Current Status of Zero Effluent Pulp and Paper Mills

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ABSTRACT:- There is no bleached Kraft pulp mill operating at the moment with zero effluent. The present status of closure of the water cycle for bleached Kraft pulp mills, about 18-20 m^3/ ADt, prerequisites segregation, stripping and reuse of the black liquor evaporator secondary condensates. The closest approach to a zero effluent bleached Kraft mill is the new Metsa-Rauma pulp mill in Finland, which started up during March 1996. This mill designed to produce TCF pulp only, is approaching 5-6 m^3/ADt in effluent amount.

There are several paper mills (without pulping facilities) in US and Europe operating with zero efflunt. These all produce relatively "low grade" products, such as recycled linerboard, corrucating medium, construction papers etc. where some contamination is not so critical. The development of closed cycle paper mill (integrated with mechanical pulp e.g. CTMP, TMP, SGW or PGW or deinking pulp) is on the way and the best newsprint mills run already at the level of 7m^3/ADt effluent flow. Typically the water consumption varies betwen 10-20 m^3/ ADt for wood containing grades and 5-10 m^3/ADt for wood free fine paper.

The evaporation process is the most effetive way to remove organic and inorganic substances from mill effluent, which is prerequisite for the reuse of process water. Zedivap™, a multi effect falling-film MVR- type evaporator, is specially designed to handle large volumes of water and to utilize waste heat. The developed evaporation technology has been an important step towards an effluent free pulp or paper mill concept. At the moment four Zedivap™ -systems are in the operation and one more under delivery.

This paper discusses the latest developments in water recycling technologies in pulping, bleaching and papermaking processes, which are important ingredients when developing zero effluent production. This paper also discuss the developed evaporation technology and how it can meet the environmental challenges of the pulp and paper industry.

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INTRODUCTION

The requirements of sustainable development, environmental protection and economical factors have changed the attitude of the pulp and paper industry. Hence, many mills today operate at much lower emission levels than the authorities limit would require. Even if the end of pipe secondary effluents treatment has been installed in many mills, further discharge reductions would rather be done by plant measures i.e. by closing water cycles. As practical situation the mill production increase can be achieved today without increasing effluent load. In some mills the main driving force for increasing system closure has been the availability and quality of clean process water.

In the Scandinavian pulp industry the discussion has recently concentrated on closed bleach plant effluent treatment. Especially so, because the recent developments in TCF-bleaching seem to offer better possibilities to integrate the treatment system into chemical recovery system without having a danger that chlorides contaminate into the process. The development work done during the past years has already led to practical mill scale applications and new equipment, which already are proven in industrial use.

PROCESS ALTERNATIVES

In TCF-bleach plants the filtrate recycling is done utilizing countercurrent washing. Most proposed configurations are such that waste water is divided into two fractions, one being alkaline and the other acidic. The alkaline filtrates contain most of the sodium and COD. The acidic fraction contains the sulfur used in pH control and the main portion of the non-process elements.

The most common concept to get the alkaline filtrate into the recovery loop is to replace the condensate used in brown stock washing with this filtrate. This means that the secondary condensate from the black liquor evaporation should be used as a wash water in the bleach plant instead of its traditional usage in brown stock washing.

Then the outcoming effluent flow can be reduced from the present 18-20 m^3/ADt level (Fig.1) down to 8-10 m^3/ADt (Fig. 2) or even below:

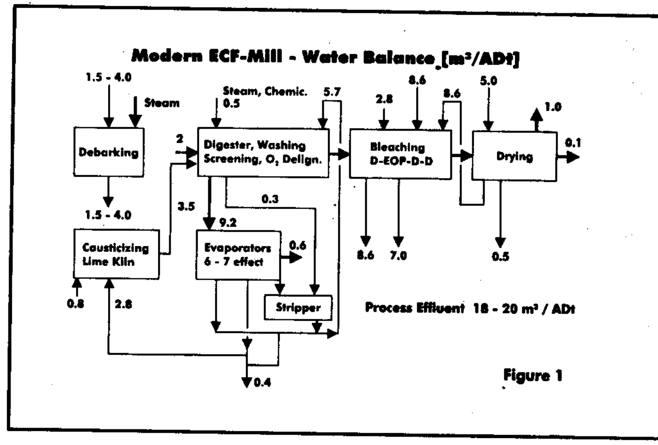

Fig. 1 Present Status of ECF - Mill Closure

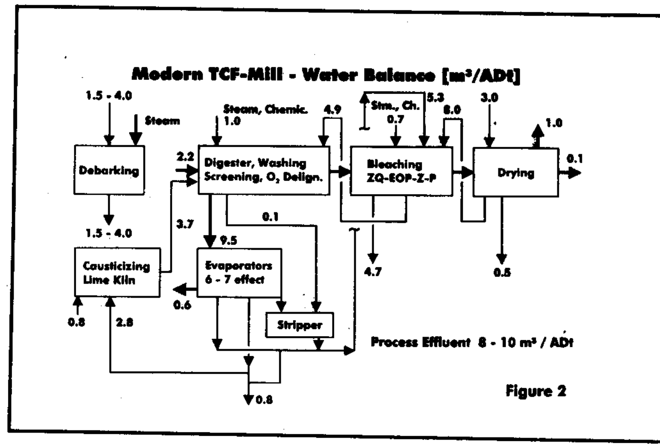

Fig. 2 Present Status of TCF - Mill Closure

Some of the acidic or neutralized filtrates up to 2 m^3/ADt can be used in recausticizing plant if the equipment is suitable and the water balance of the recausticizing plant allows this.

The next step is to evaporate the extra effluent and to use the cleaned condensate as a wash water in the fiber line or in pulp drying. The concentrate can be obviously introduced into black liquor and combusted and distroyed in a recovery boiler.

This strategy allows a step-wise approach to the closing and ends up in a situation where all the organics are finally combusted in a recovery boiler and the valuable chemicals are recovered from both alkaline and from acidic filtrate streams.

The final individual configuration of a mill water system can, however, have several other alternatives depending on the bleaching sequence and available equipment.

SECONDARY CONDENSATE AND WATER BALANCES

An example of a modern TCF- mill and of its water balance is shown in *Figure 4* where the concept is based on the usage of secondary condensate as a bleach plant wash water and the evaporation of 5.3 m³/ADt of bleach plant effluent/1/. The effluent condensate is introduced into pulp drying.

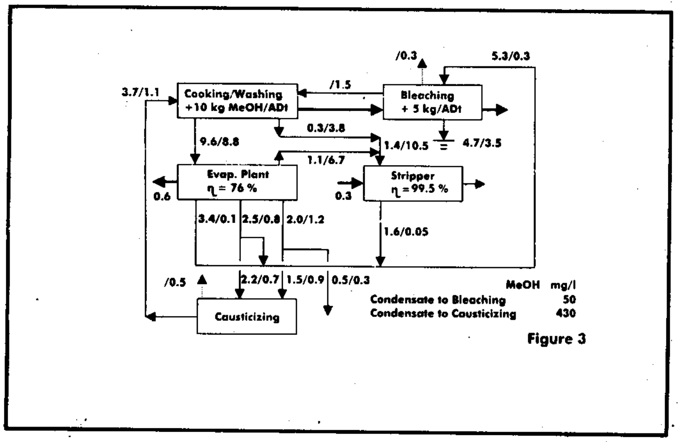

Fig. 3 Methanol Balance of Closed Cycle Mill

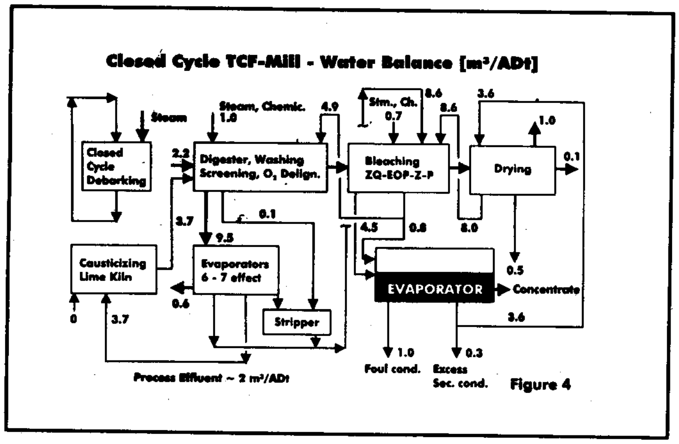

Fig. 4 Clossed Cycle TCF - Mill

The part of black liquor condensate, which is now used at the bleach plant has to meet new quality requirements when it is used to replace hot water.

The condensate quality requirements can be met with a modern evaporation plant which applies condensate segregation and steam stripping of the foul fraction from the evaporator and digester condensates.

Figure 3 shows the methanol balance in a planned modern closed cycle mill/1/. In this example the condensates are divided into three fractions:

- the first fraction is coming from the effects 2, 3 and 4
- the second fraction from 5 and 6
- the third fraction from the effect 7 and from the surface condenser

The foul condensate, which contains 75-80% of the methanol is collected from the segregated effects 2-7 and from the surface condenser and stripped with steam. The resulting methanol distribution is given in Table 1.

This distrubution allows taking of the fraction 1 and stripped condensate and a part of fraction 2 to the bleaching. The target methanol level is 50 mg/1, which gives the COD load of 200-300 mg/1. This already includes small amounts of other organics found in the condensates.

It has been shown/2/ that this COD level has no detrimental effects on pulp bleaching and can be accepted.

The excess secondary condensate having higher level impurities must be used for other purposes. It is, however, clean enough to be used e.g. in the recausticizing as weak wash if this is allowed by the water balance.

Table 1

Methanol concentrations

Fraction	MeOH Concentration mg/l	Flow M³/ADt	MeOH g/ADt
Fraction 1	30	3.4	100
Fraction 2	300	2.5	750
Fraction 3	600	2.0	1200
Stripped Concentrate	30	1.6	50

THE EFFLUENT CHARACTERISTICS

The chemical compositions of TCF-effluents have been studied carefully especially in regard to their non-process element contents/3, 4/.

An example of the inorganic compositions of these process streams is given in Table 2.

Typically the dry solids level of the filtrates is 0.5-0.7 wt-%.

Table 2

An example of TCF-bleach plant effluents Mill data. Sequence QPP

	Q-filterate (acidic) kg/admt	PP filtrate (alkaline) kg/admt
Dry solids	7.6	31.3
Sodium	1.2	8.0
Potassium	0.1	<0.1
Calcium	0.4	0.1
Iron	<0.1	<0.1
Magnesium	0.2	0.1
Manganese	<0.1	<0.1
Aluminium	<0.1	<0.1
Silicon	0.1	<0.1
Barium	<0.1	<0.1

Even though the absolute amounts of e.g. iron and manganese are low. they are important in that respect that they disturb peroxide bleaching causing increased chemical consumption and losses in pulp quality.

The dry solids analysis given in Table 3/5/ shows that combusted dry solids has in both streams a low heat value and a high alkali content. This prevents its combustion in fluid-bed type boilers.

Because the heat value is low, most obviously the moisture content will be high and when we are of course interested in recovering the alkali in a reusable form, the recovery boiler is the natural place to recover its energy value and the chemicals.

Table 3

Compositions and heat values of TCF-bleach plant concentrates

	Alkaline filterate		Acidic filterate	
	SW	HW	SW	HW
pH	9.4	10.2	4.5	4.5
C (%of ds)	16	15	11	11
H (%of ds)	1.5	1.6	1.1	1.3
N (%of ds)	0.1	0.1	0.3	o.4
S (%of ds)	10	9	15	15
Na (%of ds)	25	26	27	23
Cl (%of ds)	0.8	0.9	0.7	0.6
Cal heat value (MJ/kg ds)	5.2	4.7	3.9	4.0
So_4 (%of ds)	31	23	44	43
CO_3 (%of ds)	6.9	7.2	-	-

EXPERIENCES OF THE EVAPORATION OF TCF EFFLUENTS

In order to verify the evaporation propertieuas of TCF filtrates and their mixes and to certify the qulity of the reusable condensates. Ahlstrom Machinery has together with the Finnish Pulp and Paper Research Institute performed a set of pilot trails at a mill, which had a TCF-bleach plant. The detailed results have been reported elsewhere /5/.

The trails were done using a Zedivap (TM) falling film pilot plant of Ahlstrom Machinery having an evaporation capacity of 50-250 l evaporated water per hour.

The results of the experiments/5/ were encouraging. Filtrates were easy to evaporate separately or as a mixture. However, some precipitation of metals and especially calcium oxalate was observed but this did not cause scaling on the heat surfaces. Extra care should also be directed to fibers. The short fibers must be kept out from the heat surfaces.

The tests showed (Table 4) that the secondary condensates contained volatile impurities The main component of the impurities was methanol representing 80-95% of all organic compounds determinated. The total amount of methanol was estimated to be around 5 kg MeOH/ADt pulp. Minor amounts of ethanol and acetone were also found and also some small amounts of organic acids (formic and acetic acid) in the acidic filtrate condensate.

The conclusion was that the condensates had to be treated before their reuse and a set of trials were done using a pilot stripper.

The stripping removed 90-96% of TOC and COD. The methanol content dropped down to 20-100 mg/l and ethanol and acetone were removed almost completely. Organic acids were not removed by stripping from the condensate in the natural pH and their treatment should be considered when the reuse of water is planned.

However, the conclusion was that the condensates after stipping are clean and odorless to be used without risk on the pulp drying machine/5/. The recovered methanol, 5-10 kg/ADt has some value if it is used in a lime kiln as a fuel.

Table 4

Secondary condensates in TCF filtrate evaporation tests before stripping

Condensate	Alkaline filtrate SW	Alkaline filtrate HW	Acidic filtrate SW	Acidic filtrate HW
pH	8.2	9.5	4.0	5.3
mg/l				
TOC)	270	230	440	370
COD)	1130	960	1700	1440
Methanol	300	240	750	700
Ethanol	46	12	40	16
Acetone	6	23	16	14
Formic Acid	1	1	23	1
Acetic Acid	1	0	7	7
Propionicacid	0	0	0	1

EXPERIENCES OF NPE-SEPARATION

The build-up of elements such like iron, manganese, calcium, aluminium and silicon is often of primary concern when closed water systems are discussed in a pulp mill. Transition metals have a negative impact on oxygen delignification and bleaching, compounds like calcium and barium can form serious scaling and deposits as oxalate and sulfate salts. The increasing system closure can also increase the corrosion risks/4/.

The problem caused with oxalates was also indicated in pilot evaporation tests and some mills have faced this problem also in mill scale when the brown stock wash-water is replaced with alkaline bleach plant filtrate.

The effluent evaporation process showed to be also quite effective in that respect that due to the 30-60 fold concentration rise the evaporation precipitated already at 10 % dry solids level considerable amounts of NPE:s as shown in Table 5. This, however, requires that the evaporation is done in alkaline pH-range.

Because the major portion of NPE's is in the acidic filtrate this means that a neutralization step is required.

It is also possible to purify acidic or neutral filtrate in dilute state before it is evaporated or introduced into recovery. pH-adjustment with or without lime mud addition is shown to be an effective method/3/ to remove e.g. iron and manganese. As an example, the solubility of manganese and iron in an acid and in ozone stage filtrate drops fast when the pH rises above 8.

The metal laden concentrate from this treatment can e.g. be directed to the recausticizing department to be used as a weak wash. The precipitated metals are finally removed with green liquor dregs and the lime mud purged from the lime circulation.

Table 5

NPE's precipitation during evaporation, TCF filtrates in pilot experiments

Filtrate	Final pH	Ds (wt-%)	Precipitation (% of feed) Si	Al	P	Ca	Mg	Mn
Alkaline								
-Sw	9.4	5.0	97	100	67	78	45	67
-HW	10.2	9.7	99	100	71	84	54	100
Mixed								
-SW	9.2	9.8	44	82	5	88	1	0
-HW	6.8	11.0	59	69	21	48	4	0
Acid								
-SW	4.5	10.4	1	0	0	29	0	0
-HW	4.5	10.1	31	0	0	48	0	0

TCF-BLEACH PLANT EFFLUENT EVAPORATOR

As an example of a full scale effluent evaporation plant an alternative is presented in *Figure 5*. In the example the bleach plant represents the TCF-sequence ZQ-EOP-Z-P. Alkaline stream is connected counter-courrently into oxygen stage washing and the remaining acidic stream is 4-5 m^3/ ADt and this is introduced after neutralization up to pH 5-6, into the evaporation.

The neutralization is necessary to prevent co-distillation of organic acids.

On the steam side the process is combined with the existing black liquor evaporation plant. The vapour is taken at 50°C after last effect in three low-temperature effects where the effluent is concentrated up to 10% dry solids without external energy. The vapour from the last effect is condensed in a surface condenser or in an evaporative condenser so that no external cooling tower or coolling water is needed.

The pre-evaporated concentrate, which is now only 0.3 t/ADt can be further concentrated in a separate concentrator unit before combining to black liquor.

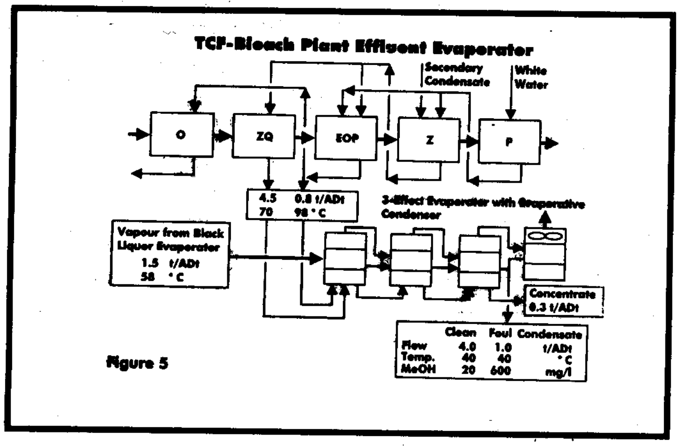

Fig. 5 TFC - Bleach Plant Effluent Evaporator

Because of the low heat value, 4-5 MJ/kg ds, the boiler heat load is increasing only 3-4% eventhough the amount of dry solids to combustion rises 6-7 % as a result of the system closing.

CLOSED CYCLE WOOD ROOM

In a new bleached kraft pulp mill woodroom effluent still constitutes 1.5-4.0 m^3/ADt, which is about to be a considerable portion of total effluent when the systems get more closed in other parts of the mill. The debarking effluent contains nutrients and toxic substances, which are not degradable in biological treatment.

The dry barking does not solve the effluent question completely. The ice and snow with the logs are coming into the system anyway and bark press filtrate has to be taken out because of the control of the dissolved solids in the system.

Our pilot plant test showed that by using evaporation the bark press effluent could be easily concentrated up to 30 % dry solids level without fouling problems. The condensate contained some acetic acid and ethanol as expected but the toxic and biologically non-gradable substances could be separated into concentrate, which can be mixed with bark of black liquor and combusted in existing boilers.

As a result of successful experiments our first commercial evaporator application for this purpose will be started in autumn 1996 in an integrated pulp and paper mill in Finland.

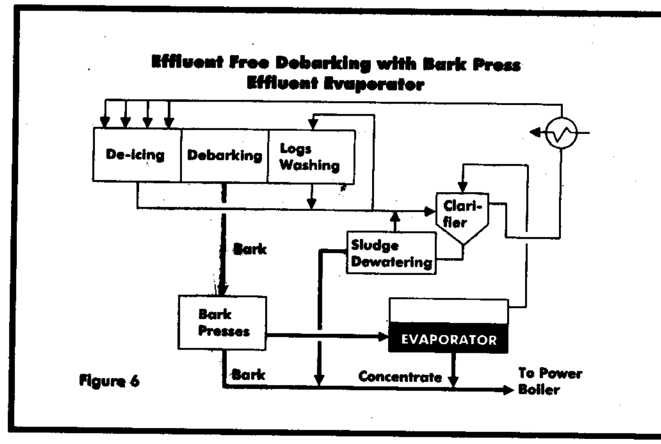

Fig. 6 Closed Cycle Wood Room

CLOSED CYCLE PAPER MILL

Paper mills integrated with mechanical pulp (CTMP, TMP, SGW or PGW) or deinking pulp production may produce Higher liquid effluent emissions than a modern chemical pulp mill. This is, because in the mechanical pulp mills there is no chemicals recovery except few CTMP mills. The development of closed cycle paper mill is in the way and the best newsprint mills run already at the level of 7m^3/ton effluent flow. Typically the water consumption varies between 10-20 m^3/ton for woodcontaining grades, 5-10 m^3/ton for woodfree fine paper and 2-10 m^3/ton for liner or corrugating medium. Effluent flow is always 1-1.5 m^3/ton less due to evaporation losses/1/1.

The water cycle can be closed to certain extent by reusing e.g. the clear filtrate of the disk filter and increasing the white water volume. Further closure would require introduction of new technical solutions to clean the white water for reuse.

The idea to use evaporation is presented in *Figure 7*. The evaporator would produce clean water only for the critical objects in the paper maching such as:

- suction roll lubrication showers
- high pressure felt cleaning showers
- sealing water
- chemicals dilution

So the demand of absolutely clean water is between 4-7 m³/ ton paper depending on the grade and the machine. The clean water should be used mainly on the paper machine and the produced white water then countercurrent in the stock preparation,

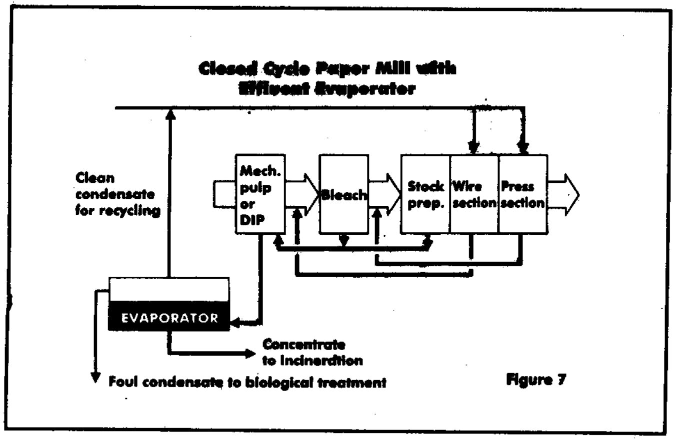

Fig. 7 Closed Cucle Paper Mill

bleaching and mechanical pulp or deinking pulp process. Good dewatering between the machine, bleaching and pulp process is required in order to prevent the dissolved matter from entering to the machine cycle and recovering the dissolved substances in the effluent flow with minimum dilution.

The evaporator would produce clean water from the pulping filtrate, which as a solids content of 0.3-0.5% ds. The dissolved substances from pulping and bleaching are mainly contained in the concentrate stream, but the volatile components have to be removed also in small amount of foul condensate. The organic acids, which are present especially in case of peroxide bleaching of mechanical pulp can be retained in condensate by controlling the pH of the evaporator feed.

An evaporator plant of TMP-filtrate has been operated in Enso Gutzeit Kotka mills from the begining of 1995. The plant has three effects and it utilizes secondary steam from the 5 effect black liquor evaporator. the plant evaporates the TMP-filtrate from about 0,3% to 8%. Then the liquor is mixed with weak black liquor and burned in the recovery boiler. The measured clean condensate quality has met the expectations and trials to use the condensate in the MFC paper machine will be done in the near future. The main data of the Kotka plant are given in the Table 6.

Table 6

ZEDIVAP Evaporator, Enso-Gutzeit Oy, Kotka Mills Main Data

Evaporator capacity	H_2O/h	70
Number of effects		3
Feed		TMP-filtrate
- Flow	l/s	20
- dry solids	%	0.3
- COD	t/d	4.0
Concentrate to be evaporated with black liquor		
- dry solids	%	8
- COD-removal efficiency	%	95
Clean cond. COD	mg/l	<150
Heat source	Black liquor evap.	
- vapour flow	kg/s	5
- saturation temperature	°C	60

Another new example will be evaporation of CTMP-effluent in Stora Billerud Fors board mill. The plant will have seven effects and it utilizes the steam from the CTMP refiners. The last effect steam is condensed in an evaporative condenser.

The latest pilot plant studies with deinking plant effluent open new possibilities to close the cycle of paper mills integrated with deinking pulp plants. The effluent can be concentrated over 30% ds without significant viscosity increase. However the inorganic solids start to precipitate and the solids may have to be separated during the process.

CONCLUSIONS

TCF-bleaching and progress in washing technology have reduced the amount of filtrates down to a level where reasonable integration in the closed recovery cycle can be realistically considered.

It is obvious that the industry will follow a step-wise starategy, which starts with the efforts to close the alkaline effluent stream counter-currently to brown stock washing and to replace hot water with secondary condensates from the bleach plant washers. Some of the key findings for this strategy are as follows:

- Modern evaporators with a well known stripping technology can produce a condensate, which is well acceptable for bleached pulp washing purposes.

- The recirculation of alkaline filtrate is already tested and going forward on its own learning curve.

- For acidic waste waters there are still several options like neutralization, evaporation, percipitation and possible use as such, treated or as condensate in a modern recaustizicing plant, pulp drying water systems and other alternative places.

- One major concern which is related to acidic waste water is the possible enrichment of NPE's. However, there are already methods of removing those compounds from the process streams.

So far the evaporation, possibly combined with chemical treatment, seems to have the biggest benefits when combined in a right way in the process. The evaporation of bleaching effluents can be done by utilizing waste heat so that the increase of primary energy use is minimized.

In spite of its potential in bleach plant effluent treatment, the waste water evaporation seems also to offer possibly interesting solution to a closed cycle wood room and paper mills integrated with mechanical pulp or deinking pulp.

When the closed TCF bleach plant is finally realized it will be more important than ever to know how to master chemical recirculation and the purity of process streams. However these challenges can be met with the appropriate process changes and with the proven equipment already being put into industrial use. Ahlstrom's recent new solutions like Zedivap™, CD-filter, and X-f Filter™ as well as TCF-bleaching on-site chemical processes have been developed based on this vision.

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