently proposed Cluster Rule regulations cover only a portion of the environmental regulations for pulp and paper operations. Discharges to the air from combustion sources and solid waste discharges are not yet a major component of the Cluster Rule. Most closed-cycle schemes basically deal with effluent discharge and often ignore the impacts on air and land discharge. Mill closure often adversely affects these other two environmental areas, VOC’s and metals concentration in dregs and ash are examples. Control of non-process elements, particularly chlorine, is essential for any of these schemes to succeed. Purges of the NPE’s must be designed into the overall mill closure arrangement. As well, all organic destruction involves oxidation of organic carbon to CO₂, whether by combustion, biotreatment, supercritical water oxidation, or some other process. Both overall destruction efficiency and total environmental impact must be taken into account with any organic disposal scheme. Work needs to be done in the areas of assessing the closed-cycle schemes for total environmental impact and identification of technologies which address total environmental impact.
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