Reducing levels of absorbable organic halogens (AOX)

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Lowering AOX by reducing or eliminating chlorine in the bleaching sequence must be achieved as cost effectively as possible, while still maintaining high brightness in a pulp of high quality.

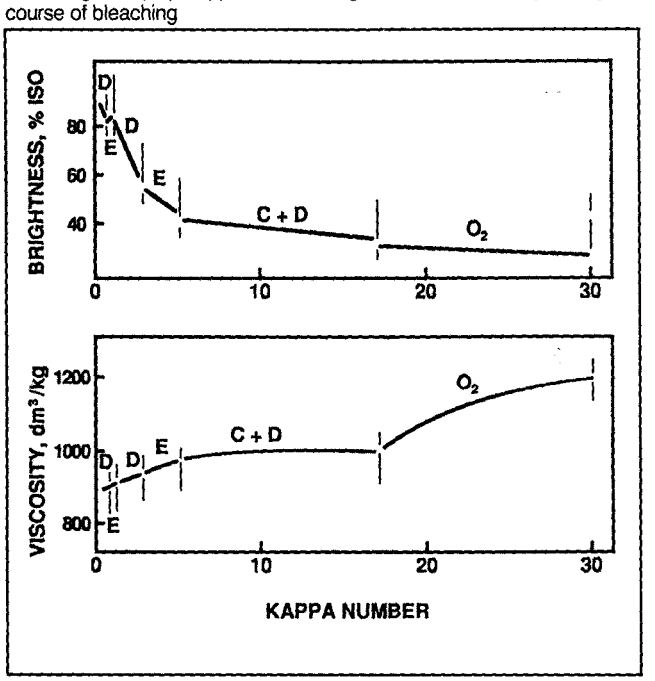
One of the most urgent problems we face in the pulp and paper industry today is that of decreasing the environmental impact of bleaching effluents. In nearly all countries that produce bleached pulp, the environmental authorities are focusing on chlorinated organic compounds in the bleaching effluents (*1-3*). Recently, Swedish Environmental Authorities passed stringent legislation concerning the total organic chlorine (TOCl) permissible in the discharge from mills. For bleached kraft, a concentration of 1.2-1.8 kg TOCl/ton of pulp will be the limit beginning in 1991. A further reduction to 0.5 kg TOCl/ton of pulp before the year 2000 and to 0.1 kg/ton thereafter is "highly recommended."

Changes in the bleaching process aimed at reducing the effluent load may detract from the quality of the product and may require further capital investment. Therefore, much research and development effort is being devoted to the task of reducing the concentration of chlorinated organics while maintaining high brightness and high quality in the product along with a reasonable profitability. Our purpose here is to examine three ways of achieving this goal.

A somewhat ambiguous situation exists concerning the methodology used for measuring the concentration of chlorinated organics. While the government legislation is expressed in kg TOCl/ton of pulp, the adsorbable organic halogens (AOX) test, which is much simpler, is favored not only in Sweden but also in other countries (*1-3*). It has been standardized recently in Sweden (*4*), and the correlation between AOX and TOCl is under study (*5*).

For uniformity, all the results presented here are AOX values measured in bleaching effluents prior to any external effluent treatment. The bleached pulp is characterized by kappa number, brightness, and viscosity. Both laboratory and mill data are presented. The regression curves in the figures represent large numbers of experiments carried out in our laboratory during the last five years. The pulps selected for study were well-washed, industrial, oxygen-predelignified, softwood kraft pulps of kappa numbers between 17.5 and 19.5. To indicate normal variability, the curves generally are presented as shaded areas. Some additional experiments were carried out, and these are illustrated with symbols in the figures. The results from mill trials are superimposed on laboratory data. The bleaching sequence was (C+D) or (DC)ED(EP)D unless stated otherwise.

1. Changes in pulp kappa number, brightness, and viscosity during the course of bleaching



Fundamentals of bleaching

The bleaching of chemical pulp is the process of removing the lignin still remaining in the pulp after cooking and oxygen delignification. During the process, changes occur in the pulp kappa number, the viscosity, and the brightness.

The kappa number of the pulp is related to the pulp lignin content, while viscosity is used here as a pulp strength parameter (*6*). **Figure 1A** shows that, to get a stable brightness of 90% ISO, the kappa number should be reduced to a value near zero. This is not simple. The pulp contains more than 95% carbohydrates at the beginning of bleaching, and these should not only be retained (for a high pulp yield) but should also be retained

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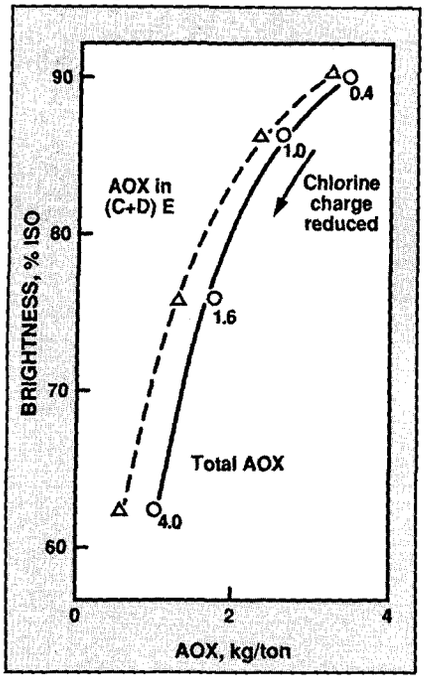
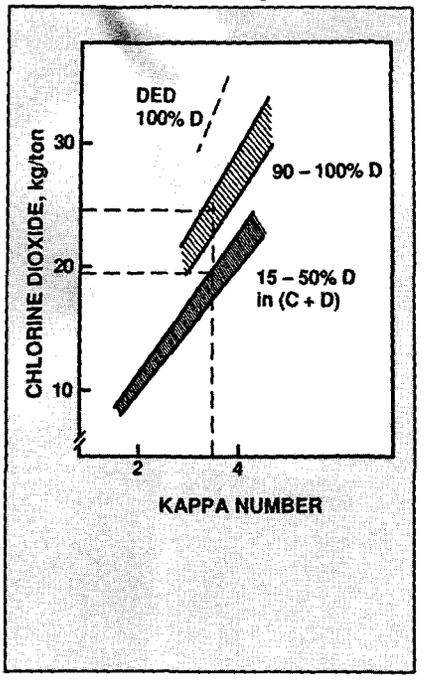
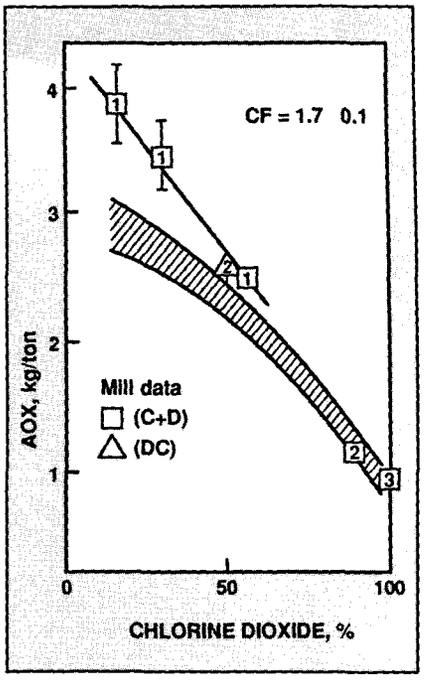
2. Final brightness as a function of AOX discharge from the (C85 + D15)EDED laboratory bleaching sequence in which the chlorine charge in the C stage was reduced from 30 kg/ton to 7.5 kg/ton



3. Chlorine dioxide requirement in D(EP)D final bleaching to 89.5–90% ISO brightness vs. the kappa number after the first E stage. The dashed line refers to laboratory bleachings without peroxide in the second E stage.



4. Total discharge of AOX as a function of different chlorine dioxide substitution levels in the C stage



in good condition, with an acceptable pulp viscosity. Therefore, the bleaching process is completed in several stages using various chemicals under different conditions.

Figure 1B illustrates how viscosity and kappa numbers vary through the sequence. As shown, chlorine is an effective and selective chemical for removing lignin, but it forms maximum amounts of chlorinated organics. While both chlorine and chlorine dioxide contribute to the AOX formation, the molecular chlorine does so to a much greater extent. The AOX formation can be roughly estimated from the chlorine and chlorine dioxide charges according to Eq. 1 (*7*):

$$AOX = k_1 [C + (D/k_2)] \quad (1)$$

where

k_1 = 0.1

k_2 = 5

AOX = AOX concentration, roughly, or total organic chlorine (TOCl)

C = chlorine charge (kg active chlorine/ton pulp)

D = chlorine dioxide charge (kg active chlorine/ton pulp).

The simplest way to lower the AOX is to decrease the chlorine charge in the C stage. This does result in a substantial reduction in AOX, as **Fig. 2** shows, but an unacceptably low final brightness is obtained if this is the only change made in the bleaching sequence.

The numbers in Fig. 2 refer to kappa numbers after the second D stage. At 90% ISO, the kappa number should be close to zero, supporting the conclusions drawn from Fig. 1. If the objective is to keep the final brightness at 90% ISO, then we have to increase the delignification during other stages if we are to achieve a kappa number lower than about 0.5 after the final D stage. We have to compensate for the lack of delignification work in the C stage, which is caused by reducing the chlorine charge.

Since the final bleaching stages—the first and second D stages—are limited in delignifying capability, we need to find a variable that can be used to predict the charges of chlorine dioxide required to reach low enough kappa numbers and correspondingly high brightnesses. The kappa number after the first extraction stage is such a variable. It has the added advantage that it can be measured on-line, which is done in several Swedish mills.

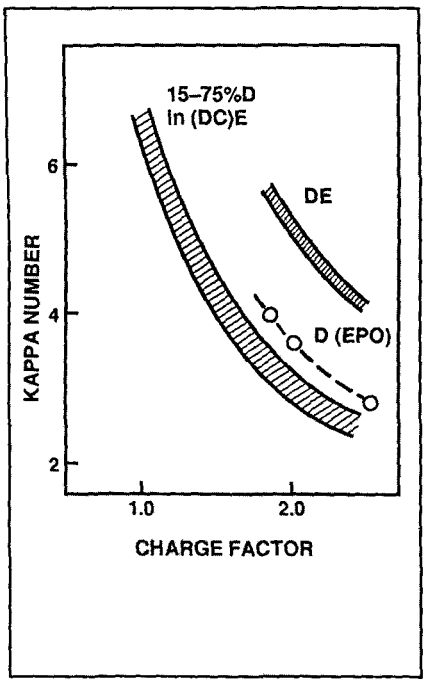
For a variety of pulps and prebleaching conditions, the kappa number after the first E stage can be used to predict the amount of chlorine dioxide required in the first and second D stages to obtain a given final brightness (*7–11*). Alternatively, at a specified final brightness and a set charge in the D stages, we can find the highest permissible kappa number after the first E stage.

For oxygen-predelignified softwood kraft, a kappa number at this point of about 3.5 seems to be a convenient, practical upper limit for obtaining 90% ISO brightness. The D(EP)D final bleaching sequence was chosen because of its superiority over the DED final sequence (*11–17*), this being particularly true at high substitution of D in the C stage, as shown by the dashed line in **Fig. 3**, denoted "DED, 100% D."

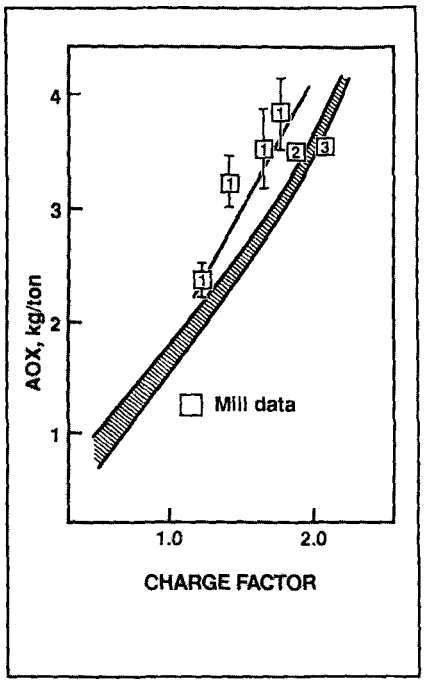
Ways of reducing the AOX concentration

When aiming at a specific final brightness, then, the amount of chlorine can be lowered only if the lack of

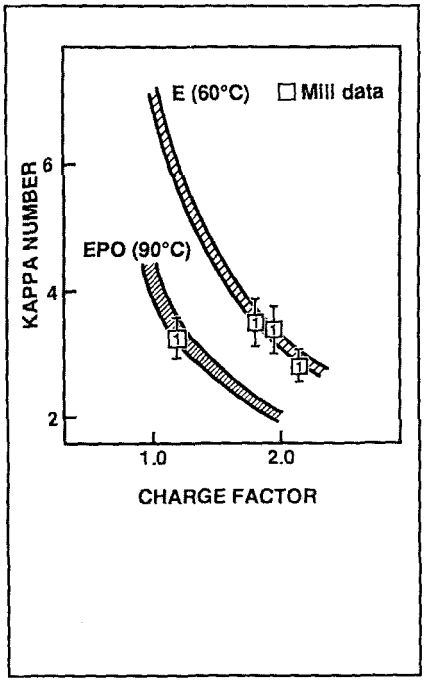
5. Kappa number after the first E stage vs. charge factor in the C stage



6. Total discharge of AOX vs. charge factor in the (C85 + D15) stage



7. Kappa number after the first E stage vs. charge factor in the (C85 + D15) stage



delignification in the first stage is compensated for somewhere in the bleaching process. This compensation can be made principally in three ways:

1. Substitution of D for C in the C stage
2. More delignification after the C stage (EPO-technology)
3. More delignification before the C stage.

Method 1: substituting D for C

When combining chlorine and chlorine dioxide in the C stage, two mill-related parameters are useful. The charge factor (*CF*) is the active chlorine (in kg/ton of pulp) divided by the kappa number prior to the C stage. The percentage of D is the percentage of active chlorine in the C stage that is chlorine dioxide.

Thus, for a given kappa number, the charge factor will define the amount of active chlorine in the first stage. **Figure 4** shows how AOX decreases as the relative amount of chlorine dioxide increases. The charge factors used at the three mills and in the lab experiments were all kept constant at 1.7±0.1.

As shown in Fig. 4, an increase in the percentage of D leads to a substantial reduction in the AOX concentration in total bleaching effluents. An increase from 15% to 75% D gives a 45% AOX reduction. Actual mill data indicate a slightly higher AOX reduction. An increase in D above 50% often leads to an increase in the kappa number after the first E stage unless a sequential mode is applied (DC) for the addition of chemicals during the C stage (*7–9*).

The importance of the kappa number after the first E stage has been discussed earlier. In **Fig. 5**, the influence of the charge factor on this variable is shown for varying degrees of substitution up to 100% D. Within the range of chlorine dioxide from 15% to 75% a charge factor of approximately 1.8 provides a kappa number of about 3.5 after the first E stage. With higher substitution, the *CF* in the C stage must be substantially increased, or the subsequent first E stage must be reinforced.

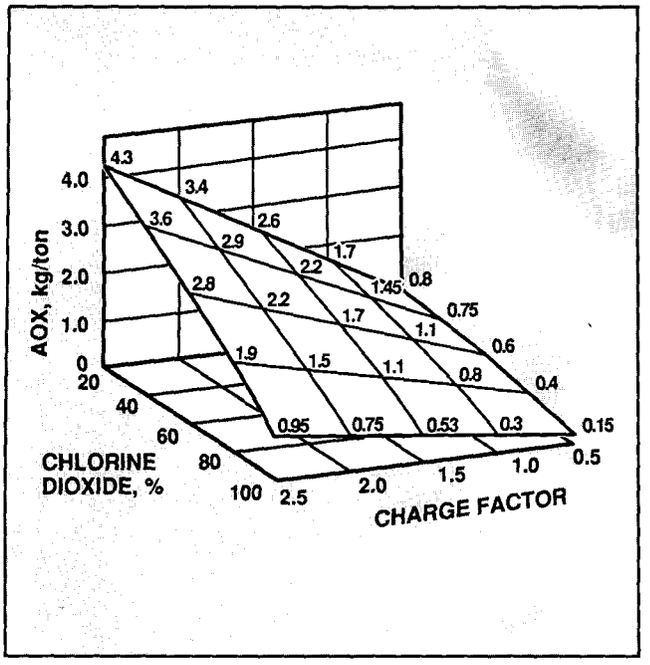
When 100% D is used in the first stage, the kappa number of 3.5 after the first E stage is impossible to obtain, at least for the conditions under which the data used in Fig. 5 were obtained. These conditions were (a) a pulp consistency in the first stage of 3.5% and (b) a temperature in the first E stage of 60°C. However, when pulp consistency in the first stage is increased to 10% and the first E stage is reinforced with peroxide and oxygen at 90°C, the target kappa number after the first E stage is easily reached at a *CF* of 2.0, indicated by the broken line in Fig. 5. The corresponding AOX reduction then is 65%, still maintaining the limit for the 90% ISO final brightness.

Method 2: more delignification after the C stage

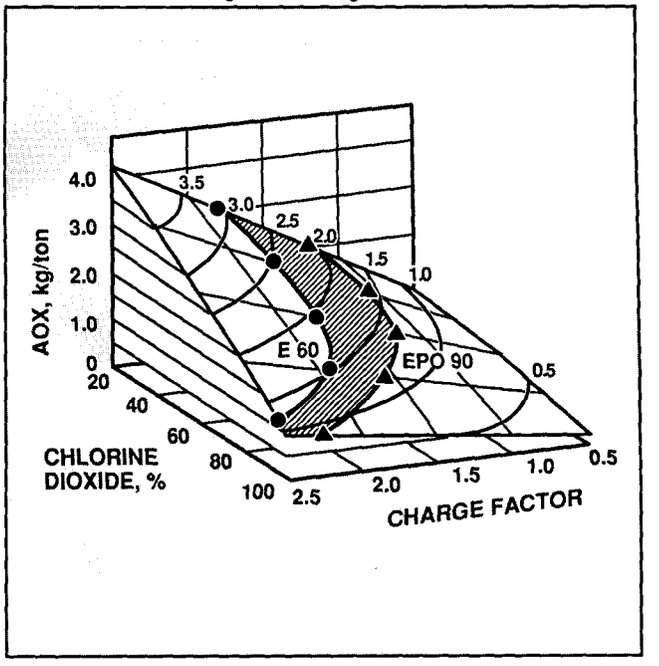
The second approach permits us to lower the chlorine charge while still maintaining the kappa number after the first E stage and still achieving the 90% ISO final brightness. **Figure 6** shows that lowering the chlorine charge is an effective way of decreasing the AOX concentration in bleaching effluents. However, when the chlorine charge is decreased, the kappa number after a typical E stage (60°C) increases (**Fig. 7**). Above a certain limit, as mentioned, the final bleaching stages no longer can achieve the required brightness.

Figure 7 indicates that a *CF* value of 1.8 is necessary for obtaining a kappa number of 3.5 after the first E stage. However, it is possible to shift delignification work from the C stage to the first E stage and thereby decrease the

8. AOX in the prebleaching effluents as a function of the percentage of D and the charge factor in the C stage



9. The shaded area defines the possibilities of combining Methods 1 and 2. The E 60 and EPO 90 curves represent the first E-stage kappa number limits for obtaining 90% ISO brightness.



charge of total active chlorine. If the E stage is reinforced with oxidative chemicals at 90°C (EPO 90), a *CF* of 1.2 is enough to reach the kappa number of 3.5. The AOX concentration reduction corresponding to a lowering of *CF* from 1.8 to 1.2 is 35% (Fig. 6). An approximate 35% reduction in the *CF* value thus corresponds to a 35% reduction in AOX. This conclusion is supported by the mill data given in Fig. 6.

Combinations of Methods 1 and 2

It is possible to combine Methods 1 and 2—that is, to further lower the chlorine charge by increasing the chlorine dioxide substitution while simultaneously decreasing the charge factor.

To visualize the influence of both charge factor and the percentage of D on AOX, diagrams in three dimensions are necessary. **Figures 8 and 9** are the result of many measurements of AOX after prebleaching an oxygen-predelignified softwood pulp (kappa no. 18) with different combinations of charge factors and degrees of substitution of chlorine dioxide in the C stage. The AOX values can be found on the oblique surface, and the grid on the surface connects lines for *CF* and % D on the axis.

The regression equation for the 3-D plot in Figs. 8 and 9, based on the results of 73 laboratory experiments, is as follows:

$$AOX = -0.21597 + 9.85 \times 10^{-3} (\%\ D) + 2.08587\ (CF) - 8.5 \times 10^{-5} (\%\ D)^2 - 0.01676\ (CF \times \%\ D) \quad (2)$$

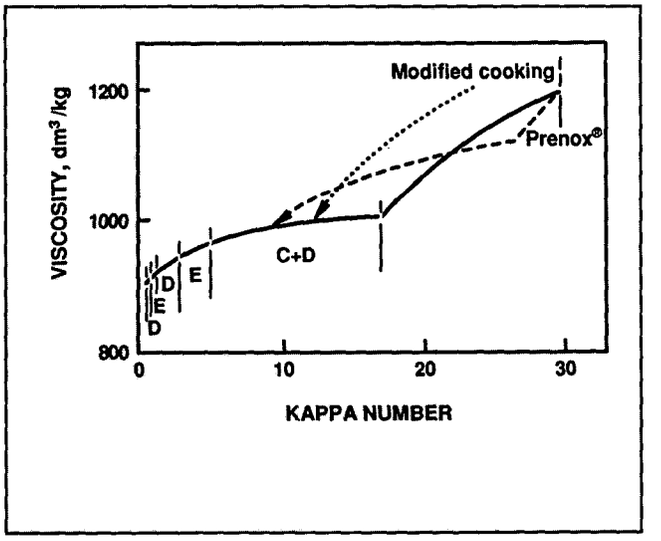
with

$r^2 = 0.963$

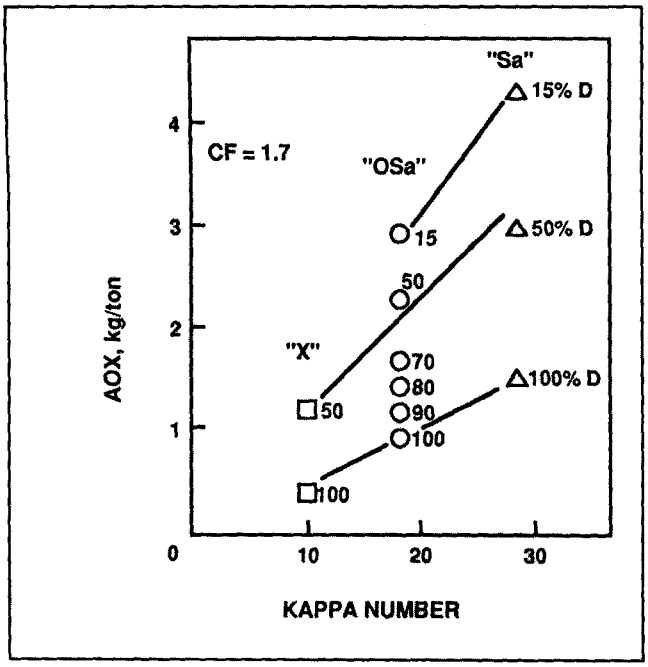
An example will illustrate how to use Fig. 8. A pulp, prebleached with 20% D in the C stage at *CF* 2.5 will give 4.3 kg AOX/ton of pulp. When *CF* is kept constant, an increase in D from 20% to 100% will reduce AOX from 4.3 kg/ton to 0.95 kg/ton. Similarly, when D is kept at 20%, a drop in *CF* from 2.5 to 0.5 will reduce the AOX concentration from 4.3 to 0.8 kg/ton. The area offers a large number of combinations of *CF* and % D that give a variety of AOX values.

However, if the objective is a bleached pulp of 90% ISO brightness, the only combinations of *CF* and % D of interest are those that give an alkali-extracted pulp with a kappa number of 3.5. Thus, it is possible to define the limits on the AOX area, outside which bleaching chemicals either are wasted or are insufficient for the required brightness. These limits are shown in Fig. 9.

10. Different ways of lowering the unbleached kappa number



11. Total discharge of AOX from laboratory bleachings to 89-90% ISO final brightness as a function of the unbleached kappa number



I. Bleaching of conventional and oxygen-predelignified, softwood kraft pulp in (C+D) (EPO)D(EP)D bleaching sequence

	Oxygen-predelignified	*Conventional*
Unbl. kappa no.	17.5	27.4
Unbl. viscosity, dm^3/kg	1058	1302
CF in Stage 1	1.7	1.7
% D in Stage 1	80	100
Chemicals added, kg/ton		
Total Cl_2 (active chlorine)	6	0
Total ClO_2 (active chlorine)	40	67
Total NaOH	19	29
Total H_2O_2	3	5
Total O_2	5	5
Brightness, % ISO	89.5	89.1
Viscosity, dm^3/kg	984	1129
AOX in filtrate, kg/ton	1.4	1.3

10% pulp consistency in all stages. Temp. in EPO = 90°C.

Curve E 60, reflecting Method 1, represents the combinations of *CF* and % D that give the first E-stage kappa number of 3.5 after the prebleaching sequence (DC)E, where E is a typical E-stage run at 60°C. Curve EPO 90, which reflects Method 2, represents the combinations of *CF* and % D that give the same first E-stage kappa number after a prebleaching sequence (DC)EPO, where EPO is a peroxide and oxygen-reinforced E-stage run at 90°C.

The area between the E 60 and EPO 90 curves gives the practical possibilities of combining Methods 1 and 2 and offers a number of alternatives. The correct choice depends on environmental restrictions and other conditions specific to the particular site. Nevertheless, when a reduction in the AOX concentration below 1.5 kg/ton is required, Methods 1 or 2 or some combination of them will result in somewhat higher costs for bleaching chemicals.

In a recent Swedish government proposition, an environmental penalty based on the quantity of purchased chlorine and chlorine dioxide is being considered. Since the proposed penalty on chlorine (5.0 SEK/kg of added chlorine) is much higher than that on chlorine dioxide (0.40 SEK/kg of added chlorine), the likely result is the eventual disappearance of chlorine for bleaching purposes in Swedish mills.

As seen in Figs. 8 and 9, despite the total elimination of chlorine, the remaining AOX concentration in the area which also provides the brightness of 90% ISO still is only slightly below 1.0 kg/ton of pulp. If AOX values substantially lower than 1 kg/ton are required, another approach has to be taken.

The AOX values in Figs. 8 and 9 represent the expected values in the bleaching effluents after prebleaching and prior to any external effluent treatments such as additional neutralization, sedimentation basins, and aerated lagoons. Compared to prebleaching, final bleaching accounts for a minor part of AOX—less than 20% of total AOX as indicated in Fig. 2. At mills that have 15-50% D in the C stage, the AOX concentration in total bleaching effluents can be reduced by up to 40% when the effluents are treated externally, as experience has shown.

Method 3: more delignification before the C stage

Theoretically, the simplest way to decrease the chlorine charge while still maintaining the 90% ISO final brightness is to decrease the chlorine requirement of the pulp by lowering the kappa number prior to the C stage. This approach may produce some practical problems. While Methods 1 and 2 can be implemented in an existing bleaching process, Method 3 requires more extensive process modifications, often necessitating additional installations.

Figure 10 illustrates the ways of reducing the kappa number prior to the C stage. The lower unbleached kappa number can be achieved by more extensive delignification either during cooking or during the oxygen-delignification stage, while still complying with the selectivity restrictions. If this delignification is carried out during cooking, the process is known as "modified" or "extended" cooking (*1, 2*). Recent Swedish experience of the modified batch softwood kraft (*18*) and the continuous softwood-hardwood kraft processes (*19*) has been reported. From the numerous pretreatments before the oxygen stage (*20-22*) aimed at improving the rather poor selectivity of the oxygen stage, the Prenox® process (*22*) seems to be the most promising.

What can be expected in terms of AOX when the unbleached kappa number is decreased? In **Fig. 11**, the influence of kappa number and the degree of substitution are shown for a constant charge factor of 1.7. For a given *CF*, the AOX discharge is proportional to the unbleached kappa number, and the degree of substitution of D for C is important. Similar curves for TOCl have been published earlier (*9, 21, 23*).

A conventional pulp of kappa no. 28 bleached with 100% D in the first bleaching stage gives approximately the same AOX concentration in the total effluents as an

oxygen-predelignified pulp of kappa no. 18 bleached with 80% D in the first stage. The details from the laboratory bleachings of these particular pulps are presented in **Table I.** The conclusion, subject to mill-scale verification, is that it may not be necessary to include an oxygen predelignification stage if the permitted AOX concentration is 1.5 kg/ton.

In Fig. 11, "Sa" and "OSa" denote the conventional and oxygen-delignified pulps at their respective kappa numbers. There is one other pulp, denoted "X," placed at kappa no. 10. This pulp is the result of development work in our laboratory concerning delignification, and it is included here to further illustrate the proportionality of AOX and unbleached kappa number. This pulp is also easy to bleach even with 100% D, which means that the total AOX discharge can be kept below 0.5 kg/ton.

Cost of bleaching chemicals

A reduction in AOX discharge from today's 3.5-4.0 kg/ton to the limit set for 1991 of 2.0 kg/ton AOX, corresponding to 1.5 kg/ton TOCl, will result in an increased cost for bleaching chemicals (excluding the oxygen stage) of 10-20 SEK/ton of pulp. However, if the goal is set lower, the cost will increase rather rapidly:

3.5 AOX: 145 SEK

2.0 AOX: 155 SEK

1.5 AOX: 170 SEK

1.0 AOX: 200-220 SEK.

Here, the proposed penalties for chlorine and chlorine dioxide are not included and would entail additional expense.

Conclusions

Full substitution of chlorine dioxide for chlorine, combined with reinforcement of the extraction stages with oxygen and hydrogen peroxide, can reduce the AOX discharge from a fully bleached, oxygen-predelignified, softwood kraft pulp down to 1.0 kg/ton. Lower AOX values, if a fully bleached market grade kraft pulp is to be produced, can only be reached either by reducing the kappa number before bleaching or by treating the effluent externally.

The costs of bleaching chemicals depend on the AOX discharge. An AOX concentration of 1.5 kg/ton will increase costs by 10-20 SEK/ton. A concentration of 1.0 kg/ton will result in a cost increase of 55-75 SEK/ton for oxygen-predelignified kraft.

Experimental procedures

Unless otherwise mentioned, the laboratory chlorinations were carried out in sealed plastic bags at 3.5% pulp consistency. The final pH for (C+D) bleachings was about 2.0 and was 1.6 for (DC), with 2 min between the stages. Alkaline extractions were carried out at 10% pulp consistency and at 60-70°C for 60 min. The final pH was between 10.8 and 11.8.

The EPO experiments were carried out according to the method described previously (*11*). Peroxide addition in the EPO stage was 2 kg/ton of pulp and 1 kg/ton of pulp in the second E stage. The chlorine dioxide bleachings were carried out at 10% pulp consistency. Like (C+D) and (DC), the first and second D-stage bleachings were optimized with respect to time and temperature, so the residual chlorine was 0.1-0.5 kg per ton of pulp. The pH in the first and second D stages was kept at 4-4.5 by adding NaOH.□

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