Progression Towards Minimizing Mill Effluent

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ABSTRACT

Union Camp Corporation had early motivation to reduce the environmental impact of its mills. An ethic was developed that supported and encouraged environmental stewardship. Goals were set for water use and effluent closure.

Because bleaching discharge represent a significant portion of the total mill effluent volume, BOD, color and AOX, a development program was designed to reduce the impacts from that source. Emphasis was placed on counter-current filtrate recycle to reuse as much water as practical. Water conservation measures were instituted including air-doctoring, high pressure recycle cleaning showers, segregation of mill water systems, spill control, condensate re-use, etc. Bleaching fundamentals were examined to develop processes that would tolerate recycle and recovery of as much of the filtrate and dissolved lignin as possible. Bleaching methods compatible with the Kraft processes were incorporated which included high consistency oxygen and ozone delignification.

At Union Camp, use of chlorine and chloride dioxide chemicals that contribute to liquor cycle problems, bleach plant corrosion and effluent toxicity is being minimized. A special OZED bleaching sequence that incorporates a (C-Free™ pulp) high consistency ozone bleaching stage facilitates closure from the extraction stage back. Only the final chlorine dioxide stage and a minor acid stage purge remain open to the sewer. There are a number of potential problems from closure, including Calcium scaling, that have been effectively controlled.

INTRODUCTION

Historically, bleached pulp production was based on core processes that were water intensive and generated copious amounts of effluent in relatively dilute streams. The Kraft process and conventional bleaching using chlorine and chlorine dioxide eventually created an efficient industry centered around chemical conservation. Water was plentiful and primary and secondary effluent treatment processes evolved that were very effective at handling pulp mill effluents, significantly reducing their toxicity and contaminant levels. As pulp mills grew in size, the quantities of effluent and water became increasingly significant to the surrounding ecological systems. Union Camp was an early leader in the efforts to minimize mill effluent due to the location of the Franklin mill on a very small river in Virginia USA. Significant effort was expended developing an efficient effluent ASB and ponding system. It was recognized however, that this would not be adequate for long term growth since water and stream resources would continue to be sought by others. Also, ecological impact could ultimately become controlling due to long term cumulative effects. A desire began to grow within Union Camp, as a good corporate citizen, to minimize the impact of the mill on the surrounding environment. This resulted in developing a strong environmental ethic and a logical progression towards a minimum effluent mill scenario.

Building an internal company wide commitment to the environment is the first step that should be taken if mill closure is to be done successfully. Everyone in the company should be aware of and supportive to the environmental program and know its' value to sustained operation and growth. This is especially true of Operators and Maintenance personnel since they have direct first line impact on the environmental performance of the existing process and environmental control systems. The Research team must discover and develop processes that viably project long term reductions in effluent volume and properties. Engineering teams must make current effluent abatement processes as effective as possible and help implement newer technology that stretches the envelope of environmental performance. This will result in a progressive process towards closure as a mechanism of permit problem avoidance and environmental stewardship.

DISCUSSION

General Elements of Mill Effluent Reduction

Once company direction is set towards closure, the key areas of effluent impact must be attacked. For a typical bleached pulp mill, of the three principle areas impacting effluent, (see Table 1): the greatest impact is from the bleach plant.

Table 1

Major Environmental Impact Areas

Bleach Plant

HAS THE GREATEST ENVIRONMENTAL IMPACT

Evaporator

Focus on Minimizing Spills
Segregate and Remove Condensate Organics

Pulp Mill

Select Good Closed Processes
Oxygen Delignification for Organic Recovery
Filtrate Management is the Key

Closing the bleaching process has complications however, and takes significant study and development work. The other two areas of impact are the evaporator and pulp mill areas. Effluent reduction measures are generally more straightforward in those areas, focusing on minimizing losses.

There are complications in the liquor cycle area with chloride and potassium build-up but that will not be covered in this paper. Buildup of non-process elements has been described by others (1,2). Union Camp has programs in place to deal with liquor cycle closure.

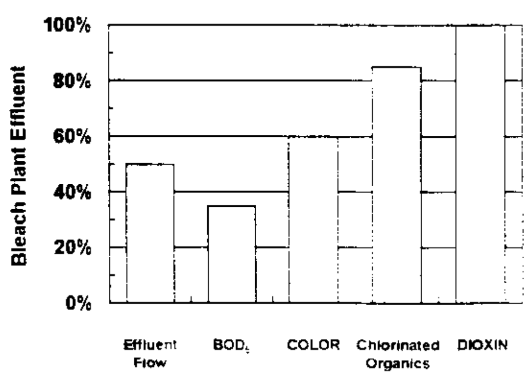
Union Camp Route to Bleach Plant Closure

Why Focus on the Bleach Plant? In the mid 1960's Union Camp began to realize that Mill Effluent would eventually become a controlling factor to mill expansion and already then had a vision for a totally effluent free bleach plant. An intensive research program was initiated to focus on developing processes and technologies that would minimize bleach plant effluent. The flow in the receiving river at Franklin is so low that environmental permits limit discharges of effluent to only four months out of the year. Thus extremely large holding ponds had to be developed in order to support such a strategy. It was also felt that in order to consider mill expansions or new site development, the exceptional environmental performance offered by bleach plant closure would help to avoid problems with ever-tightening environmental regulations in the future.

Focus was placed on the bleach plant because it represented greater than 50% of the total mill effluent flow (Figure 1). One of the major objectionable properties of mill effluent is color. Bleaching systems typically contribute 60% or more of the total effluent color from a mill. Chlorinated organics became increasingly important as environmental awareness increased. The bleach plant produces 85% or more of the chlorinated organics being discharged from the mill.

Figure 1

Percent of Mill Emissions from Bleach Plant



Finally with the surfacing of the toxicological effects of dioxin, it was found that virtually all of the dioxin being discharged from a conventional bleached mill is contained in bleach plant effluent. In addition to effluent concerns, the Franklin Mill also had desires to minimize fresh water usage.

The bleach plant contribution to total mill effluent and water consumption is further accentuated as closure activities in the rest of the mill such as closed wash and screen rooms and spill control are addressed. Table 2 shows that when the rest of the mill is closed up as much as possible the bleach plant effluent can represent 45% of the total effluent organic load (BOD_5). This percentage can actually increase to as much as 73% when modern environmental techniques are employed in the evaporator, pulp mill and paper machine areas.

Table 2

BLEACH PLANT CONTRIBUTION TO MILL EFFLUENT TREATMENT PROBLEM

	Normal Mill	Typical Closed Mill
Effluent BOD_5	35%	45%
Effluent Color	60%	85%
Chlorinated Organic Production (AOX)	85%	85%
Dioxin	100%	100%

The First Step Is An Implementation Plan. Union Camp began implementing a program 30 years ago to develop the low or minimum effluent bleach plant. Progressive goals were set and engineering and R&D resources were allocated to identify the best possible path to closure. Through assessment of the various available technologies, it was determined that the best route for Union Camp would be to recycle and recover as much of the organic material liberated in the bleach plant as possible. In addition, there was a strong desire to reduce the chloride input to the recovery and bleaching systems in order to minimize effects of bleach plant corrosion and recovery boiler water-wash frequency. Figure 2 shows the path developed by Union Camp for bleach plant closure. The first major step was to reduce effluent volume of the conventional CEDED bleaching system through counter-current washing. Next it was determined that oxygen delignification could recover 45% of the organics from bleaching effluent. High consistency oxygen was employed in order to do as much delignification as possible prior to the first bleaching stage. Union Camp mills routinely achieve 40-45% delignification on hardwood and 55% delignification on pine.

Figure 2

Union Camp Route to Bleach Plant Closure

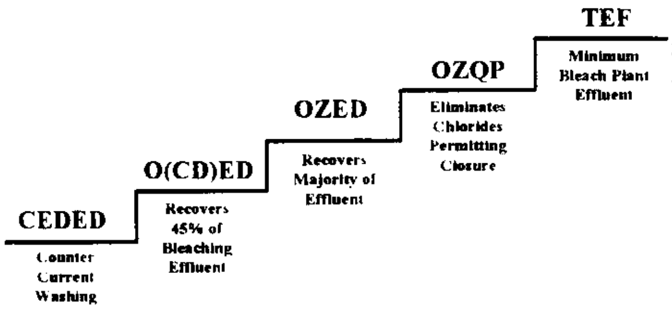


Table 3

Union Camp Bleaching Developments

30 Years Ago Set Objective of Step-by-Step Bleach Plant Close up

25 Years Ago, World's First Fully Counter-current Bleach Plant

15 Years Ago, Led the U.S. With First Oxygen Bleaching System

9 Years Ago, Built $6 Million, 25 TPD Pilot Plant to Develop Ozone

6 Years Ago, Announced Erection of World's First Ozone Bleach Line. Now In Routine Operation Since September, 1992

3 Years Ago, Spent $1.6 Million on Pilot Plant to Develop TCF

Now Focusing on Developing Last Step: Total Effluent Free Bleaching (TEF) Using TCF Sequence

The next step (in the bleach plant) to be addressed was the chlorination stage, since it still represented a significant portion of the organics being liberated in bleaching. Ozone was identified as a bleaching agent that would be compatible with the black liquor recovery system. Many years of research were devoted to developing and refining an ozone bleaching process that would replace the chlorine stage with zero to minimal effect on pulp properties. Ultimately, Union Camp developed the C-Free™ pulp high consistency ozone bleaching process. An ECF ozone bleaching sequence was developed around the patented C-Free™ pulp ozone reactor that allowed the recycle and recovery of organics from the O, Z and E stages. Only caustic and sulfuric acid are employed as major chemicals in these stages, both being compatible with the Kraft recovery process. The C-Free™ pulp ozone process at Union Camp's Franklin, Virginia mill has been in full scale operation for five years bleaching Kraft southern pine.

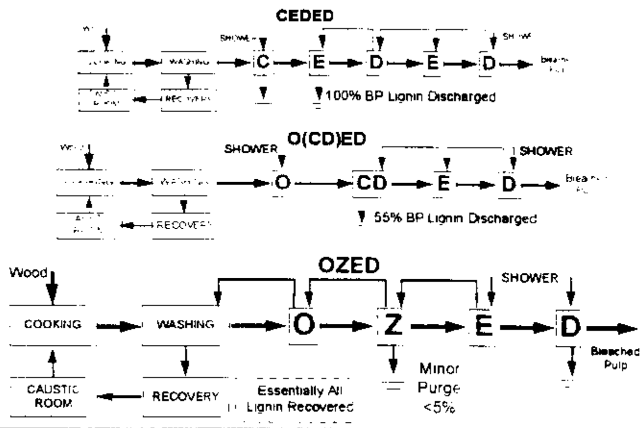
Union Camp is examining the total elimination of chloride compounds in its technological developments for use in those areas of the world where it is demanded. The most straight forward way to achieve complete bleach plant closure is to use a total chlorine compound free (TCF) bleaching process. Even then, it will be necessary to carefully handle the build-up of non-process elements. The Union Camp C-Free™ pulp bleaching technology is already being used in TCF bleaching of market pulp at the SCA Graphics Östrand Mill in Sweden where good results are reported (3), including very low effluent due to the use of an all press bleach plant supplied by Sunds Defibrator.

Table 3 provides a summary of Union Camp's bleaching development achievements over the past 30 years. The accomplishments continue to follow the route to closure set by the company. Significant funds have been allocated to pilot plant development of ozone ECF and TCF systems.

Figure 3 shows the evolution of Union Camp's bleach sequences and the filtrate management strategies employed to reduce bleach plant organic discharge. As shown in figure 3, essentially all of the lignin extracted and dissolved in the bleaching liquor is recovered in the current C-Free™ pulp ECF ozone based process.

Figure 3

Union Camp Bleaching Sequence Progression



Franklin Bleach Line Closure Achievement

In September of 1992, Union Camp started up the C-Free™ pulp ozone based bleaching process on southern pine at Franklin, Virginia. The line has been running for approximately five years producing all of the pine pulp needed to support six paper machines (4,5,6). Figure 4 shows the fiber line at Franklin. The extraction stage filtrate is cascaded counter-currently through the bleach plant and back to the black liquor system. An ozone generation gas recycle system was employed in order to conserve oxygen and to couple the ozone generation directly to the line. This minimizes the cost for ozone and produces quick response of the ozone application and control system.

Figure 4

Union Camp - Franklin, VA
C-Free™ Pulp Fiber Line

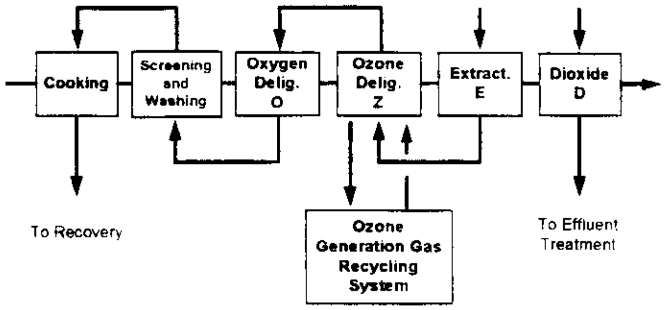
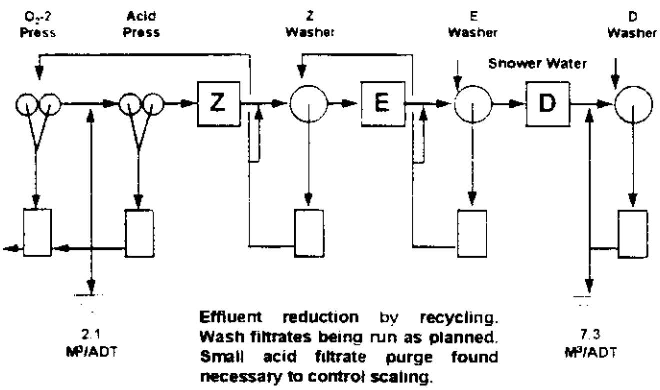


Figure 5 shows the filtrate recovery being achieved at Franklin Virginia on southern pine. Only the final D stage effluent at approximately 7.3 cubic meters/ton and a small purge of approximately 2.1 cubic meters/ton from the acid pre-treatment loop remain as effluents to the bleach plant sewer. The minor acid pre-treatment purge is employed to avoid calcium scaling in the bleach line.

Figure 5

Franklin Recycle Achievement



High consistency ozone was selected in order to maximize ozone utilization and allow for large applications of ozone to achieve a high degree of delignification. It also allowed the use of large amounts of ozone to get the greatest performance out of the ozone stage as possible. Typical ozone dosages for the C-Free™ pulp bleaching systems currently installed have ranged from 5-10 kg/ton depending on pulp species and incoming pulp characteristics. High consistency ozone also minimizes problems with filtrate recycle and recovery, since at high consistency, there is only 1.4 M³ of liquor per ton of pulp present. This minimizes the amount of dissolved organics carried into the ozone stage and reduces cooling/heating requirements of the pulp stream as well as the volume of liquor to be recycled.

The environmental achievements of the Franklin F bleach line on southern pine using ozone are shown in Table 4 against the original CEDED sequence replaced. The values given are on bleach plant discharge prior to effluent treatment. BOD and COD levels of 4.4 and 11 kg/ADMT respectively, are being achieved by the line. Color is reduced by 98%. The effluent color reduction represents only 3 kg/ADMT. Ozone effluent color is even better than oxygen based conventional sequences by 92%. All of the chlorinated organics have been dramatically reduced as indicated by an AOX value of less than 0.05 kg/ADMT. Dioxin compounds are essentially non-detectable in the effluent or the pulp. The TOX in the pulp is also dramatically reduced even over oxygen based conventional sequences.

Table 4

Effect of Bleach Sequence on Effluent and Pulp Quality

Southern Pine	Normal Emissions for Comparison CEDED	O(C+D)ED	OZED	OZED % Reduction from CEDED
Volume of Effluent, M³/ADMT	55.4	14.2	9.4	83
Effluent (Kg/AD Tonne)				
BOD_5	16	6.5	4.4	73
COD	66.5	22.5	11.0	83
Color	185	41.5	3.1	98
AOX	6.5	3.0	0.05	99
Chloroform	0.18	0.08	.002	99
TCDD (ppq)	650	60	N.D.	99+
Pulp				
TOX (Kg/ADMT)	0.28	0.12	0.04	86
TCDD (ppq)	3.4	0.8	N.D	-

The F bleach line in Franklin continues to run well and the C-Free™ pulp bleaching technology has been successfully employed at both the SCA Graphics Östrand Mill in Sweden (3) as part of a TCF bleach line on Scandinavian softwood and hardwood and at Consolidated Papers, Inc in Wisconsin Rapids USA as part of an ECF bleach line on northern hardwoods.

Necessary Parts to Completing Bleach Plant Closure

Two general areas of understanding need to be developed in order to close up bleach plant filtrates. First, process implications of changing filtrate characteristics have to be defined. Major process stream components and organics will build up in the filtrate recycle loop as each of the bleach stages are closed. Temperature and pH, as well as associated ions, change how each of the components acts in the system. The presence of pulp also influences how various ions and organics are partitioned in each of the stages and process systems. In order to learn how to close up the bleach plant one must first develop a mathematical model with capabilities to determine how each ion and compound as well as organics are partitioned within each stage. Table 5 presents the general items being examined through process modeling by Union Camp. Originally, a steady state "GEMS" type model was used. Dynamic effects are now being examined using H.A. Simon's Ideas™ model.

Table 5
Model Development

Properties	Metals	Ligands	Solids Formed In
Flow	Na	Cl	Digester
O.D. Fiber	K	CO_3	O Stage
Temp	Si	C_2O_4	Z Stage
COD	Fe, Q_{Fe}	SO_3	E Stage
	Mg, Q_{Mg}	SO_4	P Stage (if used)
	Ca, Q_{Ca}	DTPA	
	Mn, Q_{Mn}		
	Cu, Q_{Cu}		

Current model contains: Ion sorption and Lignin redeposition as functions of pH

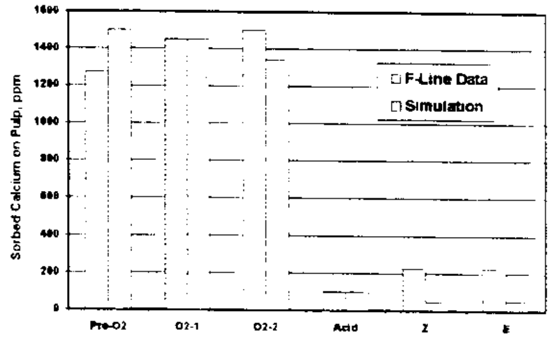
Enhancement
We have now converted GEMS to IDEAS™ to make it more user friendly and to move from static to dynamic balances.

Of particular importance is the determination of closure effects on scaling resulting primarily from calcium and its associated ligands of carbonate, oxalate and sulfate. The effects of these compounds on scaling and bleaching performance must be verified through lab, pilot and mill studies.

Finally, once the primary effects of the major components have been determined, then the process flow arrangement and equipment should be selected to produce the optimum conditions required by the bleaching process.

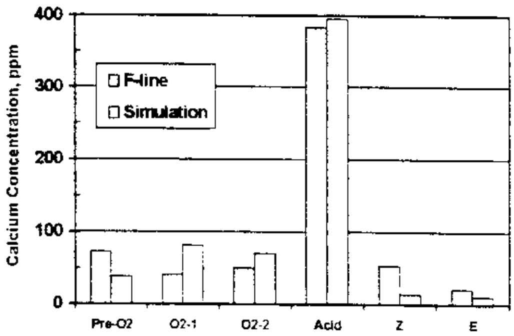
Scaling Must Be Understood. One of the most important ions to control in order to minimize scaling in the bleach plant is calcium. Union Camp has used its simulation model to predict the calcium levels and accumulation through the process. The partitioning of calcium between fiber and liquor is a function of pH and ionic strength. Figures 6 and 7 show how the simulation predictions compare to individual mill results on calcium levels for F line southern pine.

Figure 6
Sorbed Calcium: Mill Data and Simulation - Mat Samples



From the figures it can be seen that calcium sorbs readily onto pulp at alkaline pH and desorbs under low pH acid conditions. This is principally the reason for the acid loop purge. The purge is designed to keep the calcium under control by maintaining concentration below the solubility limit. This is described in more detail in reference (7)

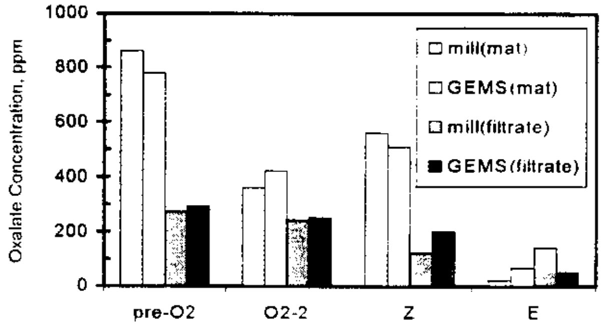
Figure 7
Calcium Concentration in Filtrate: Mill Data & Simulation



Another very important ion related to scaling is oxalate. In addition to that naturally occurring in the wood and liberated in the cooking process, oxalate has been found to be generated in both the oxygen and the ozone stages. Figure 8 shows the correspondence of the Union Camp developed computer simulation to the concentration of oxalate in both the mat and filtrates at different washer locations. Very good agreement is obtained in the model. Thus it has been used extensively to understand the effects of process changes on the generation and accumulation of calcium oxalate scale in the pulp bleaching system.

Figure 8

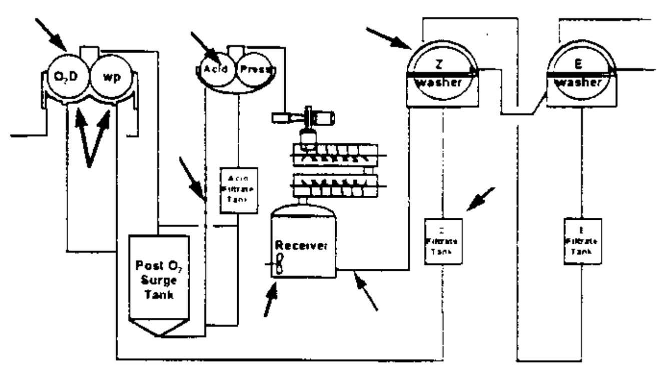
Oxalate Concentration in Mat and Filtrate: Mill Data & Simulation



With the knowledge generated by the actual mill trials and the simulation, Union Camp has developed a fundamentally sound understanding of scaling and developed operating practices that have minimized the impact of scale on operations. Figure 9 shows the potential scaling locations within the C-Free™ pulp bleaching process.

Figure 9

Potential Locations for Scaling



The potential for scaling has been reduced at each of these locations to extremely low levels through process changes. Scaling is being controlled on the C-Free™ pulp bleaching system merely by process management. Use of scale inhibitors or major equipment cleaning are totally avoided. A weekly scale monitoring program has been set in place to oversee the scale control performance of the process operation.

Bleaching Is Effected By Non-Process Elements. A necessary part to complete closure is to learn how to purge heavy metals. This can be done through the use of additives, special purging techniques or special removal processes. Ultimately, the heavy metal purge will be the most challenging part of bleach plant closure to overcome. Union Camp has been piloting and testing unique processes and filtrate management techniques that will minimize the amount of purge necessary to control heavy metals.

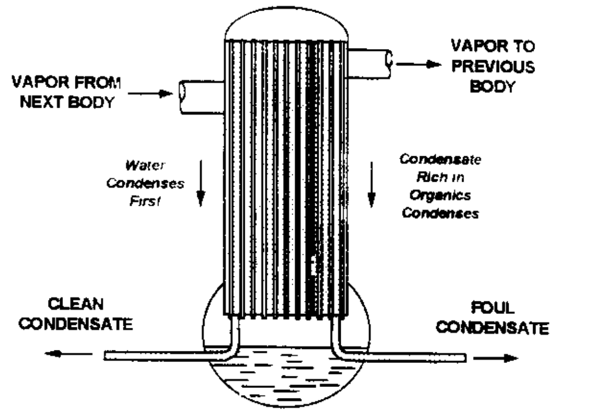
Evaporator Area

The approach taken by Union Camp in the evaporator area has been to focus on minimizing organic losses to effluent. There are three key elements to successful evaporator environmental performance: Condensate segregation, spill collection and liquor system design.

Condensate Segregation Is Important. In order to achieve a minimum effluent mill, the high organic load of the evaporator condensates must be addressed. If methanol containing condensates are discharged to the sewer, they contribute directly to the effluent. If they are used on the washing in the bleach plant, they will ultimately be discharged to the sewer at that location. Union Camp's approach to reducing the organic load from the evaporator condensate was to totally segregate the condensate in each evaporator body. This minimized the amount of clean condensate organic loading to the bleach plant as a first step. Figure 10 simply shows how this is done in an evaporator body. A separation baffle is usually employed which allows the first major section of a body to condense the water from the vapor in the first section. As the water condenses in the second section, organics begin to be stripped from the vapor thus producing foul condensate. These foul condensates are collected and stripped again with a steam stripper in order to make additional clean condensate.

Figure 10

Evaporator Condensate Segregation

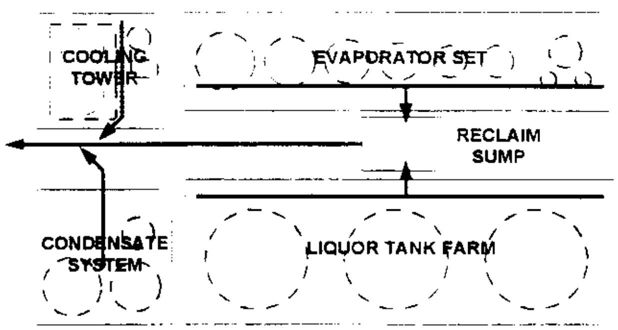


The rich organic stream that is stripped from the foul condensate is principally made up of methanol. It is also rich in sulfurous compounds. A methanol rectifying system can be used to convert the methanol into a fuel that can be used to incinerate foul pulp mill odorous gases. These gases can be collected and stripped of the sulfur containing compounds using makeup alkali thus supporting the sodium-sulfur balance of the mill. This is all accomplished very successfully at the Union Camp Eastover facility in South Carolina USA.

Spill Collection Is Crucial. A major emphasis of Union Camp in the evaporator area was in reducing the amount of liquor that is spilled in the evaporator system. The most important aspect of spill handling in the evaporator is to segregate the actual liquor areas from any water borne area. This allows the liquor spills to be picked up without undo energy requirement to evaporate unnecessary water. Figure 11 shows a simplified layout depicting evaporator sewer segregation. The cooling tower and condensate system areas are directed to the sewer separately from the evaporator and liquor tank farm drainage areas.

Figure 11

Evaporator Spill Segregation and Recovery

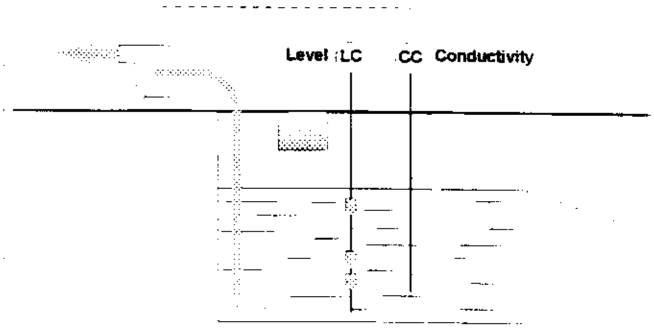


The second important element to spill collection is to have a good collection system for spills. Figure 12 shows the sump arrangements currently employed at the Union Camp Eastover mill for recovery of spilled liquor. This is an underflow-overflow sump design which under normal conditions allows rain water to pass through the sump but if a spill occurs, triggers the sump pump to collect the material before it is discharged. The key to an effective spill collection sump is to maintain reliable conductivity and level devices. A reliable pumping system must also be developed.

Liquor System Design Is Also Important. The third important element in minimizing the BOD load from the evaporator area is to have an effective liquor tank farm arrangement. Sufficient dump tank and swing liquor tank capacity should be available to hold and redistribute any spills or low concentration liquor occurrences. In addition, good tank bottom and recirculation design systems should be employed to minimize the amount of sediment that must be cleaned out of the filtrate tanks during outages.

Figure 12

Liquor Spill Collection
Underflow/Overflow Sump



As an example of what can be achieved when condensate segregation, spill collection and good liquor system designs are employed, the Eastover mill has been able to achieve BOD losses of less than 0.5 kg/ADMT from the evaporator area on a long term sustainable basis.

Pulp Mill Closure

The Key In The Pulp Mill Is Spill Avoidance. A good filtrate management strategy must be employed. Operators must have a good perspective and be thinking ahead and must know the value of filtrate spills over the concentration range through the system. It is good to have filtrate tanks as large as possible, but that still does not stop instrument or operator errors from causing filtrate tanks overflows. Thus good management practices and operator attention to detail, particularly during changing of production rates or during outages, is of critical importance.

Use of Oxygen Delignification Is Essential. Another important element to pulp mill closure is the implementation of oxygen delignification as discussed earlier. Good washing after the oxygen stage is also an important factor in minimizing effluent. For the ozone bleach line, Union Camp employs wash presses after the oxygen stage to minimize solids impact on the subsequent ozone stage and to capture of as much organic material as practical for recycle.

With oxygen bleaching, closed screens and reject handling processes with good brown stock filtrate management practices, pulp mill effluent can be extremely low. Union Camp's Eastover, SC mill achieves sustainable levels of less than 1 kg/ADMT of BOD from the pulp mill area where these brownstock measures are utilized.

SUMMARY

In summary, Union Camp believes that our industry should continue to focus on reducing the effluent from our pulp mills. We should strive to develop the lowest possible levels of effluent in order to protect our environment and co-exist within the surrounding community. Bleach plant processes should be selected that promote closure to the greatest degree possible. The following points are offered as conclusions to this paper:

1. **The principle area of effluent focus in pulp mills should be the bleach plant. Oxygen delignification should be the first step towards closure followed by steady progression of bleach plant developments aimed at effluent reduction with organic recovery.**
2. **C-Free™ pulp bleaching technology using ozone, as practiced at Union Camp Franklin, allows for recycle and recovery of OZ(EO) filtrates thereby significantly reducing effluent volume and fresh water requirements.**
3. **Use of ozone technology such as C-Free™ pulp bleaching is a key stepping stone towards either ECF or TCF bleach plant closure.**
4. **Environmental opportunities in the evaporator and pulp mill areas can be effectively examined simultaneously with the bleach plant.**

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