WAYS TO CLOSE A TCF - BLEACHING SEQUENCE

Ulf Germgård
Sunds Defibrator
S-851 94 Sundsvall
Sweden

ABSTRACT

If the bleach plant is closed up several problems can occur and process and scaling problems as well as high consumptions of chemicals and steam or cooling water are the most obvious ones. The paper discusses TCF-bleaching and our closure experience from lab and mill TCF-trials.

BACKGROUND

There is a world-wide trend in the pulp industry to reduce the impact on the environment from the production of bleached pulp and this is usually accomplished by introducing more environmentally friendly and cost-effective pulping and bleaching processes. External effluent treatment can also be used as a complement. This trend has led to the introduction of ECF-bleaching in the 1980´s and TCF-bleaching in the 1990´s. The main driving force for the introduction of both these technologies has been the desire to reduce the formation, and indirectly the discharge, of chlorinated organic compounds to the environment. As no chlorine containing bleaching agents are used in TCF-bleaching no chlorinated organic compounds are released in such bleaching.

The emission of other types of environmentally problematic substances has also been decreased considerably during the same time, but not as much as is the case for chlorinated organic substances. Therefore, other compounds in the effluent streams have taken over the role as being the most problematic substance. In Sweden the COD-emission is today considered as being the most problematic one.

However, to solve specific problems associated with specific effluent parameters in a case by case manner is no longer cost effective. A more general approach is currently being implemented in the mills. Today this usually includes closure actions in the mill and especially in the bleach plant. However, bleach plant closure involves more than a straightforward recycling of bleaching filtrates.

One of the main obstacles with recycling of conventional bleaching filtrates is that chlorine containing bleaching agents are used in the bleach plant, and chloride and chlorine compounds are therefore recycled to the closed part of the mill. This can lead to considerable corrosion problems especially in the recovery boiler. Bleach plant closure development has therefore started in mills that utilize chlorine free bleaching.

There are today several TCF-mills in Sweden and Finland that are semiclosed, i.e. they recycle the alkaline filtrates and the resulting bleaching filtrate emission is therefore only 5-10 m^3 per ton of pulp. Lower filtrate emissions can be foreseen in the future. However, closure of the bleach plant must be done with great care, otherwise different process problems can occur.

There are a few important issues that have to be considered. First of all an intelligent closure technique must be used that both recycle as much as possible of the polluting substances but also suppresses scaling tendencies and process problems. Secondly, we have to carfully control the calcium levels in the bleach plant as calcium is in many cases the cation in inorganic scaling. An simple alternative to deal with scaling is to use additives in critical positions but these can never compensate for a poor closure manner. Finally, good pulp washing between the stages is important as this means that we can keep problematic ions apart. If presses are used instead of filters we can also in a better way prevent temperature and pH shocks as less water is carried over with the pulp to the next stage.

RESULTS AND DISCUSSIONS

TCF-bleaching

There are many bleaching developments taking place all over the world as new demands have been put on the bleaching processes. A new trend is that market forces have taken a leading role in specification of how pulp is bleached and especially how much the bleaching process will be allowed to negatively affect the environment. This has resulted in the development of totally chlorine free (TCF) bleaching, as there is a fear among the final consumers that chlorine containing bleaching chemicals will lead to the formation and the discharge of chlorinated organic substances that are environmentally harmful. It is also apparent that the customers are willing to pay a price premium for TCF pulp.

The first TCF-bleaching process for kraft pulps was the Lignox process developed by EKA Nobel in 1990 (1). This two stage process consists of an initial stage with a chelating agent, like EDTA or DTPA, which releases heavy metals from the pulp followed by a good washing stage. The second step is a powerful hydrogen peroxide stage where usually 20-40 kg H_2O_2 per ton of pulp is added. However, the Lignox process alone will not result in softwood kraft pulps of full brightness (88-90% ISO).

The rapid development of TCF-bleaching has resulted in new bleaching alternatives based on pressurized (PO)- bleaching, on ozone bleaching and to a limited extent on the introduction of totally new chemicals, like peracetic and Caro´s acid. By combining a Lignox-sequence with other bleaching stages, full brightness can be achieved on softwood kraft pulps while still maintaining market pulp quality (2).

Closure of the bleach plant

One of the key issues in modern pulp production is the reduction in water consumption. Much has happened in recent years, *figure 1*. From the old case, to the left in the figure, where filters were used, the water consumption was 50 m³/t or in some cases even more. We have since then moved to the right in the figure, and today the most modern bleach plants are emitting only about 5 m³/t. It may be possible to reduce this volume further, and in the "future case" it is speculated that the water emission is only between 0-2 m³/t. Note, it is suggested that such a tightly closed mill will be of the TCF-type.

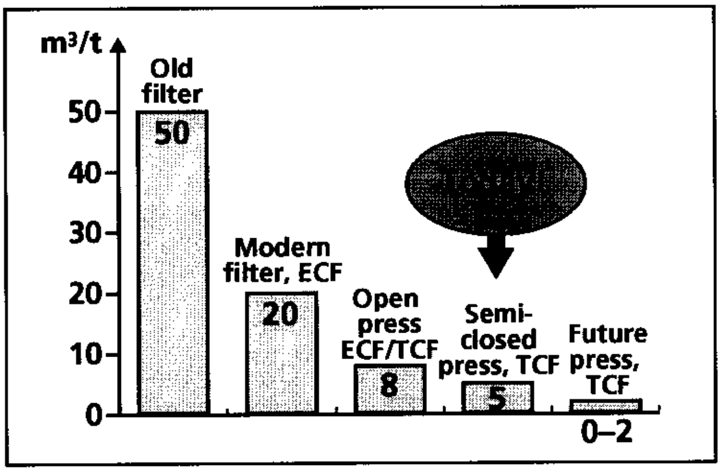

Figure 1 The water emission from bleaching of pulp in old and new mills respectively.

A similar closure technique will work in ECF-sequences, but because of the presence of chloride compounds in the filtrates significant corrosion problems can be expected, if the degree of closure is high and efficient chloride removal techniques are not in use. However, if the chlorides are purged in a controlled way, a high degree of closure can be used in that case without corrosion problems. One attempt in this area is the BFR-process that is now started up in the Champion mill in Canton, NC, USA (3).

However, it is important not only to look at the effluent volume as such, but also at the actual emission of harmful substances. *Table 1* shows the results from a TCF-mill trial in a softwood kraft pulp mill where internal closure and recycling of filtrate to the oxygen stage was studied.

Table 1 The COD discharge in a mill trial where the bleach plant was closed up from 25 to 5 m³/t.

Case	m³/t	COD, kg/t
Reference	25	27
Semi-closed	5	12
% Reduction	80%	56%

This mill uses presses after the oxygen stage and a filter/press combination in the bleach plant. In this study the bleach plant filtrate volume was reduced from about 25 m³/t down to 5 m³/t, which is a reduction of 80%. The COD emission was however only reduced from 27 to about 12 kg/t or about 56%. This was a considerable reduction in COD, but it also indicates that the resulting emission of polluting substances is not reduced in proportion to the water volume. Thus, total elimination of polluting emissions from the bleach plant requires zero filtrate emission.

The requirements for the pulp washing equipment used in a highly closed TCF-bleach plant are high. One reason is that costly bleaching chemicals are being used, which means that losses of bleaching chemicals due to high carry-over of COD or acid/alkali between the stages can no longer be accepted. A second reason is that hydrogen peroxide and ozone are sensitive to the presence of transition metals on the ppm-level, as such metals lead to decomposition of the bleaching chemicals. A washer that acts as a barrier to such metals is therefore preferred. In the case of hydrogen peroxide the presence of manganese is especially problematic. A metal chelating stage, denoted a Q-stage, and a good pulp wash are therefore usually used in TCF-sequences prior to peroxide and ozone stages (1).

If the sequence includes an ozone stage, this usually has a temperature of only 40-45 degree C, while the other stages in the sequence before and after the ozone stage are kept at 80-100 degree C. Such temperature jumps in the sequence further increase the importance of limited carry over of water between the stages. If for example the pulp leaving the washer has a low water content (a high consistency) the amount of water carried over to the next stage will be low and a barrier effect will be obtained.

The reasons above have resulted in an industrial trend to invest in new, more efficient pulp washing equipment, and this has resulted in an increasing number of presses in the fiberline. The built-in potential in the press to minimize the wash water addition and indirectly to reduce the volume of polluting emissions has further strengthened the interest for press washing (4,5).

Scaling

Our experience of scaling in closed bleach plants is that the major scaling problems come from the inorganic salts in *figure 2*. As can be seen the cation is either barium or calcium and the anion is carbonate, oxalate, hydroxide or sulfate. The table also shows that the solubility of these salts increases downwards. However, the amount of calcium is usually significantly dominating over barium in a pulp mill so scaling is therefore mainly a calcium problem.

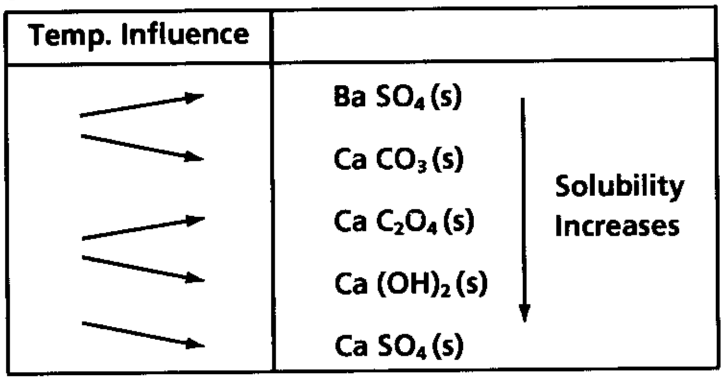

Figure 2 The most common inorganic scaling salts found in a highly closed bleach plant ranked in solubility order. The arrows to the left indicate if the salt is more or less soluble at higher temperature.

To the left in the table it is indicated that the solubility of these salts is either increased or decreased with increasing temperature. Thus, calcium carbonate, calcium hydroxide and calcium sulfate are all less soluble at higher temperature while barium sulfate and calcium oxalate are easier to dissolve at increased temperature. It can be concluded that the system is complex, and this is especially the case if we also include scaling effects from pitch and lignin. In Scandinavia, bleaching of birch pulp in a highly closed mill is therefore especially difficult due to the high concentration of neutral resins in the pulp.

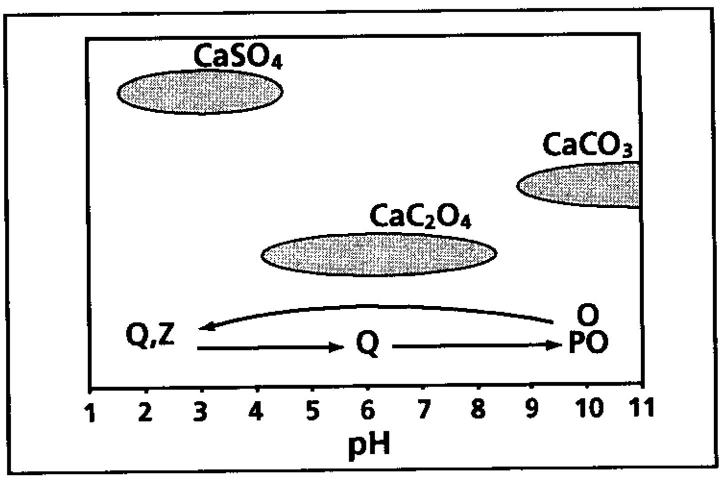

Figure 3 The pH areas where three problematic types of calcium scaling usually occur. In the lower part of the figure the path for the pulp in a O(QZ)Q(PO)-sequence is indicated

The pH is a very important parameter for scaling as is shown in *figure 3* where approximate pH-intervals are given for these three calcium salts. As can be seen the type of scaling that occurs is different at different pH-levels. For example, at neutral pH calcium oxalate is the most dominating one. Calcium sulfate scale is seen at lower pH while calcium carbonate is found at pH above 9. This has implications in a closed bleach plant.

For example in the lower part of figure 3 it is indicated that if the TCF-sequence O(QZ)Q(PO) is used, the pulp is transported from pH of about 10 in the oxygen stage to a pH of 2 in the ozone stage. The pulp is then going back to about pH 6 in the Q-stage and it finally returns to about pH 10 in the (PO)-stage. Thus, the pulp and the recycled filtrates will pass areas where there are scaling risks from at least these three types of salts. Note especially that the second Q-stage is in a risk zone for calcium oxalate!

An interesting mill result is shown in *table 2* for a highly closed TCF bleach plant with a press after the second Q-stage. Initially, the Q-stage was carried out at about pH 6 and a problematic scaling of calcium oxalate was soon observed on the following press. It was soon realized that something had to be done and a pH adjustment to low pH was suggested according to figure 3. As is shown in the table the pH adjustment solved the problem, and no scaling is now seen on the press.

Table 2 The influence of pH on the amount of calcium oxalate found in a Q stage at pH 6 and pH 2 respectively.

	On the following press
"Old" Q-stage at pH 6	Significant CaC_2O_4-scaling
"New" Q-stage at low pH	No scaling

The current situation for closed bleach plant technology is that it is more important to use bleaching and closure conditions that avoid problematic scaling than to minimize the bleaching agent consumption. Hopefully, when the principles of scaling are better understood, it will again be possible to focus more on the bleaching agent consumption. Good washing between the stages will naturally always be of high importance.

Ways to purge calcium from the bleach plant?

We have earlier concluded that calcium is a problematic cation in a closed mill, and ways need to be found to purge calcium to avoid scaling problems. In the traditional open bleach plant the calcium was usually not a problem, as it was liberated from the pulp in the chlorine stage and purged via the chlorine stage filtrate, *figure 4*. The traditional case for calcium removal is in the figure denoted as "Today".

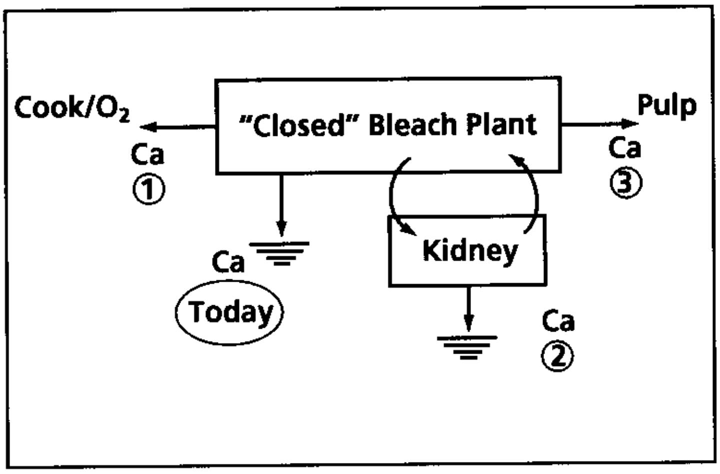

Figure 4 Three ways to purge calcium from a closed bleach plant excluding the open reference case denoted "Today".

If there are no filtrate emissions from the bleach plant there are only three more possibilities left to get rid of calcium. These are: 1) to send it back as dissolved calcium in the wash liquor that is returned to chemical recovery, 2) to purify an internal stream in the bleach plant with respect to calcium using some type of kidney and 3) to keep it attached to the fibers and to send it away with the bleached pulp. It has been found that an increasing degree of calcium chelation is beneficial for purge via route 1 but detrimental to purge via route 2. Thus, the route that is best suited for calcium control in a specific mill is totally dependent on the local situation.

Fiberlines with presses

The Union Camp F-line in Franklin, VA, USA is bleaching Southern Pine kraft pulp according to the sequence OQZ(EO)D, *figure 5*. This bleach plant was started up in September 1992, and it was then the tightest closed bleach plant in the world with an effluent volume of about 7-9 m^3/t. The bleach plant uses presses up to the ozone stage and filters in the final bleaching. The effluent volume comes from the D_1-stage (7 m^3/t) and from a purge from the acidic loop (0-2 m^3/t) (6). The acidic purge reduces the calcium concentration and thus avoids scaling in that position. The COD emission from the bleach plant, measured before external treatment, is about 11 kg/t of which only 4 kg/t comes from the open D_1-stage (6). Thus, when a better technique for calcium purge is installed the COD emission will be significantly reduced.

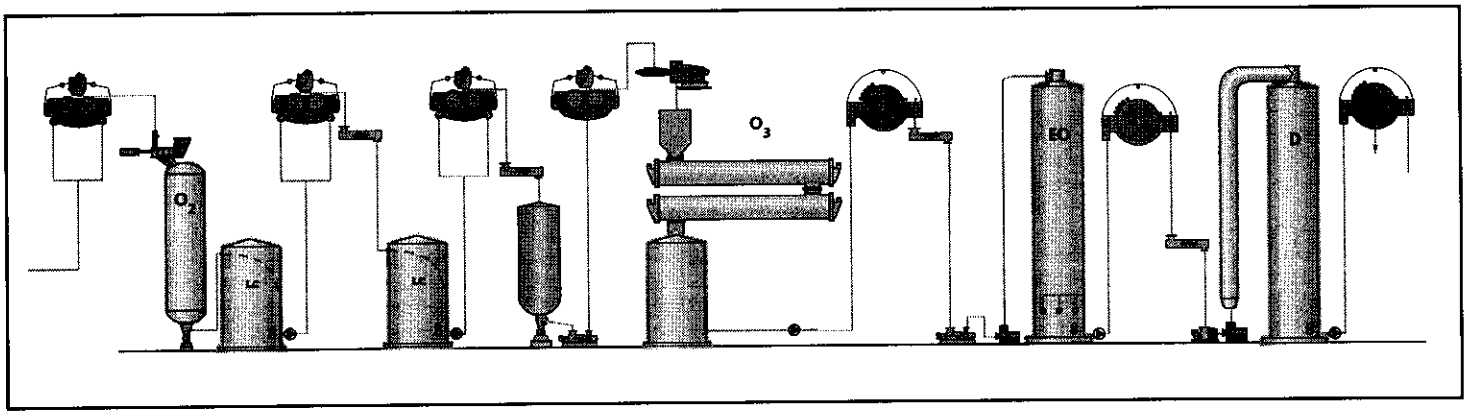

Figure 5 The Union Camp Franklin mill is using the OQZ(EO)D sequence which is closed up in a counter-current mode from the (EO) stage.

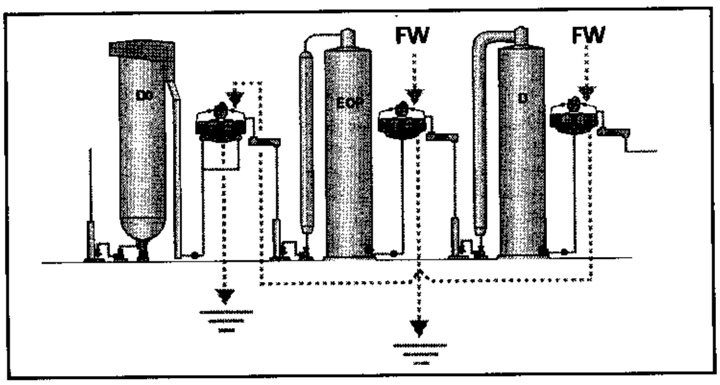

Figure 6 The Advance Agro ECF bleach plant uses presses as washers. The filtrate flows are shown as dotted lines.

Because of the use of the high consistency ozone stage in the Franklin mill, the bleaching cost is considerably reduced compared with both conventional bleaching of either ECF or TCF-type (6).

A simplified flow-sheet of the Advance Agro ECF-bleach plant is shown in *figure 6*. This bleach plant was started up 1995 and discharges only 8-9 m^3/t, although no filtrates are recycled to the post oxygen washers. This is the result for a totally open bleach plant with presses as depicted in figure 1. However, if for example, the alkaline filtrate can be recycled the remaining effluent volume will only be about 5 m^3/t.

Note also that two types of presses are used in the bleach plant (2); a displacement press is used after the first D-stage, as the washing requirement is greatest in that position, and two dewatering presses are used after the second and third stages. A dewatering press is slightly less efficient but the investment cost is significantly lower and is therefore the preferred press in less critical positions.

The new ASSI Lövholmen TCF-bleach plant was started up in 1995 and is one the latest press based bleach plants, *figure 7*. The sequence used is OQ(PO), and the (PO)-filtrate is recycled to the oxygen stage press. This mill is interesting as the 4-5 m^3/t of Q-stage pressate is recycled to the parallel liner pulp mill where it is used as wash water together with fresh water on the brown stock washers. Thus, in reality, the bleach plant is totally closed.

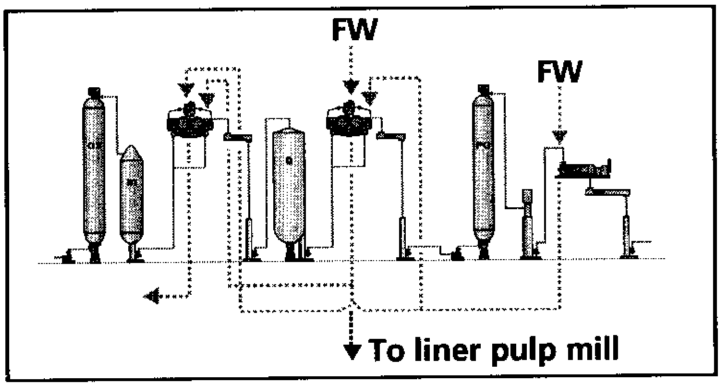

Figure 7 The ASSI Lövholmen TCF-bleach plant for birch pulp uses presses and an existing screw as washers. The Q filtrate is taken to the parallel liner pulp mill.

In the liner pulp mill the calcium from the Q-filtrate will either go out with the washed brown pulp, or if it is chelated enough, go back with the wash water to the chemical recovery system.

The SCA Östrand TCF press based bleach plant was started up in May 1995, and the sequence used is OQ(OP)Q(ZQ)(OP). The bleach plant is closed up to about 5 m^3/t, where the COD-rich alkaline pressate is recycled to the oxygen stage presses, *figure 8*. Calcium and metals, together with some COD, are purged via the pressate from the Q-stage.

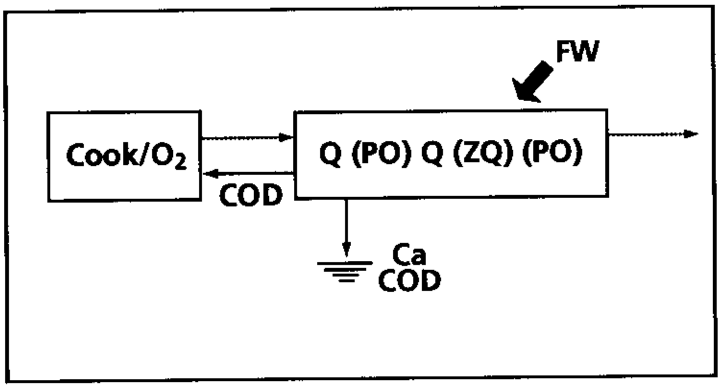

Figure 8 The SCA Östrand bleach plant uses the TCF-sequence OQ(OP)Q(ZQ)(PO) and the alkaline filtrate is recycled to the post oxygen washers. The calcium rich Q-filtrate is purged.

The concentration of calcium in different parts of a closed bleach plant is an important parameter as problematic calcium scaling can easily occur if the calcium level is high. The calcium concentration in the bleach plant has therefore been analysed in detail at the Östrand mill during the stepwise closure procedure, from the open reference case of about 15 m^3/t to the semi-closed case of about 5 m^3/t. The results are shown in *figure 9*, which is a plot of typical average numbers for calcium in the pulp after each bleaching stage. The figure is valid for bleaching of softwood kraft pulp.

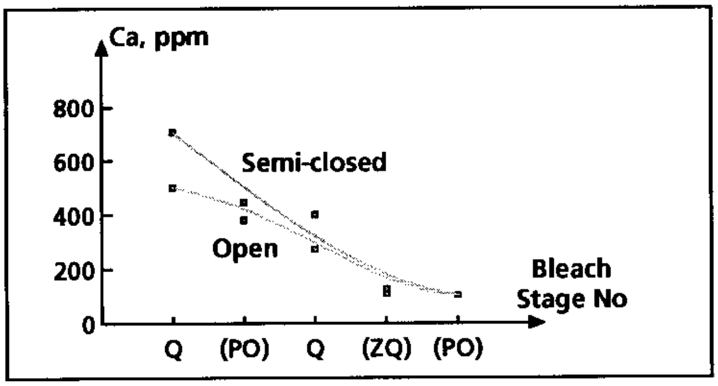

Figure 9 The total concentration of calcium in the pulp after each stage in the bleach plant is shown for the open reference and for the semiclosed 5 m^3/t case

Thus, it has been possible to avoid high build up of calcium in the bleaching stages, although a considerable closure action has been taken. Note also that in the final bleaching stages there is practically no difference between the open and the closed cases.

CONCLUSIONS

It is currently possible to run a TCF-bleach plant at low water emission and less than 5 m^3/t effluent is possible to achieve in mill scale today. One way to keep the water consumption down is to use presses as bleach plant washers. In addition, a good knowledge of scaling chemistry is essential when running closed bleach plants. The problems associated with closed bleach plants have so far been unexpectedly few when good design and process strategy are employed.

ACKNOWLEDGEMENT

Thanks to due to Frank Steffes for constructive criticism of the manuscript and to Mona Bergström for the final manuscript preparation.

REFERENCES

1. Basta J, Holtinger L, Lundgren P, Fastén H
   Proceedings, The International Pulp Bleaching Conference, Stockholm, Sweden, June 1991 p.23-33

2. Germgård U., Nordén S.
   Proceedings, The International Pulp Bleaching Conference, San Diego, CA, USA, June 1994 p.53-58

3. Maples G., Ambady R., Caron J.R., Stratton S., Vega Canovas R. Proceedings, International Pulp Bleaching Conference, June 1994, p 253-262

4. Germgård U., Norstedt Å., Sjödin L.
   Pulp and Paper, March 1994

5. Germgård U., Norstedt Å.
   Paper Asia, May 1995, p.58-62

6. Sundin M., Griggs B.
   Proceedings, SPCI 96´, Stockholm, Sweden, June 1996