Generation of Halogenated Compounds in Bleaching without Chlorine

Can TCF be chlorine-free?

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1. Abstract

The chemicals applied in pulp bleaching as the alternatives to chlorine are strong oxidizing agents. They are capable to generate chlorine in-situ from chloride ions. In ECF bleaching the positive effects of a combined application of peracids and chlorine dioxide are accompanied by the in-situ formation of chlorine. The result is an increase of the AOX load.

In TCF bleaching the presence of chloride ions similarly affects the delignification and generates AOX and OX. The residual of halogenated compounds in pulps bleached with distilled peracetic acid in the presence of chloride ions can be as high as in normal ECF bleaching. Thus the OX level in a bleached pulp does not necessarily allow to draw conclusions about the bleaching process applied.

2. Introduction

Without any doubt the environmental situation in pulp mills is improved with the elimination of elemental chlorine from the bleaching process and the conversion to ECF technology. The substitution of chlorine with chlorine dioxide results in a significant decrease of the AOX load. Compared with chlorine bleaching the decrease of the AOX amount can reach between 80% and 90%, depending on the design of the bleaching sequence. Unfortunately the effectiveness of ClO_2 in delignification is lower compared with chlorine. Therefore it is important to apply in addition other chemicals in order to improve the results. Typically oxygen and hydrogen peroxide are used to improve lignin extraction and brightening of the pulp. Recently also the combined application of peracetic acid with chlorine dioxide was recommended [1].

In addition to the amount of AOX detected in the effluent, also a residual of halogenated compounds remains in the bleached pulp. The term OX describes this residual of halogenated compounds. The OX residual decreases by about 50% with the switch from chlorine to ECF bleaching [2]. In theory the bleaching process applied on a pulp should show up in the level of the residual OX. A high OX would indicate chlorine bleaching and a low one ECF bleaching. TCF pulps should have no OX at all, at least they should have a very low level of OX. In practice, things are more complicated.

3. Generation of chlorine in delignification with ClO_2

Delignification with chlorine dioxide requires acidic conditions. The initial reaction of the chlorine dioxide radical is the abstraction of a hydrogen atom from a phenolic group. The resulting products are a phenoxy radical and $HClO_2$. The phenoxy radical is oxidized in a second step with another molecule of ClO_2. One reaction path is the cleavage of the side chain, which results in the formation of a quinone. The chlorine dioxide part of the molecule is eliminated as hypochlorous acid. The other reaction path is the demethoxylation of the phenoxy radical by another attack of ClO_2 and the elimination of methanol and hypochlorous acid. It is important to note that the demethoxylation only takes place with phenols, phenol ethers are not attacked by chlorine dioxide, at least not initially. The chlorous acid formed in the initial step can disproportionate to yield again chlorine dioxide and hydrochloric acid ($5\ HClO_2 \rightarrow 4\ ClO_2 + HCl$).

The intermediately produced hypochlorous acid plays an important role in the delignification process. The presence of hypochlorous acid, respectively chlorine, accelerates the delignification. Chlorine cleaves phenol ethers in the residual lignin. Thus the in-situ generation of chlorine is important for the destruction of the lignin. In consequence a lower pH improves the delignification, because it supports the intermediate formation of chlorine. On the negative side the lower pH results in an increased AOX load. These effects were described earlier [3]. The positive side of the low pH is a low lignin residual. Because low Kappa numbers are required to achieve brightening, the in-situ generation of chlorine has to be accepted, the alternative would be a higher demand for chlorine dioxide in the final bleaching stages with a higher AOX load there. As long as the total AOX load remains low, an intermediate generation of chlorine is acceptable.

4. Oxidation of chloride ions

The oxidation potential of some bleaching agents is high enough to generate chlorine from chloride ions present in the pulp. The standard oxidation potential (E°) for chloride to chlorine is 1.358 V. Bromide is even easier oxidized, its potential is only 1.066 V. **Table 1** has the data for the oxidation potential of different bleaching agents, applied in ECF and TCF bleaching processes.

Table 1: Standard oxidation potentials for bleaching agents [4]

compound	reaction	pH	oxidation potential (E°/V)
ozone	$O_3 + 2H^+ + 2e \rightarrow O_2 + H_2O$	0	2.08
	$O_3 + H_2O + 2e \rightarrow O_2 + 2OH^-$	14	1.24
persulfate	$S_2O_8^{2-} + 2H^+ + 2e \rightarrow 2HSO_4^-$	0	2.12
Caro's acid [5]	$HSO_5^- + 2H^+ + 2e \rightarrow HSO_4^- + H_2O$	0	1.81
chlorine dioxide	$ClO_2 + e \rightarrow ClO_2^-$	0	0.93
hydrogen peroxide	$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$	0	1.80
	$HO_2^- + H_2O + 2e \rightarrow 3\ OH^-$	14	0.87

Under acidic conditions the oxidation potentials of ozone and Caro's acid definitively are high enough to generate chlorine in-situ from chloride ions. It can be expected that the oxidation potential of peracetic acid is not much different, under acidic conditions it should be very close to the potential of H_2O_2. Therefore the level of chloride ions in the water circuit of an ECF or TCF bleach plant can have an impact on the AOX level in the effluent.

The effect of the oxidation of chloride ions was described by Francis [6] as an option to achieve a more effective delignification with Caro's acid. The consumption of Caro's acid was found to be poor in the absence of chloride ions. Only 40% of an amount of 6.64% H_2SO_5 were consumed. The addition of 1% chloride (on pulp) increased the consumption to 94%. At 10% consistency this corresponds to an amount of only 0,1g/l of chloride. Such a concentration is not uncommon in pulping liquor if wood was transported in seawater [7].

Francis found the amount of AOX produced by a treatment with Caro's acid in the presence of chloride ions and followed by extraction to be 0.68 kg/t. The corresponding value for a similar treatment with the stages D_0Eo was 0.66 kg/t. Thus the Caro's acid treatment with halide activation generated the same level of AOX as ECF bleaching. Because of the higher cost for the generation of Caro's acid [8] compared with chlorine dioxide, there are neither ecological nor economical advantages.

Similar effects can be expected if distilled peracetic acid is applied in combination with chlorine dioxide in a D_0 stage. Peracetic acid alone reacts very slowly with pulp. A temperature higher than 70°C is required even for the consumption of smaller amounts. In the presence of chlorine dioxide peracetic acid reacts much faster. The reaction is further accelerated with the addition of chloride ions. **Figure 1** has the data on the effect of a combined application of ClO_2 and CH_3COOOH on delignification and on the resulting AOX load. The reference is the increase of the active chlorine charge. A higher active chlorine factor lowers the Kappa number and increases the AOX. The addition of peracetic acid to a low amount of ClO_2 (factor 0.15) only has a small impact on the Kappa number measured after the Eo stage. The effect becomes more pronounced with the addition of 1% NaCl to the ClO_2/Paa stage. The impact of the NaCl addition on the AOX load is significant.

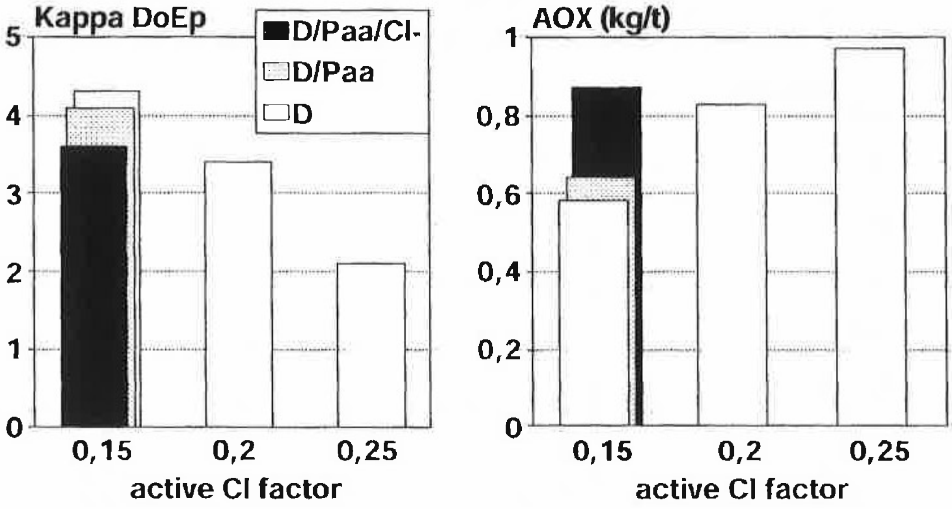

Figure 1: Delignification of softwood kraft pulp with ClO_2 with and without peracetic acid and NaCl; oxygen delignified Kraft pulp, Kappa 17; D_0 stages at 60°C, 1h, pH <3, dist. Paa 1%, NaCl addition 1%; Ep stage with 1.8% NaOH, 0.5% H_2O_2, 75°C

Jäkärä [9] reported advantages of a combined application of ClO_2 with peracetic acid in a final bleaching stage. There were no data presented about the AOX generation in this treatment, it can, however, be expected that there will be more AOX in the effluent as the result of the oxidation of chloride ions.

Hydrogen peroxide is acting as a reducing agent in the presence of hypochlorite and chlorine. The reaction products are chloride ions and oxygen ($H_2O_2 + ClO^- \rightarrow O_2 + H_2O + Cl^-$ and $H_2O_2 + HOCl \rightarrow O_2 + H_3O^+ Cl^-$). This reaction can yield a red chemoluminescence as the result of the formation of singlett oxygen. Under alkaline and neutral conditions therefore no chloride oxidation will take place. Despite of the high oxidation potential for H_2O_2 under acidic conditions an oxidation of chloride ions does not take place in diluted solutions. Strong acid conditions and high concentration are required to oxidize hydrobromic and hydrochloric acid with H_2O_2. Technically this reaction is applied in organic synthesis [10], dominantly to decrease the demand for Br_2 in bromination reactions by reoxidizing HBr to Br_2.

4. Generation of OX in TCF bleaching

Another alternative to chlorine bleaching is the total substitution of all chlorine containing chemicals. TCF bleaching uses only oxygen, hydrogen peroxide, ozone or peracids for delignification and brightening. Peracids like Caro's acid and distilled peracetic acid were recommended to bleach kraft pulp [8, 11]. In theory in TCF bleaching no AOX or OX is generated. This concept is threatened by the potential in-situ generation of halogenated compounds via side reactions. Especially in narrow water loops with a low water intake the chloride concentration might increase to a level that can cause effects. Laboratory tests with peracetic acid in the bleaching sequence in the presence of NaCl resulted in an extreme increase of the OX residual in the pulp. **Figure 2** has the resulting OX-values of a softwood kraft pulp bleached with the sequence O-AQ-Op-Paa-P-Paa. The OX-values were measured after the final Paa stage. The effect of the in-situ chlorine generation becomes not only visible as OX, it also results in a two points higher brightness and a final Kappa number of only 1.3 compared with 2.2 in the reference blank test. In the reference test without chloride the Paa residual was high after the treatment (1% Paa in the first stage and 0.5% in the second were applied). The residual became lower with increasing chloride addition. It was close to zero in the experiment with the highest NaCl input, another indication for the side reaction. The increase of the OX level is dramatic. The addition of 1% NaCl on pulp (i.e. 0.1% on liquid) causes a jump from the "nearly nothing" level to very significant amounts. The advantage for the bleaching process turns out to be very negative for the OX values.

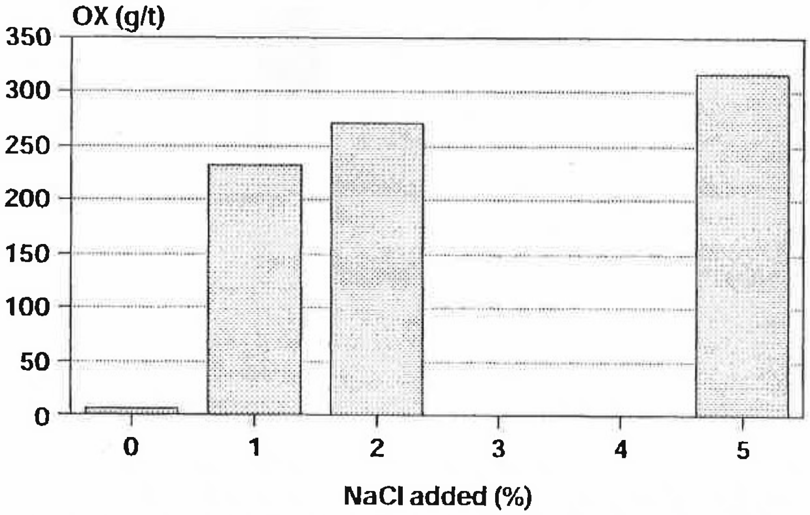

Figure 2: OX levels in pulp after the final Paa stage with increasing presence of NaCl in both Paa stages. Softwood kraft pulp, sequence O-AQ-Op-Paa-P-Paa; Paa stages at 75°C, 1h, 1% dist. Paa in the first stage, 0.5% in the second Paa stage

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The OX profile during the bleaching process shows the typical pattern well known from ECF bleaching [2]. The OX increases sharply in the acidic Paa stage and decreases in the subsequent alkaline P stage. The alkaline treatment with caustic soda partly decomposes and extracts the halogenated compounds. The second Paa treatment again increases the OX, while the final P stage lowers the value. The data are visualized in **Figure 3**. The final OX level of the pulp is as high as it would be with "conventional" ECF bleaching. In fact, optimized ECF bleaching can yield pulps with a much lower OX residual [12].

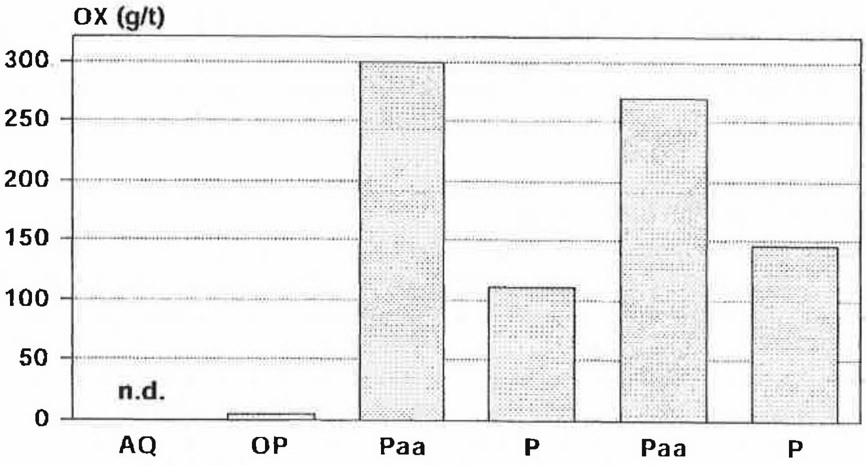

Figure 3: Development of the OX profile during TCF bleaching with the sequence O-AQ-OP-Paa-P-Paa-P in the presence of NaCl; NaCl addition in both Paa stages 2% on pulp, resp. 0.2 g/l. Paa amounts 1% and 0.5%, 75°C, 1h; all stages at 10% cons. (n.d. = not determined)

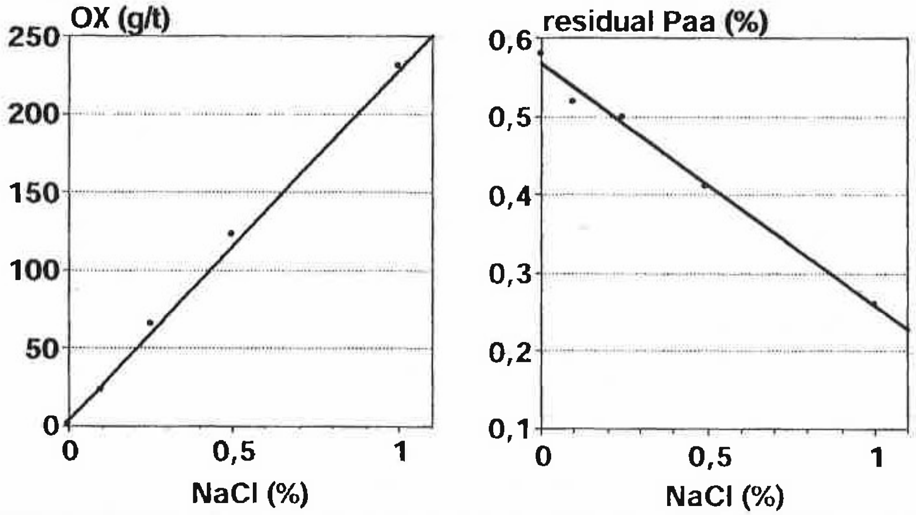

Figure 4: Effect of trace amounts of sodium chloride in a peracetic acid stage following O-AQ-OP delignification on the amount of OX generated in the pulp and the consumption of peracid; const. 1% Paa, 75°C, 1h, 10% cons.

These high levels of OX in the bleached pulps raise the question with how little chloride present an OX formation can be started. Additional experiments were made running just the first Paa stage in the presence of increasing small amounts of chloride. **Figure 4** has the data for the treatment of pulp with peracetic acid after the predelignification with the stages O-AQ-OP to Kappa 6.4. In the left part the OX level detected after the Paa stage is shown. The impact of the small amounts of chloride is very visible. Already the smallest amount of chloride applied, did trigger the formation of OX in the pulp. Within the range analyzed in this test, the dependence was linear. The right part of the graph shows the increasing turnover of the constant amount of Paa added. The more chloride is present, the more peracetic acid is consumed and, not shown here, the delignification effect improves. The amounts of H_2O_2 generated as hydrolysis product from peracetic acid remain nearly constant at 0.07%, an indication that the side reaction with the chlorine destroys most of it. These results set a limit to the closure of the water loops in Paa stages. Even the recycling of Paa filtrate needs to be closely monitored. Any increase of the content of chloride in the water has to be avoided, otherwise the conditions would certainly be not anymore "TCF".

In order to learn about the quenching effect of hydrogen peroxide experiments were made with the same pulp and sequence, however, now with constant chloride charge in the Paa stage and increasing H_2O_2 addition. The results are presented in Figure 5. The positive effect of the presence of hydrogen peroxide on the OX residual in the pulp becomes visible. Thus the option exists to lower the negative effects of a chloride presence in the Paa stage with an excess of H_2O_2. This is, however, not a very attractive approach. Distilled peracetic acid is prefered in pulp bleaching over equilibrium peracetic acid because of the higher costs of the mixture of peracetic acid with an excess of H_2O_2 and acetic acid.

A similar bleaching sequence was applied to analyze the effect of chloride ions on ozone delignification. The amounts ozone applied were slightly lower, because ozone is significantly more reactive compared with peracetic acid. In the sequence O-Q-OP-Z-OP-Z-P for the addition of the ozone a high consistency fluidized bed reactor [13] was used. Again an amount of 1% NaCl was added to the pulp in the Z stages, each with 0.4% O_3. The resulting OX generation in the pulp was much smaller. The OX increases in the ozone stages to amounts of 10g/t (Z_1) and 11g/t (Z_2) and decreases again in the subsequent P stages to levels well below 10g/t. Very obviously the reaction of ozone with the lignin is much faster then with the chloride ions and the amounts of chlorine generated remain very low. It seems unlikely that medium consistency ozonation would result in a different reaction pattern.

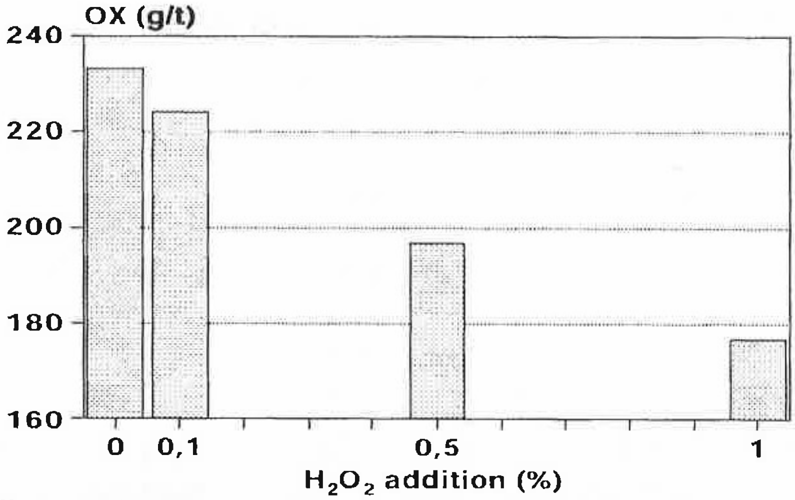

Figure 5: Effect of chlorine quenching by H_2O_2 addition to a Paa stage with chloride presence. Predelignification with O-AQ-OP to Kappa 6.4, subsequent Paa stage const. with 1% dist. Paa and 1% NaCl and variable addition of H_2O_2 at 75°C, 1h, 10% cons.

In order to learn about the level of OX in technical TCF pulps two available Nordic pulp samples were analyzed. One sample, a TCF birch pulp had an OX of 27 ± 4 g/t, the other one, a softwood pulp only 7.1 ± 0.3 g/t. Because neither the applied bleaching sequence (with or without peracide or ozone) nor the relevance of these two samples in respect to the "typical" levels of OX in TCF pulps are known, these results only indicate that slightly higher OX levels do occur.

It seems to be very important in TCF bleaching to keep chloride ions away from the stages with peracids. Water reuse and all closed loop systems become more complicated. Pulp mills with alternate production of ECF and TCF grades or mills running these in parallel lines will have to be very careful with any water exchange between the lines. If membrane technology is used to reuse washing water, the membranes should be capable to hinder chloride ions from passing through the membrane.

Rather low residuals of halogenated compounds, OX, are possible in pulps bleached with "ECF light" technology [14]. Amounts well below 100 g/t are detected after OD_0EopD_1P bleaching and values even lower than 50 g/t resulted from OZDP(O) bleaching. In consequence, the differences in terms of the residual of halogenated compounds become neglectable. Other parameters, e.g. fiber quality, brightness and recources consumption (yield on wood) will gain in importance in the diffferenciation between both bleaching strategies.

5. Conclusions

- In ECF bleaching the application of strong oxidizing compounds like Caro's acid or peracetic acid in combination with chlorine dioxide has limited advantages. There is no positive impact on the AOX load.
- Because the generation of peracids is more expensive compared with chlorine dioxide, there is no economical reason for their use.

- TCF bleaching with peracids in the presence of traces of chloride ions clearly generates halogenated by-products which are detected as an OX residual in the pulps.
- Closing the water loops becomes critical if this increases the concentration of chloride ions. In principle "closing" of mills becomes more complicated if the chloride ions level has to be kept very low.

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