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HYDROGEN PEROXIDE IN CHEMICAL PULP BLEACHING
-an overview-

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Abstract

If applied under appropriate conditions, hydrogen peroxide is a very effective bleaching chemical. The very wide application range will be described, starting with boosting the brightness in an existing bleach plant in any extraction stage, as well as in an additional final treatment in the high density storage tower. In addition hydrogen peroxide decreases the demand for chlorine dioxide in the final bleaching stages of an ECF sequence. Significant savings are the result of peroxide addition in the second extraction stage. The replacement of one chlorine dioxide stage in D_1-D_2 final bleaching with peroxide and the application of a D_1-P treatment also cuts the active chlorine demand.

With hydrogen peroxide the kappa number in the first extraction stage can be lowered and the substitution of chlorine with chlorine dioxide made more efficient.

In TCF sequences hydrogen peroxide is the chemical of choice to gain the required brightness. The conditions of peroxide bleaching are described and the benefit of magnesium salt addition and buffering with very small amounts of sodium silicate is demonstrated.

In addition the effect of alkaline hydrogen peroxide on the corrosion of titanium is reviewed and underlined with laboratory data. Basically, corrosion does not take place under the typical reaction conditions for peroxide bleaching in an ECF sequence.

Introduction

In 2001 the worldwide production of hydrogen peroxide was estimated to have reached more than 1,8 million metric tons. The dominating amount of hydrogen peroxide is used in bleaching processes. Hydrogen peroxide is generally supplied as an aqueous solution, typically in concentrations between 35% by weight and up to 70% by weight. These acidic solutions of hydrogen peroxide in water are very stable. Hydrogen peroxide can be stored for months in stainless steel tanks without significant changes of the content.

Compared to water, the energy content of hydrogen peroxide is much higher. For water the heat of formation (ΔH, eq. 1) from the elements is as low as -286 kJ mol^{-1}, for hydrogen peroxide (eq. 2) the coresponding value is only -188 kJ mol^{-1}[1]. In consequence hydrogen peroxide is less stable and can disproportionate into water and oxygen.

(1) $H_2 + ½O_2 \rightarrow H_2O$ $\Delta H = -286\ \text{kJ mol}^{-1}$

(2) $H_2 + O_2 \rightarrow H_2O_2$ $\Delta H = -188\ \text{kJ mol}^{-1}$

Since the activation energy for the cleavage of the oxygen-oxygen bond is rather low ($\Delta H = -71\ \text{kJ mol}^{-1}$)[2], traces of contaminants can start this reaction. Basically the decomposition is a redox process. Hydrogen peroxide either supplies electrons and yields oxygen or accepts electrons and yields water. Metal salts of each state of oxidation can start the decomposition reaction. The first step can be the reduction of iron according to equation (3):

(3) $2\ Me^{2+} + H_2O_2 \rightarrow 2\ Me^{+} + \mathbf{O_2} + 2\ H^{+}$

The alternative is the oxidation of a metal according to equation (4):

(4) $2\ Me^{+} + H_2O_2 + 2\ H^{+} \rightarrow 2\ Me^{2+} + \mathbf{2\ H_2O}$

The reaction certainly can also start with the reduced form of metal. The overall reaction is identical, it is the formation of water and oxygen from hydrogen peroxide and the redox system of the metal is acting as the catalyst [1].
The decomposition of hydrogen peroxide is in addition catalysed by alkali. These are the reaction steps:

(5) $\mathbf{H_2O_2} + OH^{-} \rightarrow H_2O + HOO^{-}$

(6) $HOO^{-} + H_2O_2 \rightarrow \mathbf{H_2O} + \mathbf{O_2} + OH^{-}$

Since bleaching with hydrogen peroxide requires alkaline conditions, this decomposition reaction is very important for the practice.
Single electron transfer reactions of hydrogen peroxide with catalysts yield radicals. These decomposition reactions take place with metals or enzymes like catalase. Radicals formation can also be the result of a thermal cleavage of the oxygen-oxygen bond.

(7) $H_2O_2 + Me^{+} \rightarrow OH^{-} + {}^{\cdot}\mathbf{OH} + Me^{2+}$

(8) $H_2O_2 + {}^{\cdot}OH \rightarrow H_2O + {}^{\cdot}\mathbf{OOH}$

(9) $H_2O + {}^{\cdot}OOH \rightarrow {}^{\cdot}\mathbf{OO}^{-} + H_3O^{+}$

The hydroxyl radical, the hydroperoxy radical and the superoxide anion radical are important intermediates. They cause side reactions in bleaching processes, with delignification as positive and depolymerisation of the cellulose as negative result. Generally radicals produce more negative effects than positive results on delignification. Therefore, transition metal ions are normally eliminated before a peroxide treatment.

In pulp bleaching the formation of the perhydroxyl anion (eq. 5), a nucleophile intermediate, is responsible for the oxidation of chromophores in lignin through the cleavage of side chains [3]. The effect of a hydrogen peroxide treatment is dominantly an increase of the brightness. Delignification with hydrogen peroxide is to a large extent the result of the action of the radicals produced in equations 7, 8 and 9 [3, 4]. At moderate temperature, under buffered conditions and in the absence of transition metals, the delignifying effect of hydrogen peroxide is limited. The degradation of polymerized lignin, which can be the result of high intensity pulping conditions, with hydrogen peroxide is limited. The perhydroxyl anion, being a nucleophile, cannot attack the electron rich aromatic rings of the residual lignin.

Application of hydrogen peroxide on mill scale

Bleaching reactions with hydrogen peroxide are conducted in stainless steel reactors or in rubber coated carbon steel towers, to avoid decomposition of the peroxide and corrosion of the reactors. Alkaline peroxide solutions are not corroding stainless steel. Peroxide solutions are diluted and premixed with caustic soda before they are added to the pulp. The alternative is the addition of the technical grade solution of hydrogen peroxide (50% to 70%) to the pulp without dilution, which requires an efficient mixer in order to avoid local overconcentration. The advantage is the addition of a lower volume of diluting liquid which permits a higher consistency. Generally the consistency in a peroxide bleaching stage should be as high as possible. The increase of the relative concentration of the chemicals to the pulp and the elimination of dissolved organic compounds improves the efficency of the bleaching.

Very alkaline peroxide solutions are agressive against another material which is widely used to in the construction of bleach plants: titanium. The corrosion of titanium through alkaline peroxide solutions is strongly depending on the peroxide concentration and the pH value. Table 1 and figure 1 have the results of laboratory tests with titanium metal treated with alkaline hydrogen peroxide at 80°C.

Table 1: Corrosion of titanium with alkaline hydrogen peroxide. Effect of peroxide concentration and pH value. A continuous flow of peroxide and alkali was applied to maintain the concentration of the chemicals, the amount of chemicals is calculated on liquid, it has to be multiplied by ten to correspond (at 10% consistency) to pulp.

H_2O_2 (%)	NaOH (%)	Na_2CO_3 (%)	resulting pH	corrosion rate (mm/year)
0,2	-	0,1	10,3	0
0,2	-	0,2	10,6	0
0,2	0,1	0,1	10,8	0
0,2	0,2	-	11,6	0,06
0,2	0,4	-	12,0	0,22
0,5	0,2	-	11,6	0,28
0,5	0,4	-	11,9	1,62

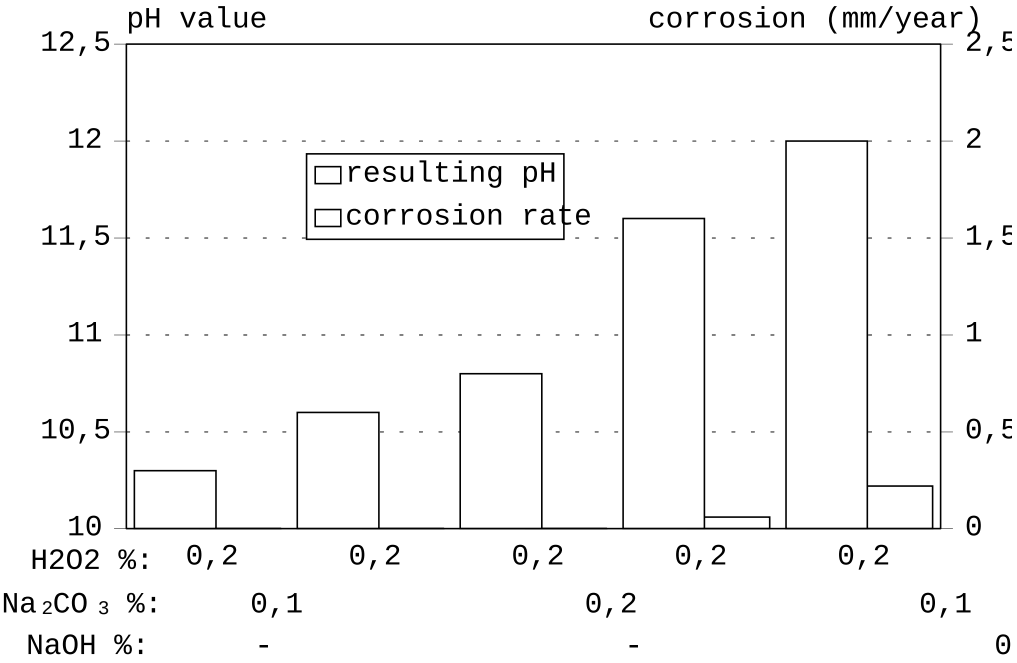


Figure 1: Corrosion of titanium with alkaline peroxide, effect of pH level

The results indicate a significant increase of the corrosion level at high pH-values. In addition, the losses of material increase with increasing hydrogen peroxide concentration. On the other hand, at a pH below pH 11, no corrosion takes place. Hydrogen peroxide starts the corrosion only at higher concentration levels. The highest corrosion rate in the table coresponds to a hydrogen peroxide charge of 5 % H_2O_2 on pulp at 10% consistency, an addition value, which is far away from typical peroxide charges. The same is valid for the charges of caustic soda. These are typically in the range of 2% to 3% NaOH on pulp in an extraction stage and are significantly lower in a final peroxide bleaching stage. In addition, in peroxide bleaching the pH level and the peroxide concentration decrease during the reaction. Thus, in the upper part of a bleaching tower the pH and the peroxide concentration are significantly lower. The optimum parameters for hydrogen peroxide bleaching and, with restrictions, also for hydrogen peroxide delignification are not within the range of strong corrosion of titanium metal. The corrosion of titanium is inhibited with calcium ions (water hardness) or magnesium salts [5, 6, 7]. Already 1 ppm of calcium has a pronounced effect [5]. Sodium silicate also inhibits corrosion [5]. Since magnesium is normally added to peroxide bleaching processes, a corrosion of titanium under typical mill conditions becomes very unlikely, if the amount of chemicals added is properly controlled.

Prerequisites of hydrogen peroxide application

Transition metals are decomposing hydrogen peroxide. A controlled decomposition with a well defined generation of radicals would be desirable from the point of an improvement of the delignification. Unfortunately untill today no selective generation has been described. Typically the radicals produced through metal catalysed decomposition are inselective and fiber damage dominates, as a result of cellulose depolymerisation. In consequence, metal impurities have to be removed from the pulp before a subsequent peroxide treatment [8, 9, 10]. The amount of transition metals being present in pulp differs in a wide range and is depending on the soil where the wood has been grown. Normally manganese and iron are dominating, other metals like copper and cobalt are present only in traces around 1 ppm. In sulphite pulping the removal of metal is very easy. During the acidic and reducing conditions of the pulping process, metals become water soluble and are easily removed during brown stock washing.

In kraft pulping the transition metal ions become insoluble during the pulping process. They are reduced to a low state of oxidation and precipitated as sulphides. These sulphides are very insoluble under alkaline and neutral conditions, so normal washing does not remove them. During oxygen delignification they might be oxidized to a higher state of oxidation, but the resulting hydroxides are still insoluble under the conditions of oxygen stage washing. They become water soluble under mild to strong acidic conditions. In conventional bleaching processes transition metals are removed during the acidic bleaching stages. Since hydrogen peroxide typically is applied in ECF bleaching only after the first D stage, the metal profile normally is already low enough and no specific measures are required. Figure 2 demonstrates the effect of the pH value on the elimination of iron and manganese from kraft pulp.

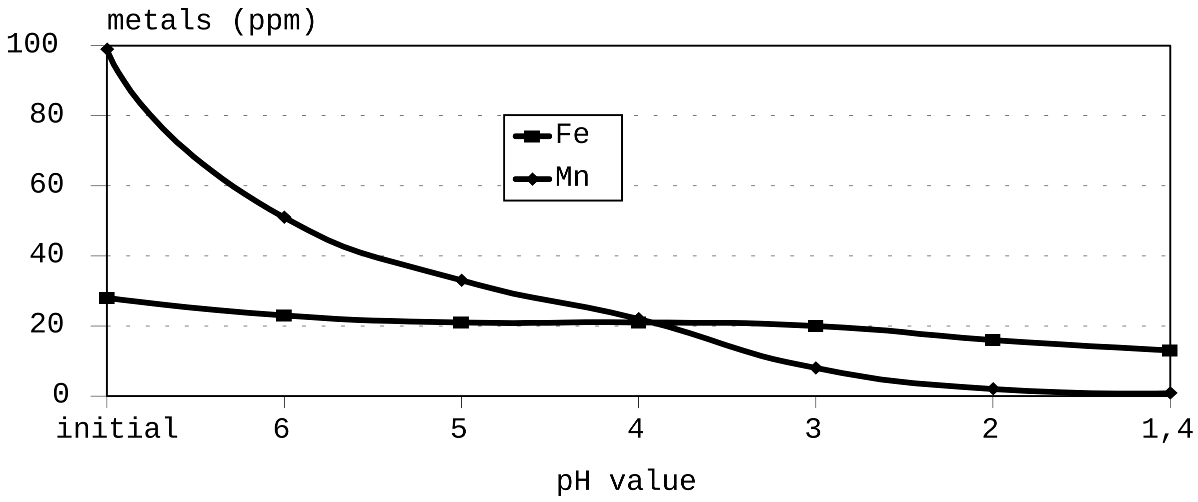


Figure 2: Removal of iron and manganese from softwood kraft pulp with increasing acidity. All trials at 3% cons., 60°C, 0.5h with H_2SO_4 for acidification.

In comparison to iron the removal of manganese obviously is much easier. Strong acidic conditions are required to lower the amount of iron. In TCF bleaching the removal of the metals becomes more important, because hydrogen peroxide is applied early in the sequence at much higher charges.

As demonstrated in figure 3, the elimination of the metals is improved with the addition of chelating agents. Since compounds like EDTA are good chelating agents for double-charged metal ions, the addition of a small amount of sulphite improves the chelation. DTPA can chelate also higher charged metal ions. The metal ions present in the pulp are very likely bound to lignin or cellulose. EDTA and DTPA are competing with these compounds for the metal ions. In addition, alkali earth metals are also chelated by DTPA or EDTA, depending on their chelation constants. Metals like iron do have chelation constants, which are about two tenth powers higher, but this is compensated by the fact that the calcium concentration may be more than one hundred times higher compared with the concentration of iron. In kraft pulps calcium concentrations of about 5000 ppm are found. If the concentration of calcium is so much higher compared to the concentration of iron, then despite the higher chelation constant, the alkali earth metals are the preferred compounds for chelation. The demand for DTPA will therefore be higher than the stoichiometric equivalent calculated for iron and manganese.

The results shown in figure 2 and 3 demonstrate a much stronger binding of iron to the residual lignin or to the cellulose compared to manganese. Even very high charges of DTPA do not affect the iron content at pH 6. In contrast, manganese values are significantly lowered. In consequence, an efficient removal of transition metals needs higher acidic conditions, even in the presence of a chelating agent. The necessity of efficient washing goes without saying. Table 2 gives an example for the metals removal from eucalyptus kraft pulp using acidic conditions with and without chelant addition.

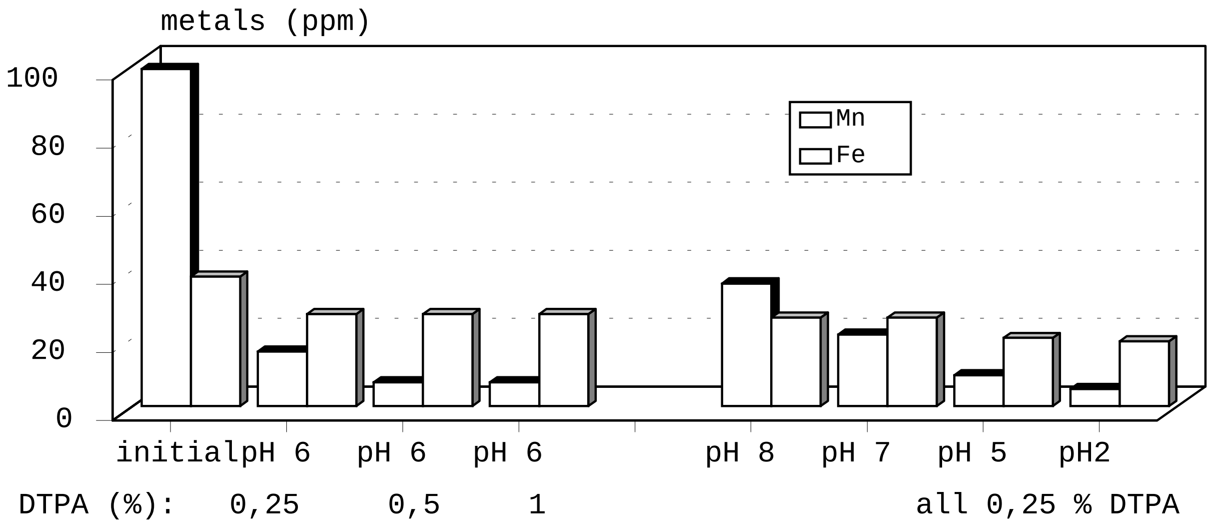


Figure 3: Removal of iron and manganese from softwood kraft pulp with DTPA and increasing acidity. All trials at 3% cons., 50°C, 0.5h with H_2SO_4 for acidification.

Table 2: Removal of transition metals from oxygen delignified eucalyptus kraft pulp. Conditions: 3% consistency, 60°C, 0,5 h, 1% H_2SO_4, 0,5% $NaHSO_3$, pH 2,3

	pH value	Fe (ppm)	Mn (ppm)
oxygen delignified		25	5
$A_{(W)}$	2,3	11	<1
$A_{(Q)}$ with 0,1% EDTA	2,3	10	<1

Bleaching experiments demonstrated, that it is not necessary to decrease the metals content to extremely low levels. The addition of a small amount of metal ions to a superchelated pulp has a more pronounced negative effect compared with the same amount of metal as residual. I.e. pulp chelated down to 20 ppm iron bleaches better than pulp superchelated down to 5 ppm iron and enriched artificially with another 5 ppm. Very obviously the normal residual of iron or other metals is tightly bound to the pulp and is not available for the decomposition reaction. In consequence there is no advantage of a further drop of the iron level.

It is very difficult to describe a threshold value for a "no effect“ level for iron or manganese, because of the chelation of these metals to the pulp or the lignin. Typically the residual remaining after an acid wash/chelation treatment for iron differs between 10 and 30 ppm and for manganese between 1 and 5 ppm. If washing was efficient, the bleaching performance is all right within this range of residual metal ions.

Hydrogen peroxide in pulp DELIGNIFICATION

Hydrogen peroxide in ECF sequences

As mentioned above (chapter 2), alkaline hydrogen peroxide has a limited delignification ability. In ECF bleaching it is applied to improve the lignin removal in the extraction stage. In the extraction stage the oxidized lignin is solubilized. The solubility of these compounds in water becomes much better under alkaline conditions, because salts are formed. The oxidation with chlorine dioxide produces less free phenolic groups and carboxylic acid groups on the high molecular residual lignin compared with chlorine. In consequence the combined effect of a chlorine dioxide treatment and a subsequent extraction stage is inferior compared with the result of chlorine plus extraction. This becomes visible in figure 4.

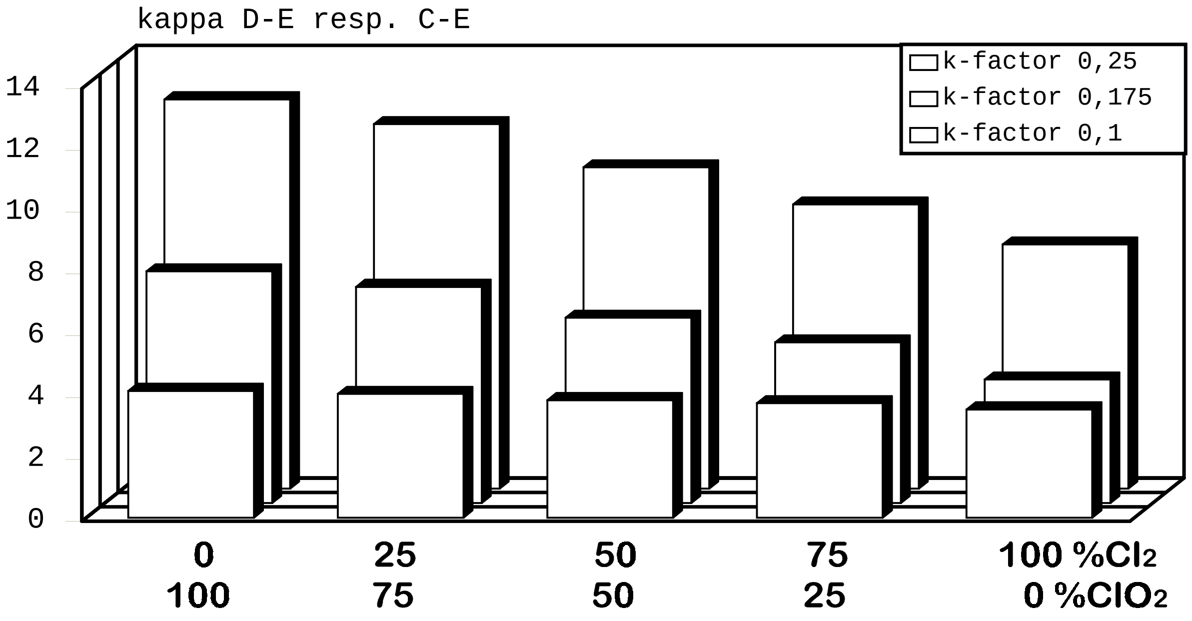


Figure 4: Delignification of eucalyptus kraft pulp with sequence C-E resp. D-E and mixtures of Cl_2 and ClO_2

The addition of small amounts of oxygen to the extraction stage is a technical possibility since high shear mixers permit a fluidization of the pulp at medium consistency. Oxygen gas is added to the pulp in the form of micro bubbles, and a homogenous mixture of pulp, gas and water is generated. In 1979 the combined addition of oxygen and hydrogen peroxide was first introduced in a pulp mill in southern Germany. Both chemicals oxidize lignin into better soluble, lower molecular weight fragments. Oxygen reacts primarily as an electrophile with the phenolic structures, but produces also peroxo intermediates, which cleave side chains on the residual lignin in a nucleophile reaction.

The amount of oxygen is normally set between 5 and 10 kg per ton of pulp. It is generally accepted to overdose oxygen, because oxygen is inexpensive. The consumption of oxygen is a function of the reaction temperature and the mixing efficiency. Increasing the pressure from 2 to 3 bars to higher levels, normally is only of benefit, if the mixer is inefficient. If the oxygen bubbles are really small and properly distributed, a pressure increase cannot produce much effect. With injectors or spargers gas bubbles of a larger diameter may result. Therefore under these conditions a compression can be effective.

Because of the limited effect of hydrogen peroxide on deligification it does not make sense to apply larger amounts. Normally the amount of hydrogen peroxide is kept strictly well below 10 kg per ton of pulp. Typically about 3 to 5 kg/t are applied in an EOP stage. Figure 5 compares the effect of an E, an EO and an EOP treatment after chlorination and after chlorine dioxide treatment.

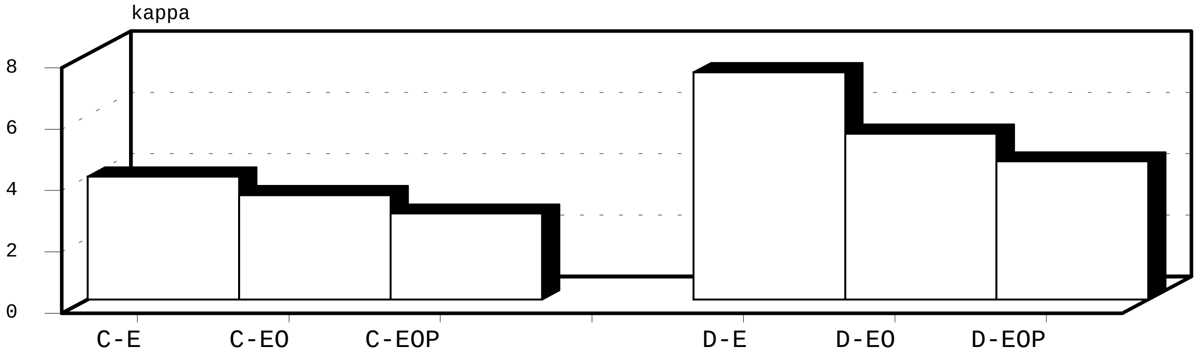


Figure 5: Effect of oxidative reinforcement of the extraction stage with oxygen and oxygen plus hydrogen peroxide. Eucalyptus kraft pulp kappa 16.2; active chlorine multiple 0.15; ~ 0.5 % O_2, 0.5 % H_2O_2.

The positive effect of the addition is clearly visible. It is smaller, if chlorine is applied and more pronounced after the less effective delignification with chlorine dioxide. The effect of an increasing hydrogen peroxide charge is given in Figure 6. In the temperature range of 70°C to 80°C, the effect on the kappa number reduction is pronounced within the addition range from zero to 0.5 % H_2O_2. Higher hydrogen peroxide charges lift the brightness, but do not alter the lignin content very much. Under these reaction conditions, a residual of peroxide at the end of the treatment demonstrates the absence of lignin structures which are easily oxidized.

However, this effect can be improved in terms of brightness increase and delignification under more drastic conditions, e.g. higher temperature and higher peroxide dosage. Table 3 gives a comparison of the results achieved with increased temperature and pressure on a D_0 pretreated pulp.

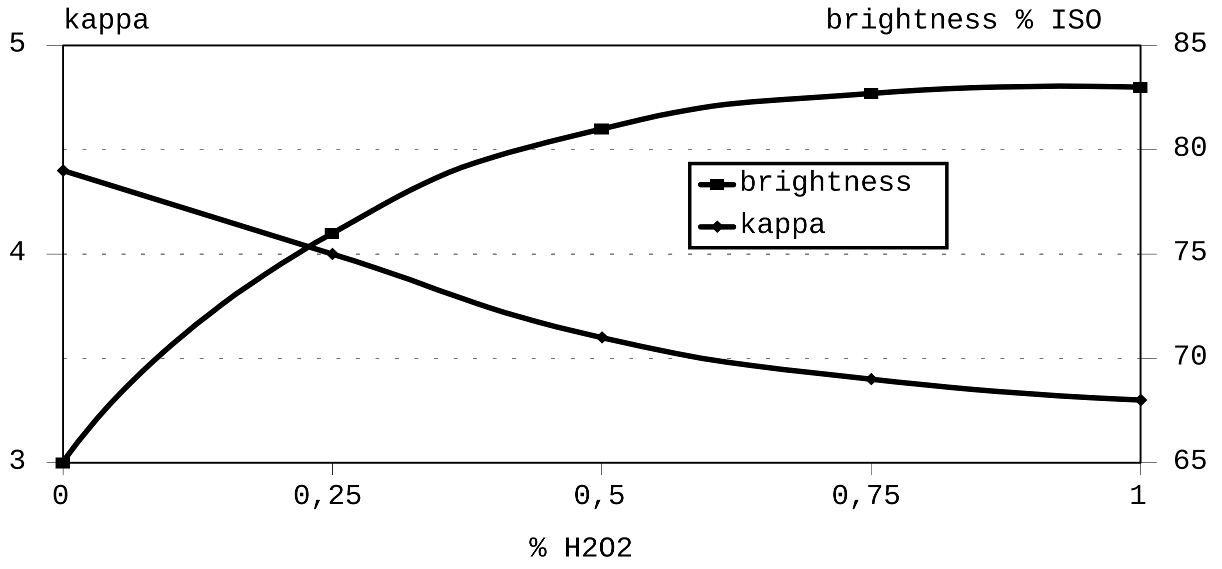


Figure 6: Lignin degradation and brightness increase of eucalyptus kraft pulp with increasing hydrogen peroxide charge in EOP subsequent to the D_0 treatment with 0.15 active chlorine multiple: EOP conditions: 10 % cons., 75°C, 30 min., 0.3 MPa O_2 pressure, 60 min. without pressure.

Table 3: Effect of temperature and pressure in an EOP treatment of eucalyptus kraft pulp on kappa, brightness and viscosity. D_0 with 0.15 % active chlorine multiple. Constant conditions in EOP: 1,8% NaOH; 10 % cons., 0.5 h pressure, 1.0 h without pressure (simulation of upflow tube and downflow tower).

temp. (°C)	H_2O_2 (%)	oxygen (MPa)	kappa	brightness (% ISO)	viscosity (mPa·s)
80	0.5	0.3	4.0	81.4	11.2
80	1.0	0.3	3.8	82.5	11.1
100	0.5	0.3	3.2	81.6	10.3
100	0.5	0,5	3.3	81.7	10.3
100	1.0	0.5	3.1	82.8	9.2

The more drastic conditions yield lower residual lignin levels. While the effects on the Kappa number reduction remain moderate, the increase of the temperature basically lowers the pulp quality. At the higher temperature level, the viscosity of the pulp becomes lower. The improved delignification and the possible savings of chlorine dioxide are traded for a lower quality. In addition the higher temperature does have a negative impact on the temperature profile of the sequence. Normally the temperature changes from stage to stage should not be too high, because this might cause difficulties with the temperature level of the washing water circuits. The increase of the pressure does not produce a better peroxide performance. On mill scale certainly pressure can be important, especially if poor oxygen mixing has to be compensated, but this has no impact on the performance of hydrogen peroxide.

The addition of magnesium salts improves the viscosity levels especially at higher temperature. Figure 7 illustrates an example for softwood kraft pulp. The increase of the EOP stage temperature only yields a moderate drop of the lignin level from kappa 3,4 to 3,1 (which is about 10%), and the viscosity losses can kept moderate, if magesium salts are added.

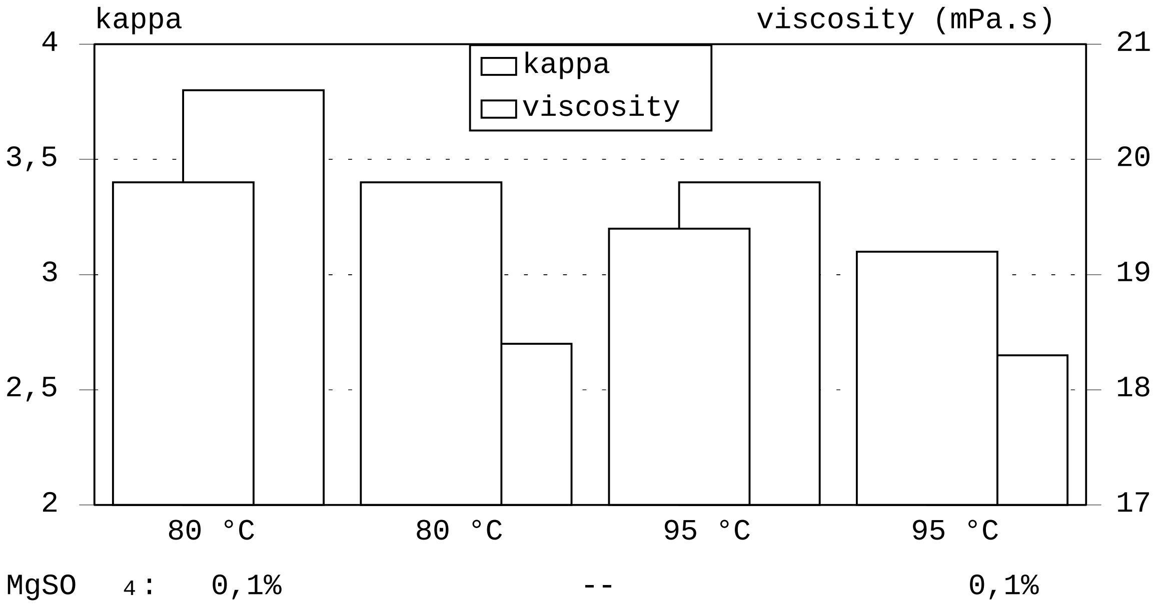


Figure 7: Effect of temperature increase and $MgSO_4$ addition in EOP treatment of softwood kraft pulp. Sequence O-D_0 with kappa-factor 0,175 in D_0. Reaction in EOP with 1,8% NaOH, 0,3% H_2O_2

With the addition of oxygen and peroxide in the extraction stage a decrease of the residual lignin level down to kappa numbers between 3 and 4 can be achieved with an active chlorine multiple in the D_0 stage as low as 0.15 to 0.2. Temperatures above the usual level of 75°C to 85°C in an EOP stage cannot be recommended since the benefit in terms of delignification is moderate and the pulp quality suffers.

In ECF bleaching the addition of hydrogen peroxide to the first extraction stage has these advantages:

- H_2O_2 improves the delignification and increases the brightness
- small amounts of H_2O_2 already yield a pronounced effect
- H_2O_2 addition can be combined with oxygen
- standard E stage temperature produces good results.

Hydrogen peroxide in pulp BRIGHTENING

Hydrogen peroxide in ECF sequences

Hydrogen peroxide is applied in the final stages of an ECF bleaching sequence with the target to optimize the requirement for bleaching chemicals. Basically in each extraction stage of a bleaching sequence the addition of hydrogen peroxide is possible. The question is, whether such an addition offers an economical advantage. For northern softwood and the bleaching sequence CD-E_1-D_1-E_2-D_2 this question was positively answered already in 1981[12]. The addition of a small amount of hydrogen peroxide in the E_2 stage was economical, because it lowered significantly the chlorine dioxide requirement for final bleaching.

Another variation of the addition of hydrogen peroxide became very typical in the United States: high density storage addition of hydrogen peroxide. It allowed pulp mills to boost the brightness in an additional bleaching stage without spending capital. In the race for top market pulp brightness and the resulting top selling price advantage, the additional two to three brightness points which are easily achieved with as little as 2 kg to 3 kg of H_2O_2 do pay off. Certainly high density storage application of hydrogen peroxide is only a compromise. Nevertheless, it makes sense, because the capital requirement for an additional bleaching stage is high, and despite the always changing conditions in a storage tower, the results are rather satisfying. The good results of high density storage bleaching open another alternative: a final bleaching stage run with hydrogen peroxide.

The application of hydrogen peroxide in a final bleaching stage is an answer to the concept of shortening the bleaching sequences and also the answer to the elimination of the second extraction stage. Instead of a D_1-E_2-D_2 sequence the D_1-D_2 alternative was created to cut investment costs. It certainly needs more active chlorine compared with the longer sequence, but the savings in capital for one tower and one washer were believed to pay for. On the other hand, in some mills the higher chlorine dioxide requirement causes problems because of the limitation in the installed chlorine dioxide capacity. An increasing pulp production and the implementation of ECF bleaching can also tighten the availability of chlorine dioxide.

Bleaching an eucalyptus kraft pulp with the sequence O-D_0-EOP-D_1-D_2 requires about 3,3 kg of active chlorine, to produce the market pulp target brightness of 90^+ ISO. The lowest demand results with an active chlorine multiple of 0,15 to 0,175 in D_0. The combined active chlorine multiple for the D_1-D_2 stages is relatively high, a kappa factor of 0,5 is needed to achieve the target brightness. The typical increase of the brightness during the D_1 and D_2 stages is demonstrated in figure 10.

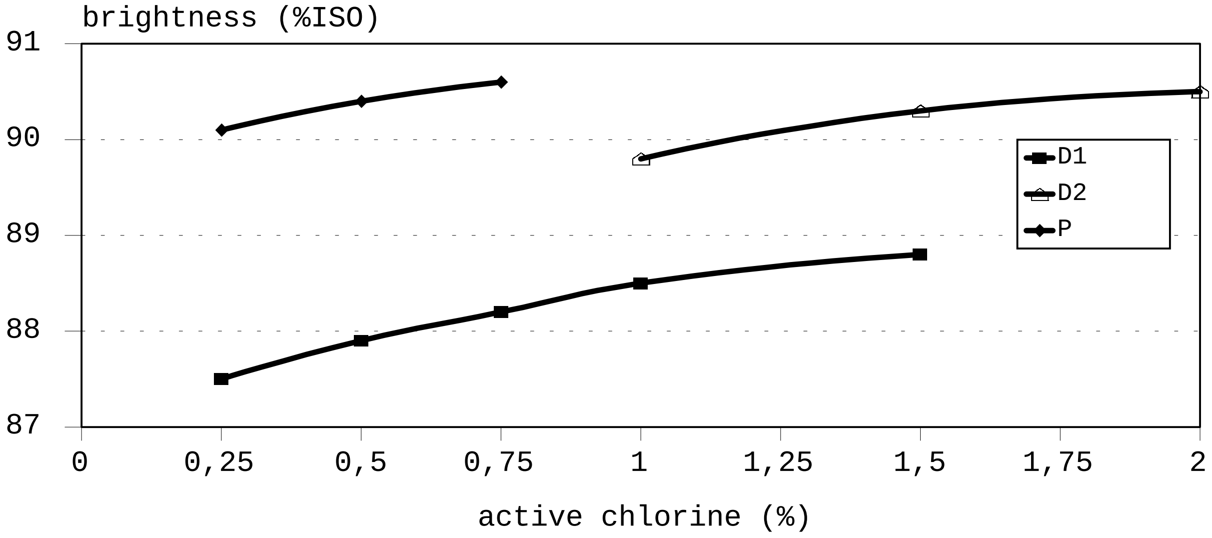


Figure 10: Brightness increase of an O-D_0-EOP prebleached eucalyptus kraft pulp (kappa number 3.5 and 82.1 % ISO brightness) with ClO_2 or H_2O_2 applied in final bleaching at 10 % cons. D stages 75°C, 3 h, P stage: 0.25 % H_2O_2, O.4 % NaOH, 80°C, 3 h.

In the D_1 stage increasing amounts of chlorine dioxide yield a significant brightening effect. Nevertheless, this effect levels of at higher chlorine dioxide charges. After an inital steep increase of the brightness, a doubling of the ClO2 charge does not significantly further lift the brightness. With only 0.5 % active chlorine the brightness is lifted from 82,1% ISO to 87.8 %, with twice the amount of chlorine dioxide (1 % active chlorine), only 88.4 % ISO result. The curve for the brightness development in D1 becomes very flat, thus even very high charges of ClO2 do not produce brightness levels above 89 % ISO. This is the reason why indeed an additional stage (D_2) is required and in the past a D_1-E_2-D_2 treatment was applied. The desired final brightness above 90 % ISO is achieved only after washing and the addition of more chlorine dioxide in the second D stage. Under these conditions a total input of 1.5 % active chlorine yields 90 % ISO brightness.

Changing the bleaching conditions, for example the pH environment from acidic to alkaline, or applying a different bleaching agent, normally results in an advantage compared with the repeated addition of the same chemical. So, instead of two subsequent chlorine dioxide treatments, a chlorine dioxide stage followed by an alkaline peroxide stage should be more efficient. This becomes obvious in the left part of figure 10. Very low levels of chlorine dioxide in D_1 yield a sufficient activation to achieve the required brightness increase in the peroxide stage. In consequence, a significantly lower demand for chlorine dioxide is needed to achieve the brightness target. For another pulp sample the results are very similar, as is demonstrated in figure 11. Mill scale trials have reproduced these results and demonstrated its general applicability [13]. This effect can be very attractive to mills with a limited chlorine dioxide capacity, or for mills which want to increase pulp production but not their chlorine dioxide generator capacity.

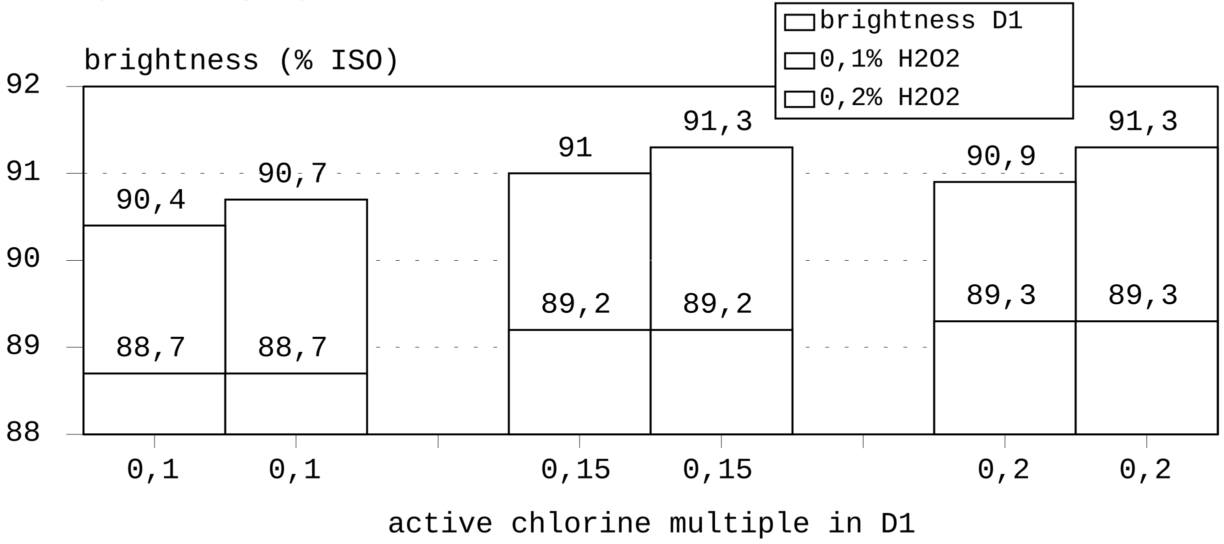


Figure 11: Brightness increase for different kappa-factors in D_1 and peroxide charges. Pre-bleaching with sequence O-D_0-EOP-D_1 with oxygen stage kappa 11,1; kappa-factor 0,15 in D_0; P stage with 0,1 % $MgSO_4$, 75°C, 1,5 h 10% consistency

The amount of hydrogen peroxide needed to boost the brightness is rather low. Figure 12 demonstrates the brightness increase achieved with an increasing hydrogen peroxide charge. Very small amounts of hydrogen peroxide already produce a brightness increase of about two points. In addition the brightness stability is improved. A comparison of the results achieved with a final D_1-D_2 and a D_1-P treatment demonstrated a decrease from the average 4 to 5 points brightness loss after D_1-D_2 to only 2 to 3 points after D_1-P. In consequence, the target brightness on mill scale can be decreased. A calulation of the savings in chlorine dioxide against the demand for hydrogen peroxide shows a replacement ratio of up to 9 kg of chlorine dioxide (as active chlorine) with only 1 kg of hydrogen peroxide. The active chlorine multiple for the D_1-D_2 stages can be lowered from 0,5 to a level as low as 0,1 for the D_1-P combination.

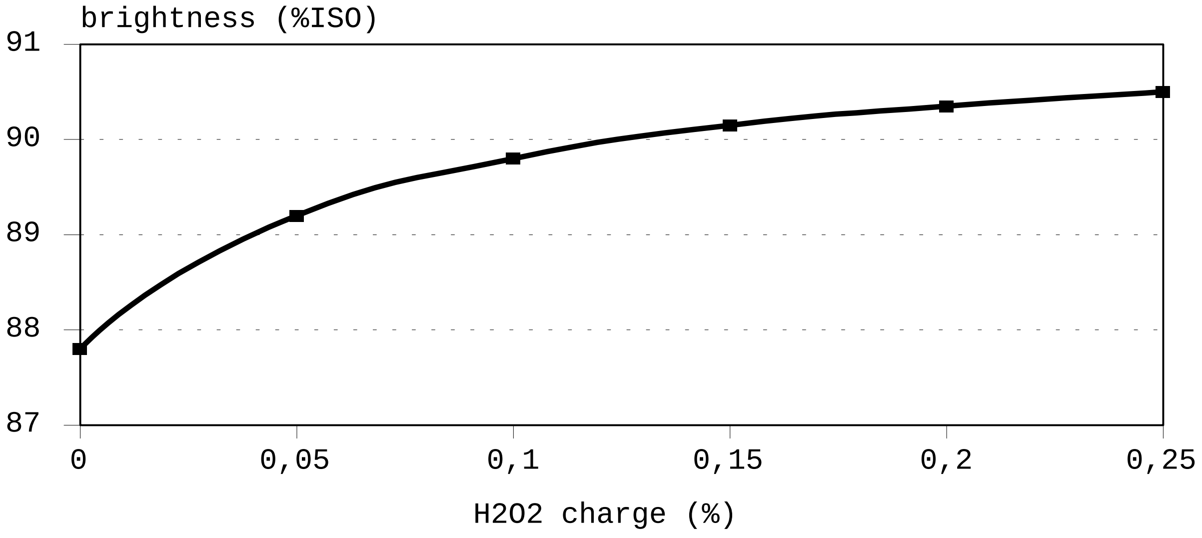


Figure 12: Effect of an increased hydrogen peroxide charge in postbleaching. Bleaching of an O-D_0-EOP-D_1 prebleached pulp. Kappa-factor in D_0 0.17, in D_1 0.2.

The viscosity level in the final peroxide stage can be controlled with the addition of magnesium salts. As expected, the temperature of the P stage has an effect on pulp viscosity. A high peroxide residual also has a negative impact on the viscosity, especially at higher temperature and neutral pH. Table 5 gives the results for a variation of the bleaching conditions in the final peroxide stage. The much better thermal stability of the peroxide bleached pulps becomes obvious, if heat aging brightness losses are compared with standard D_1-D_2 bleached pulp.

Table 5: Improvement of the final viscosity after peroxide bleaching of eucalyptus kraft pulp. Pulp prebleached with O-D_0-EOP-D_1 to 87.7 % ISO brightness. Constant: 10 % cons., 2 h.

chemicals addition (%)				temp. (°C)	residual H_2O_2 (%)	bright-ness (% ISO)	viscosity (mPa.s)	heat ageing (points)
H_2O_2	NaOH	$MgSO_4$	sodium silicate					
0.25	-	-	-	70	0.02	87.6	8.5	7.2
0.25	0.4	-	-	70	0.01	90.2	10.8	2.0
0.50	0.4	-	-	70	0.10	90.8	10.1	2.8
0.25	0.4	0.1	-	70	0.04	90.5	11.2	2.6
0.25	0.3	0.1	0.25	70	0.04	90.7	13.4	2.6
0.25	0.3	0.1	0.50	70	0.05	90.8	13.8	2.4
0.1	0.3	0.1	0.50	70	0.03	90.5	13.9	2.4
0.1	0.3	0.1	0.50	90	0.01	90.7	12.8	2.5
0.2	0.3	0.1	0.50	90	0.01	90.9	12.5	2.6
control (D_1D_2 treatment):				75	-	90.4	13.2	4.6

In a final peroxide stage the application of pressure was recommended [14]. It is very difficult to understand why this recommendation was made. A small amount of hydrogen peroxide reacts already at 80°C within two hours without the application of pressure. Figure 11 illustrates this. At higher temperature the viscosity values suffer and the brightness is not tremendously improved. In consequence for the application of hydrogen peroxide in the final stage of ECF sequences our recommendation is not to decide for drastic conditions, but for a smooth reaction at moderate conditions. A final P stage offers these advantages:

- Small amounts of hydrogen peroxide yield high brightness gains already at conventional temperature levels -
- the brightness stability is significantly inproved.

The selection of the best conditions in the P stage has to be made with following facts:

- magnesium salt addition increases viscosity -
- buffering yields maximum brightness at highest viscosity -
- high temperature increases the brightness but yields lower viscosity -
- viscosity is negatively affected by residual peroxide at neutral pH.

Summary

The final conclusions in this look over peroxide application and performance in chemical pulp bleaching can be made as follows:
Hydrogen peroxide is a very versatile bleaching agent. It can be applied in a wide range of conditions:

- **Temperature** range: (starting at about 20°C)
    normally: 75**°C** to 8**5°C**,
    in special cases up to 100°C.
- **Retention time** range: (starting with about 30 min.)
    normally: **1,5 h** to **2 h** and up to 16 h,
    in special cases 1 day to 3 days.
- **Consistency** range: not below 8 % consistency,
    normally: **10%** to **15%** consistency,
    in special cases up to 30% consistency.

- **In ECF bleaching sequences** the application of hydrogen peroxide offers significant economical benefits. The addition of hydrogen peroxide in the extraction stage improves the delignification and allows lower kappa factors in D_0.
- Final bleaching with hydrogen peroxide cuts the requirement for chlorine dioxide in D_1. A very low input of hydrogen peroxide allows kappa factors in D_1 as low as 0,1 to 0,15.
- The decreased demand for chlorine dioxide yields lower cost, lower AOX of the effluent and a lower OX in the pulp.
- The moderate conditions (pH and concentration) required for bleaching with hydrogen peroxide do **not** result in a corrosion hazard for titanium equipement.

ECF light

Introduction

Halogenated compounds are generated during bleaching with chlorine containing compounds. These by-products of the bleaching process are well known as the AOX load in the effluent. It is not so common that a certain amount of halogenated compounds remains in the pulp, even in pulp bleached to full brightness. The amount of halogenated compounds can be analyzed using the same method as for AOX, the difference is that not an effluent is passed through active carbon and the washed carbon is burnt. To measure the halogenated residual in the pulp, the pulp is ground to a fine powder and processed with the same method used for the AOX analysis, i.e. it is washed with potassium nitrate solution to remove chloride ions and finally burnt with oxygen. The amount of chlorine and bromine as HCl or HBr in the combustion gases is analyzed.

The amount of pulp that can be burnt under these conditions is limited. Therefore extremely low levels of residual are are outside of the detection range. This results in a treshold for the amount of chlorine, that can be detected. In addition there is an amount of chloride ions naturally present in the pulp that cannot be removed totally with the washing procdure. All these factors result in a background noise, a naturally present amount for halogenes of about 0,4µg to1µg. This can be translated into a background level of 15g to 20g of organically bound halogen (OX) in the pulp. This level is normal also for totally chlorine free bleached pulps. In order to stay on the safe side, it is normally assumed to set 30g/t OX in pulp as the treshold below which pulps are definitely bleached without chlorine containing compounds.

OX in fully bleached pulp

Conventional bleaching methods result in rather high levels of OX remaining in the pulp. The analysis of several different kraft pulps gave values between 200g/t and 600g/t of OX. Pulps bleached with a chlorine stage do have a higher OX residual, however, there are also pulps bleached with an oxygen stage and chlorine dioxide which have high OX values [1]. In contrast to the effects on the AOX in the effluent, the switch from chlorine to a partial or complete substitution with chlorine dioxide does not necessarily result in a significantly lower OX of the pulp after the final bleaching stage. The OX level remaining in the pulp is obviously affected also by other parameters.

The halogenated residual of a bleached pulp can be partially removed with a simple a hot water extraction. Table 1 has the results of an extraction of two kraft pulp samples in a soxhlet apparatus.

The amount of OX decreases with such a treatment by about 10%. Obviously the solubility of the residual in water is limited.

Table 1: Decrease of the residual of halogenated compounds (OX) with hot water extraction (1h reflux), fully bleached softwood kraft pulps

sample	OX (initially) (g/t)	OX (extracted) (g/t)	decrease (%)
A	274 ± 21	252 ± 31	9
B	562 ± 14	493 ± 23	12

Saponification and extraction are another possibility to decrease the amount of halogenated residual. In Table 2 the effect of the treatment of different kraft pulps with caustic soda is listed. The drop of the OX level with the extraction is between 15% and more than 30%, with the best effect on the pulp with the highest OX. Alkaline stages not only decrease the OX with their ability to extract organic material, they in addition saponify and decompose some of the chlorinated compounds. This becomes visible in the moderate amount of AOX in the effluent, which is lower than the amount of OX removed from the fibers. Since higher amounts of alkali do not improve the extraction effect further, the chemical structures which are decomposed by caustic soda represent only a smaller fraction of the halogenated compounds.

Table 2: Decrease of the OX content in three different kraft pulps with a mild alkaline treatment (1h, 60°C, 10% cons.), bleaching sequences not available

sample	NaOH (%)	initial OX (g/t)	OX extracted (g/t)	AOX generated (kg/t)
A	0,5	274	233	0,01
B	0,5	562	384	0,02
	1		376	0,02
	2		380	0,02
C	0,5	324	264	0,03

Postbleaching is another option to decrease the OX content. Pulp B, the pulp with the highest residual, had not only a high OX but also a brightness only in the mid eighties. It was treated with a small amount of ClO_2 and H_2O_2 in two additional bleaching stages. This increased the delignification and improved the brightness. From these data it can be concluded that a high OX can also be the result of incomplete delignification, for example in semibleached pulp and in addition an effect of poor washing. In consequence, really low OX levels can only be obtained with a change of the bleaching strategy.

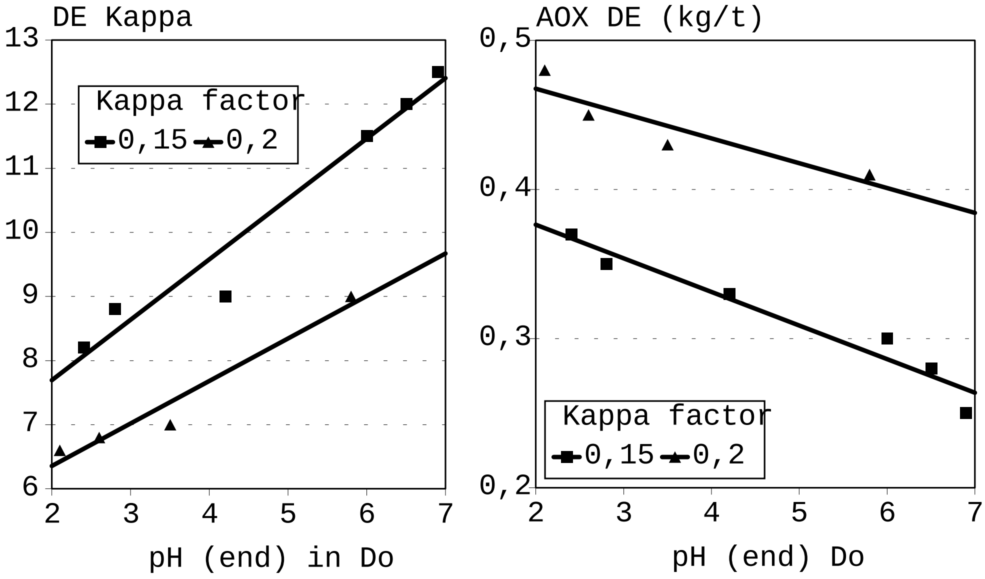
Table 3: Postbleaching of softwood kraft pulp with the stages DP, conditions: D: 0,3% act Cl, pH 5, 70°C, 2h, 10% cons; P: 0,2%H_2O_2, 0,3% NaOH, 70°C, 1,5h, 10% cons.

treatment	Kappa	OX (g/t)	brightness (%ISO)
untreated	1,8	562	84,9
D		423	88,2
P	<1	256	90,4

OX and delignification

ECF bleaching offers the best prerequisites for low OX values. With an oxygen stage in front, the lignin amounts are low. The same is valid for the demand for delignification chemicals. In ECF bleaching the workhorse is chlorine dioxide. The amount of AOX and OX generated during a D stage is depending not only on the amount of ClO_2 applied but in addition on the pH value during the treatment. The lower the pH value, the better the degradation of the lignin becomes. This effect is caused by the increasing in-situ formation of HOCl resp. chlorine during the delignification process with ClO_2. In consequence a lower pH in the D_0 stage yields also more AOX in the effluent [2,3]. Figure 1 illustrates this effect for the delignification of an oxygen delignified softwood kraft pulp with Kappa 20. In order to achive the best decrease of the lignin content, it is important to run the D_0 stage at low pH, however, at the same time this results in a higher level of AOX. Because of the limited effect on the lignin content, high pH conditions are not only ineffective but also expensive. Therefore it is necessary to run the D_0 stage at low pH and accept the resulting AOX formation.

Figure 1: Effect of pH in D_0 on delignification and AOX in the effluent, Kappa 20 softwood kraft pulp; D_0 at 60°C, 1h, 10% cons., E with 2,2% NaOH, 70°C, 1,5h, 10% cons.



The lower the residual lignin content and the input of ClO_2, the lower the AOX and OX formation should be. Thus the basis for a low OX level in a fully bleached pulp is a low Kappa number in pulping and the existence of an oxygen stage.

During the bleaching process the lignin residual is oxidized and extracted. After the first two stages, in conventional bleaching in the Cd and E stage, in ECF bleaching in the D_0 and the E stage, delignification is already nearly complete. The Kappa numbers after the Eop stage are typically well below 2 for Cd treated pulps and below 3 for D bleached grades. The final bleaching stages dominantly increase the brightness, the small residual of lignin is oxidized further into compounds with a lower molecular weight, which are in addition more hydrophilic. The same happens to the compounds which have been halogenated during the oxidation process. The halogenated residual is high in the begining of the bleaching process. The amount of residual OX decreases with ongoing oxidation of the lignin and with its extraction. Figure 2 shows the decrease of the OX content in a bleaching sequence for an oxygen delignified eucalyptus kraft pulp. The amount of OX remaining in the pulp is significantly lower compared to the results cited for softwood pulps above. This is mainly caused by the lower total demand for ClO_2 because of the lower Kappa number of the oxygen delignified hardwood pulps.

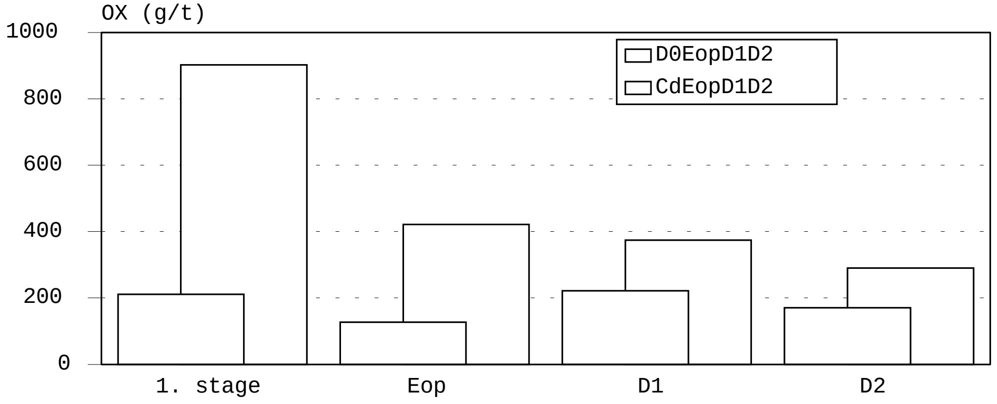


Figure 2: Decrease of the amount of halogenated compounds in eucalyptus kraft pulp during the bleaching process. Oxygen delignification to Kappa 11,8. Conventional bleaching with $CdEopD_1D_2$ (20% substitution in Cd) and ECF bleaching with $D_0EopD_1D_2$. Kappa factor 0,15, total amount of active Cl: 3,8%, final brightness >90 %ISO

The conventional bleaching conditions with chlorine and a ClO_2 substitution of 20% result in an initially very high amount of OX in the pulp. The first extraction stage already decreases the OX level significantly, the halogenated compounds are saponified and become water soluble as AOX. The final treatment stages D_1D_2 further oxidize the residual lignin and the halogenated compounds, thus lowering the content stepwise to about 300g of OX per ton of pulp. The application of ECF conditions result in a significantly smaller initial generation of OX. The Eop stage decreases the OX to a value well below 200g. However, the application of more ClO_2 in the final stages increase the OX again. The final value of 170g OX is not far away from the value achieved with conventional conditions.

Lower OX values in fully bleached pulp will be possible only with the application of less chlorine dioxide. One option to cut the ClO_2 demand is to replace the final D stage with a P stage. This modification was presented already during the ABTCP conference in 1995 [4]. A final P stage lowers the demand for ClO_2 in the D_1 stage. In consequence the OX already after the D_1 stage becomes lower, despite of the addition of ClO_2. Obviously the halogenation of the residual lignin is more than compensated by the simultaneous degradation. In addition the final P stage, run with a very small amount of H_2O_2 (0,2%), again extracts and destroys halogenated compounds. Figure 3 shows the result of the modification of the bleaching sequence with the substitution of the final D stage by a final P stage.

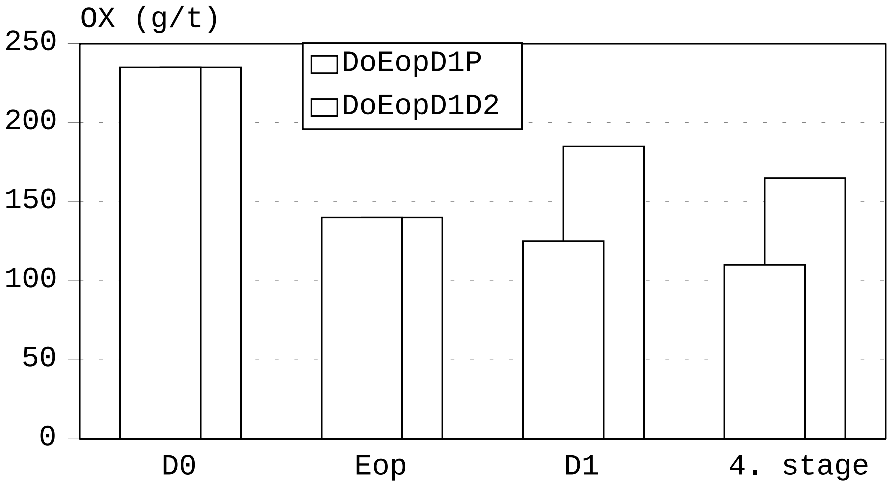


Figure 3: Effect of replacing the D_2 stage with a final P stage in an ECF sequence with the stages $D_0EopD_1D_2$, amount of ClO_2 as active Cl: 1,2% in D_1D_2, 0,3% with D_1P, final brightness >90 %ISO

The amount of chlorine dioxide applied in the first bleaching stage has an influence on the OX of the end-product. If the lignin is not oxidized thoroughly, the residual remains high. Thorough oxidation on the other hand generates a high residual. Therefore a compromise is required to decompose the lignin just enough to allow final bleaching with peroxide, without generating too much halogenated residual during the delignification process. On the other hand the second D stage also contributes to the OX, as it increases its level again. If the Kappa factor in the first D stage is very low, more chlorine dioxide is required in the second D stage. This would increase the OX values again.

Tab. 4: ECF bleaching with OD_0EopD_1P to 90%ISO brightness. Kappa factors in D_0: 0,2 and 0,1; 50°C, 1h; Eop at 80°C with 0,5 or 0,75% H_2O_2 and 1,5% NaOH, 1,5h; D_1 at 70°C,2h and P at 80°C, 2h; all stages at 10% cons.

act Cl in D_0 (%)	act Cl in D_1 (%)	total act Cl (%)	H_2O_2 in Eop + P (%)	final OX (g/t)
1,72	0,5	2,32	0,7	94
0,86	0,6	1,46	1,25	80
0,86	1	1,86	1	92

Table 4 shows the moderate effect of a low and normal Kappa factors in the D_0 stage on the final OX value. Because of the higher demand for ClO_2 in the second D stage the advantage of a low OX generation in the first stage with a low Kappa factor remains limited. It therefore makes sense to use in a first D stage amounts of ClO_2 which are high enough to decrease the Kappa number to a level below Kappa 4. In comparison to the standard sequence the OX levels are lower because of the increased effect of extraction and oxidation in the reinforced E stages. The OX in all experiments is below 100g/t.

Low OX with high intensity peroxide bleaching

The intensity of a peroxide stage can be increased with an increase of the temperature. However, because of the more agressive conditions, very high temperature and prolonged retention time can cause viscosity drops and losses in yield. This is due to the peeling reaction of the celulose in the presence of alkali and to decomposition reactions of hydrogen peroxide at very high temperature. Therefore any increase of the reaction temperature has to stay within a certain temperature range. This temperature range has been described earlier [5]. Above approximately 90°C to 95°C these side reactions start to become more pronounced. Therefore the temperature in the bleaching trials with a high input of hydrogen peroxide was kept at this level.

The initial approach was to keep the bleaching sequence, however, to change the input of chemicals. The sequence D_0EopD_1P was run with a very low amount of active chlorine in both D stages. The D_0 stage was run at 95°C in order to hydrolyze hexenuronic acids [6,7] and the input of hydrogen peroxide to the Eop stage and the final P stage was increased to compensate for the lower usage of ClO_2. Table 5 summarizes the results.

Table 5: Bleaching with D_0EopD_1P, oxygen del. to Kappa 9,8, D_0 at 95°C with factor 0,1; Eop with 0,75% H_2O_2; final P with 2,5% H_2O_2 at 90°C

D_0 act. Cl (%)	Eop Kappa	D1 act. Cl (%)	brightness (%ISO)	reversion (points)	OX (g/t)
1	5,6	0,25 0,5	89,9 90,1	- 8,1 - 7,5	54 ± 6 65 ± 3

The OX values are rather low, however, the aging properties of the pulp are not very good. The other alternative is to apply more chlorine dioxide but only in the first D stage. Final bleaching was made after the high intensity delignification with D0Eop directly with the P stage. Table 6 has the results of a set of experiments with this sequence D_0EopP. In order to learn about the limits for the demand of ClO_2 the variation for the Kappa factor was between 0,2 and 0,1. The peroxide charge to the Eop stage was increased to 0,75% H_2O_2 and a final P stage was conducted at 90°C with 2,5% H_2O_2.

Table 6: Bleaching with only one D stage in the sequence D_0EopP, Eop at 90°C, 0,75% H_2O_2, P with 2 to 5h at 90°C and 2,5% H_2O_2. Initial Kappa number 10,3 after O. Aging with 2h at 100% humidity and 100°C (Tappi T 260)

D_0 act Cl (%)	D_0 temp (°C)	Eop Kappa	brightness (%ISO)	reversion (points)	OX (g/t)
2,06	50	4,0	89,5	- 8,1	74 ± 12
1,55	50	4,6	89,9	- 7,4	71 ± 4
1,03	50	5,8	89,2	- 8,4	57 ± 4
1,03	**90**	5,0	89,3	- 7,3	53 ± 7

Despite of the high amount of H_2O_2 applied, it was impossible to reach the target brightness of 90 %ISO. It seems as if the lack of delignification is responsible for the inability to push the brightness ceiling above the 90 %ISO level. However, brightness was very close to the top level. It has to be noted that the stability of the brightness was not as good as with normal active chlorine amounts and more moderate conditions in the P stages. The harsh aging conditions of the Tappi test T 260 are normally responsible for a drop of the brightness by only 4 to 6 points.

Ozone reinforced D stages

The chemicals chlorine dioxide and ozone can be combined in one treatment stage. Because the application of ozone decreases the demand for active chlorine, it can be expected to achieve lower OX levels in bleaching sequences with this combination. Table 7 has the results of the application of O_3 and ClO_2 in a sequence with an oxygen stage in front.

Table 7: Bleaching of eucalyptus kraft pulp with moderate amounts of ClO_2 and O_3 and higher charges of H_2O_2 in final brightening. Pulp O_2 del. to Kappa 9; ozone charge 0,4%; aging with Tappi T 260

sequence	active Cl (%)	H_2O_2 (%)	brightness (%ISO)	reversion (Points)	OX (g/t)
Z/D_0EopD_1P	1,4 + 0,6	0,3 + 0,25	92,3	-5,4	39,4 ± 1,2
Z/D_0EopP	1,4	0,3 + 1	90,4	-4,9	24,3 ± 0,5

The application of ozone results in a very low final OX value. The level is very low, even if a second stage with chlorine dioxide is applied. The results imply the assumption that the treatment with ozone destructs the residual lignin into compounds with a very high solubility.

The level of the OX can also be low, if the treatments with chlorine dioxide and ozone are separated from each other. The sequence OD_0EopZP allows a low input of chlorine dioxide because the bleaching response of the pulp to the final bleaching with hydrogen peroxide is accelerated with ozone. However, such a sequence is technically difficult because of the different temperature profiles of the peroxide stages and the sandwiched ozone stage. Table 8 has data for bleaching tests made with the sequence OD_0EopZP. The level of the pH in the chlorine dioxide stage is more affected by the pH in the D stage than by the amount of active chlorine applied.

Table 8: Bleaching with low levels of active chlorine and the sequence OD_0EopZP

D_0 active Cl (%)	D_0 pH end	O_3 (%)	H_2O_2 (Eop + P) (%)	brightness (%ISO)	OX (g/t)
0,9	3,6	0,4	0,5 + 1	90,2	18 ± 6
0,9	2,9	0,4	0,5 + 1	90,5	35 ± 6
1,4	3,5	0,4	0,5 + 1	90,3	40 ± 3

A comparison of the OX results from the experiments in table 7 and 8 allows the conclusion, that the OX is influenced by the number of D stages and the pH-values in the D stage and by the intensity of the peroxide treatment. Againg the small amount of ozone has a significant effect on the residual of OX and on its removability. In cases where a very low OX is the target, the combination of the application of O_3 and ClO_2, either in one stage or in two separated stages is best guaranty to achieve low OX and at the same time a high brightness.

7. Summary

- During bleaching with halogenated compounds not only AOX but also OX is generated.
- These compounds are partially degraded during the bleaching process.
- The residual of halogenated compounds (OX) in conventionally bleached oxygen predelignified eucalyptus pulps is in the range of 250g to 300g/t.
- Conventional ECF bleaching decreases this level to values between 150g and 200g.
- The sequence D_0EopD_1P can be modified to reach even lower low values between 50g and 100g/t by applying less active chlorine and higher peroxide charges.
- The modification of the delignification conditions with a combination of ozone and chlorine dioxide results in extremely low OX values. The range well below 50g is easily reached.
- These pulps do have a good brightness stability, their OX values are nearly identical with those of TCF pulp.

HOT PEROXIDE BLEACHING

Abstract

Recently the number of reports on high temperature peroxide bleaching has increased sharply. While for years the best temperature level for peroxide bleaching was believed to be between 40°C and 70°C, now the temperatures recommended reach levels above the boiling point of water. In papers published recently, the temperature had already reached 110°C and an end of this increase seems not to be reached yet.

It seems to be necessary to compare the results of peroxide bleaching at different temperature levels, to consider the effects of retention time and caustic soda activation on the performance of the bleaching process and to balance this with yield and COD load. In addition the amounts of hydrogen peroxide needed to reach a given brightness target, need to be compared at different temperature.

The paper will compare the effects of temperature:
- on delignification with hydrogen peroxide,
- on the caustic soda demand,
- on the effluent COD load,
- on pulp viscosity and
- on pulp yield.

The results of a hydrogen peroxide treatment at high temperature in an ECF sequence will be compared to the effects of "conventional“ peroxide bleaching of eucalyptus kraft pulp.

Basics of hydrogen peroxide bleaching

For the development of brightness hydrogen peroxide needs alkaline bleaching conditions. The perhydroxyl anion is a strong nucleophile and cleaves side chains in the residual lignin, thus destructing chromophores. Lignin degradation takes place in addition via radicals resulting from the decomposition of hydrogen peroxide. The disadvantage of these radicals is their inselectivity, the side reactions are cellulose oxidation and subsequent cleavage of the polymer chains. Basically, all reactions, which produce peroxide decomposition are not favorable. In consequence, careful removal of transition metals from the pulp is a prerequisite of hydrogen peroxide bleaching. Acidic washing of the pulp, or the treatment with chelants is the standard procedure for successful peroxide bleaching.

Peroxide bleaching is activated with alkali. At higher pH the equilibrium of equation (1), is pushed to the right side to the formation of the reactive compound, the perhydroxyl anion:

(1) $H_2O_2 + OH^- \longleftrightarrow H_2O + \mathbf{HOO^-}$

Higher alkalinity therefore accelerates the consumption of hydrogen peroxide. On the other hand, at higher alkalinity more hydrogen peroxide is consumed in a side reaction. The disproportionation to water and oxygen is catalysed with alkali (equ. 2):

(2) $HOO^- + H_2O_2 \rightarrow H_2O + OH^- + \mathbf{O_2}$

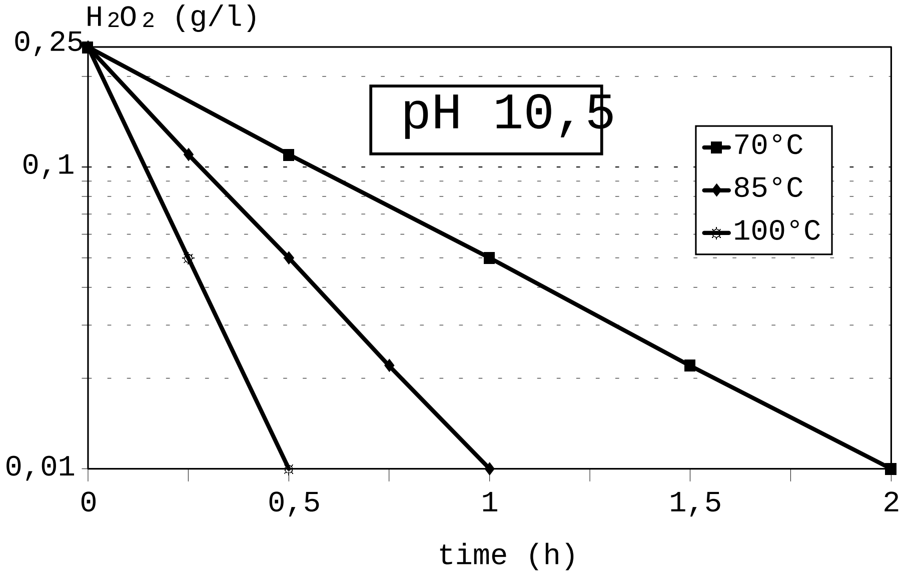


Figure 1: Decomposition of hydrogen peroxide under buffered conditions at pH 10,5 at different temperature levels in the presence of 0,1 g/l $MgSO_4$

Figure 1 illustrates the decomposition of hydrogen peroxide in demineralized water in the absense of pulp. Within a rather short time at high temperature the side reactions consume the added amount of 0,25g/l H_2O_2, (which would be equivalent to a charge of 2,5% on pulp at 10% consistency). In presence of pulp this decomposition is less pronounced, however the reaction still takes place.

The reaction of hydrogen peroxide in a bleaching process will certainly be accelerated with higher charges of alkali, because this increases the amount of perhydroxyl anions. However, the side reaction (2) will also become more pronounced and take place at a higher rate. In consequence, a higher turnover of peroxide might not reflect an advantage for the bleaching process. In addition, high alkali charges have an increasing extraction effect. Hemicelluloses and oxidized cellulose chains become water soluble. The advantage of this extraction is a higher viscosity of the remaining pulp, the disadvantage on the other hand is a simultaneous negative effect on the effluent load and the yield of the bleaching process.

Higher temperature also accelerates the thermal decomposition of hydrogen peroxide into hydroxy radicals according to equ. 3:

(3) $H_2O_2 \rightarrow \mathbf{2{\bullet}OH} \rightarrow \rightarrow$ decomposition products

Thus, very high temperature might accelerate the consumption of hydrogen peroxide, whether this results in an advantage for the brightening process, remains to be demonstrated in a valid comparison. Inevitably, above a certain temperature the decomposition reaction and other side reactions become dominant and a higher turnover of the peroxide will not yield a better bleaching effect.

Laboratory scale application of hydrogen peroxide

Basically it is very easy to conduct hydrogen peroxide bleaching on laboratory scale. Preheated pulp is mixed with diluted solutions of the chemicals needed, typically caustic soda, hydrogen peroxide and epsom salt. The reaction is conducted in plastic bags in thermostated water baths. It is easy to achieve efficient mixing at the required temperature level and to gain results which are compareable to large scale. Only if the temperature level should be above 100°C, efficient mixing and maintaining the temperature becomes difficult. On mill scale steam would be added to the pulp and the chemicals would be mixed with the pulp within seconds after steam addition. Therefore, the bleaching reaction starts immediately. On laboratory scale it is very difficult to run trials with such an accuracy. Especially if bleaching is conducted at temperature above 100°C, mixing is made at lower temperature and the pulp is heated without much agitation in a bath to the final temperature. In consequence, the reaction is not conducted at e. g. 110°C for 60 minutes but at 90°C to 110°C for maybe 30 minutes and only 30 minutes at the top temperature. This difference can have an important impact on the bleaching result.

Slow heating to temperature results in an inhomogenious reaction:
- the pulp inside the reactor reaches the target temperature with delay,
- the consumption of chemicals is retarded,
- the fibers outside react faster and to a higher extent,
- the consumption of chemicals is accelerated, as are side reactions.

Table 1: Effect of rapid or slow heating to the target temperature on brightness, peroxide consumption and viscosity in final peroxide bleaching. Sequence D_0EopD_1P, constant addition of chemicals: 2% H_2O_2, 1,2% NaOH, 0,1% $MgSO_4$, total time 1 h

temperature (°C)		time to target temperature	H_2O_2 residual	brightness	viscosity
begin	target	(min)	(%)	(% ISO)	(mPa.s)
90	90	preheated	0,13	89,3	12,0
20	90	15	0,76	89,7	13,8
110	110	preheated	0,03	88,8	11,0
20	110	20	0,18	89,6	11,1

Table 1 compares laboratory bleaching at 90 °C with pulp preheated to the temperature and the bleaching solution added at temperature and a pulp with chemicals added at room temperature and heated to the target temperature within 15 minutes, respectively 20 minutes. Slow heating to temperature gives lower peroxide consumption, better brightness and higher viscosity. However, the reality on mill scale would be a rapid temperature increase in the steam mixer. In consequence, the selection of the best conditions for the practice would not be the recommendation to increase the temperature to 110°C, but to stay at 90°C and start possibly trials with lower temperature and longer reaction time.

In order to avoid these differences between laboratory scale and practice, in the Degussa laboratory all bleaching trials at very high temperature are conducted in a stainless steel high shear mixer. The pulp is preheated to temperature and the bleaching chemicals are injected and immediately mixed.

Hot hydrogen peroxide in delignification

The addition of hydrogen peroxide to oxygen stages yields a higher delignification effect. However, since transition metals decompose hydrogen peroxide, higher addition levels of H_2O_2 require a pretreatment with an acidic washing stage. Since such a washing stage is difficult to implement into the countercurrent alkaline washing water flow from a normal oxygen stage into black liquor recovery, the addition of hydrogen peroxide normally is restricted to the application in a second oxygen stage. A typical sequence for a high intensity combined oxygen/hydrogen peroxide treatment therefore would be $OA_{(Q)}Op$. As an alternative a hot hydrogen peroxide/oxygen delignification can follow an acidic washing stage directly after brown stock washing. However, the laboratory results described in literature are difficult to translate into practice, because the experiments were carried out in plastic containers inside of autoclaves [7, 8], or mixing was conducted at room temperature [9]. In consequence the bleaching temperature inside the plastic containers is reached with a significant time delay. Without any doubt the consequences for peroxide consumption and the homogeneity of the pulp are similar to the effects described in table 1.

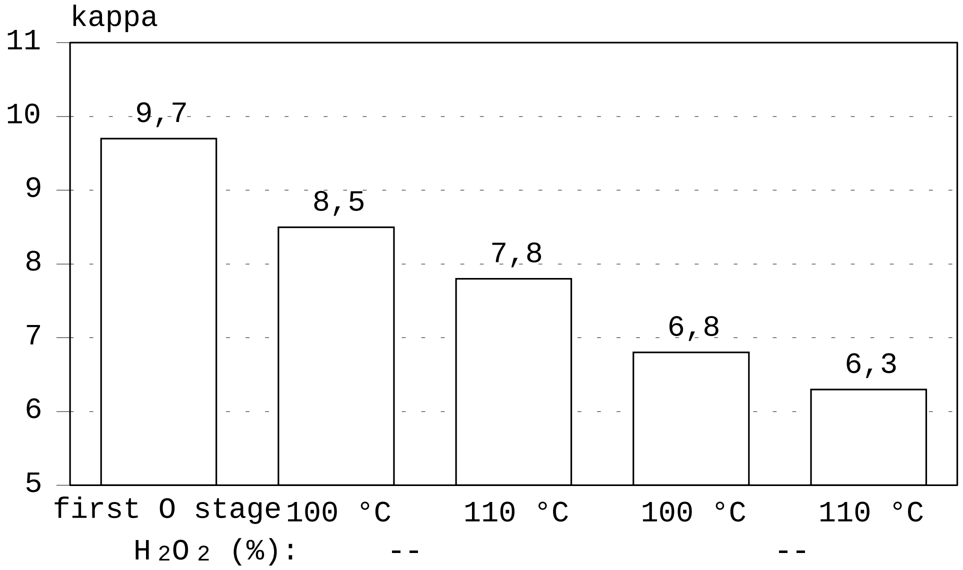


Figure 2: Delignification of eucalyptus kraft pulp with a second oxygen treatment with and without hydrogen peroxide addition. Effect of temperature and hydrogen peroxide addition on Kappa number.

In our laboratory the pulp is preheated inside a high-shear mixer to the target temperature and all the chemicals are injected simultaneously into the mixer. Figure 2 shows the effects on delignification of a high intensity second oxygen stage with and without hydrogen peroxide addition. The pulp was pretreated with EDTA under under acidic conditions to avoid decomposition reactions with transition metals.

If delignification is the most important target, the positive effect of the addition of hydrogen peroxide will certainly be appreciated. The addition of 2% of hydrogen peroxide improves the delignification by nearly two additional kappa units. However, there are some side effects, which are shown in figure 3. Despite the absence of metals, pulp degradation takes place. The moderate drop of the viscosity with the second oxygen treatment is intensified with the addition of peroxide. Very obviously side reactions, like the thermal cleavage of peroxide into hydroxyl radicals, result in an attack on the cellulose chains. An attack on the cellulose as a result of metal induced decomposition is very unlikely, because both trials had a residual of hydrogen peroxide. The degradation of the cellulose becomes also visible, if the effluent loads are compared. The COD values increase with rising temperature, and on top of this with the peroxide charge. If the kappa number drop is compared with the COD increase, the significant increase of the COD load can be attributed to an increase of the degradation of cellulose.

In consequence the advantage of the better delignification has the negative price tag of inferior yield and lower viscosity, therefore on mill scale the applicability will be limited. The lower viscosity has been attributed to the use of stainless steel equipement and the possibility of wall effects. However, similar results with a steep drop of the viscosity have been described in experiments using teflon lined containers [23]. Therefore it seems to be rather unlikely that a contamination with metal ions is caused by the stainless steel of the reactor.

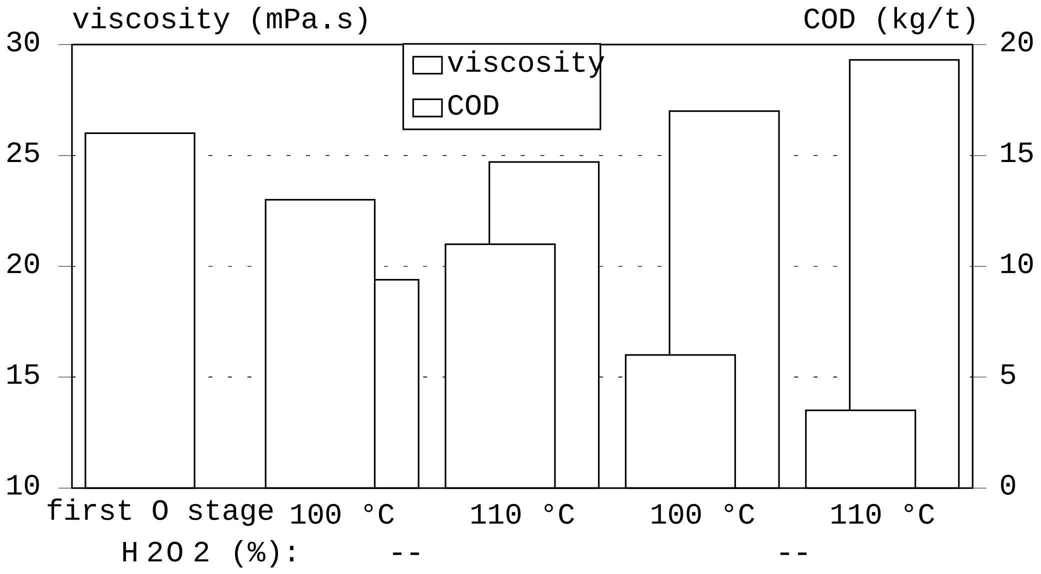


Figure 3: Delignification of eucalyptus kraft pulp with a second oxygen treatment with and without hydrogen peroxide addition. Effect of temperature and hydrogen peroxide addition on viscosity and effluent load.

Hot extraction stages with hydrogen peroxide

In ECF bleaching hydrogen peroxide is applied in the first and second extraction stage to increase lignin removal and brightness. The almost classical approach is the improvement of the effect of the first extraction stage with hydrogen peroxide and oxygen. The typical conditions of a standard E stage remain more or less unchanged. The temperature in an Eop stage thus is normally between 75°C and 90°C.

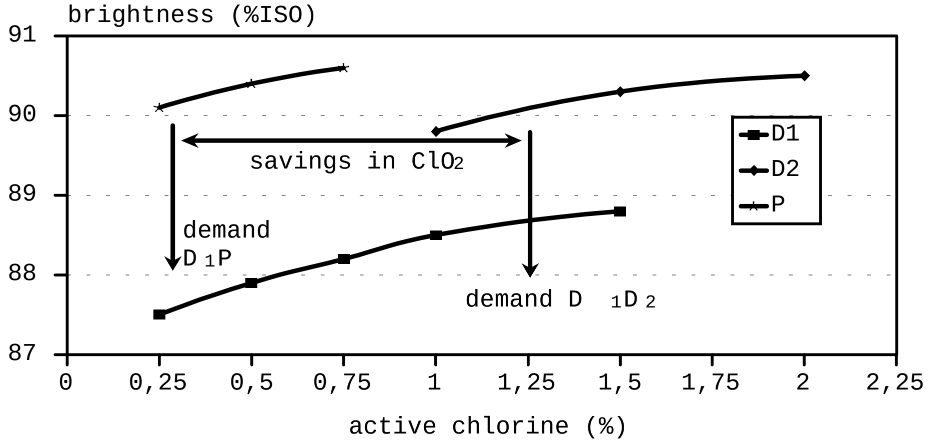


Figure 4: Substitution of chlorine dioxide in ECF bleaching of eucalyptus kraft pulp with peroxide addition to the D_2 stage. Sequences $OD_0EopD_1D_2$ respectively OD_0EopD_1P. D_2 and P stage at 80°C, peroxide charge constant 0,25% H_2O_2.

In the second E stage hydrogen peroxide can be used to lower the chlorine dioxide demand in the D_1 stage. An additional side effect is the possibility to eliminate the D_2 stage. The temperature for this H_2O_2 application is normally also within the range of 70°C to 90°C. This does make a lot of sense, because for a countercurrent water flow the temperature profile in a bleaching sequence should be rather steady. It is certainly easy to increase the pulp temperature with steam, but it requires a lot of water to cool hot pulp. A high water demand seems to be a contradiction to the philosophy of narrow circuits and closed loops with minimum effluent. In consequence, wide swings in the temperature from stage to stage cause problems and would only make sense, if the advantages would be very pronounced.

In ECF sequences hydrogen peroxide is successfully applied to cut the demand for chlorine dioxide in the final bleaching stages. There is a pronounced advantage in the addition of hydrogen peroxide, because only a small amount of peroxide is needed in a final P stage to achieve a significant brightness increase. At the same time this small amount of H_2O_2 substitutes a relative high amount of chlorine dioxide. The replacement ratio for chlorine dioxide in a D_1D_2 sequence reaches levels of 1:6 and 1:10 and more for the D_1P alternative. If 1 kg H_2O_2 substitutes 10 kg ClO_2 (as active chlorine), the addition of hydrogen peroxide becomes very economical [1]. This replacement is achieved at the normal temperature level of bleaching stages, typically between 75°C and 80°C. Such a replacement ratio is demonstrated in figure 4. The kappa factor for the active chlorine demand in the stages D_1 and D_2 is normally 0,5, it is lowered to 0,1 through the addition of hydrogen peroxide.

Running the Eop and the P stages at very high temperature allows even higher replacement rates and could open ECF technology also to mills which do not have an oxygen stage and in addition a limited chlorine dioxide capacity. Table 2 summarizes the modifications of the sequence, the lower kappa factors in the D stages, the increased temperature in Eop and P and the higher peroxide charges. The intensified conditions in the E stages cut the chlorine dioxide demand half. However, the pulp quality suffers. The bleaching results are listed in table 3. Viscosity is significantly lower. The lower chlorine dioxide charge to the D_0 stage produces less COD in this stage, but in the subsequent stages the COD load explodes, because of severe cellulose degradation and because this degraded cellulose is extracted easily at the very high temperature.

Table 2: Modification of an ECF bleaching sequence (eucalyptus kraft pulp, kappa 16,8) with a final P stage at moderate or high temperature and a hot Eop stage.

sequence	kappa factor		addition of H_2O_2 (%)		temperature (°C)	
	D_0	D_1	Eop	P	Eop	P
$D_0EopD_1D_2$	0,15	0,5	0,3		80	-
D_0EopD_1P	0,15	0,1	0,3	0,15	80	80
D_0EopD_1P (**hot**)	0,1	0,1	0,5	0,5	100	110

Table 3: Comparison of viscosity and COD at moderate or high temperature conditions in Eop and P stages

sequence	brightness (%ISO)	viscosity (mPa.s)	effluent COD (kg/t)				
			1.	2.	3.	4.stage	Σ
$D_0EopD_1D_2$	90,0	25,6	19	20	4	2	42
D_0EopD_1P	90,2	24,7	19	20	4	4	43
D_0EopD_1P (**hot**)	88,6	18,7	10	24	5	15	54

A higher COD value for the effluent indicates a lower yield in bleaching. It might be possible to lower the COD level, if lower caustic soda charges are applied. At very high temperature less caustic soda could be required for the activation of the bleaching reaction. On the other hand, the necessity to produce the perhydroxyl anion as the reactive intermediate sets a narrow limit for lower caustic soda charges or a lower alkalinity. In bleaching processes for mechanical pulp a partial substitution of caustic soda with sodium carbonate (soda ash) is possible, however, sodium bicarbonate does not produce enough alkalinity to activate the consumption of H_2O_2 [2]. If the caustic soda charge is too low, peroxide consumption remains poor. In Figures 5 to 8 a comparison of the effects of different caustic soda charges is made at different temperature levels in the final P stage. Prebleaching of a softwood kraft pulp was conducted with the sequence OD_0EopD_1 to a brightness level of 83,5 %ISO. Standard kappa factors and conditions were used in D_0 (0,2; calc. on O kappa) and D_1 (0,7; calc. on Eop kappa), the Eop stage kappa was 3,8. As expected the high peroxide charge was not consumed at low temperature and at low alkalinity. Figure 5 shows the increase of the peroxide consumption with increasing temperature. Even at the low alkali charge peroxide is consumed, despite a nearly neutral pH level.

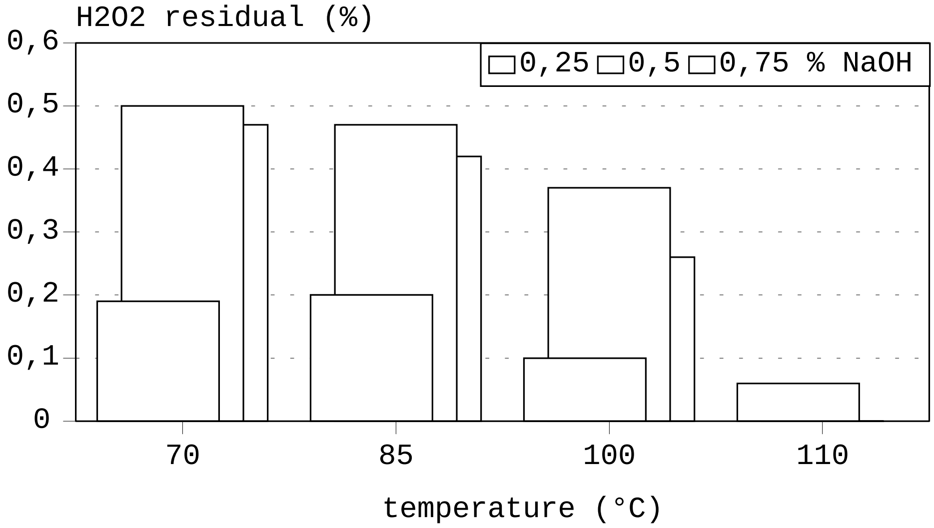


Figure 5: Increase of peroxide consumption in a final P stage with increasing temperature and alkali charge. (constant: 0,7% H_2O_2, 0,1% $MgSO_4$, 2h at 70°C, 1h all other temp. levels)

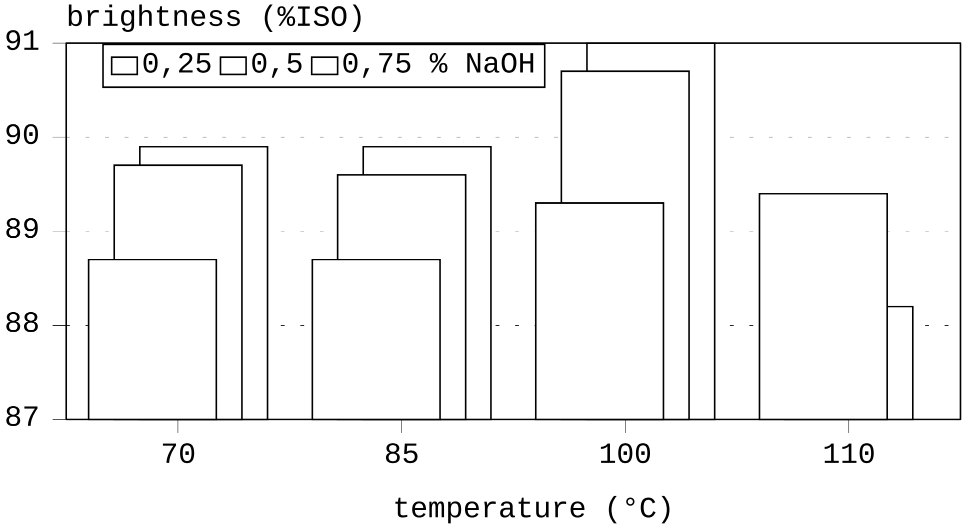


Figure 6: Increase of brightness with temperature and caustic soda charge, (constant: 0,7% H_2O_2, 0,1% $MgSO_4$, 2h at 70°C, 1h all other temp. levels)

The better consumption at higher temperature has a positive effect on the brightness increase (fig. 6). There is a gain of about one brightness point with the increase of the temperature from 85°C to 100°C. Only at very high temperature this benefit vanishes. Both, increasing alkalinity and higher temperature yield a higher brightness. At constant alkalinity the increase of the temperature accelerates the brightening reaction. The first conclusion therefore would be the recommendation of a high temperature and a high alkalinity for the process.

However, before a final conclusion is drawn, in addition other parameters have to be checked. One of these is the effluent load. As expected, with increasing alkali charge the extraction of organic compounds increases. In addition, higher temperature also increases the effect of the extraction. This effect is well known and used to improve the extraction effect, for example in the production of dissolving pulp. On the other hand, prolonged reaction at a high alkali level and temperature results in yield losses due to the peeling reaction on the cellulose chains. The additional point of brightness achieved at 100 °C carries a price tag: a slightly higher COD load. These effects are compared in figure 7.

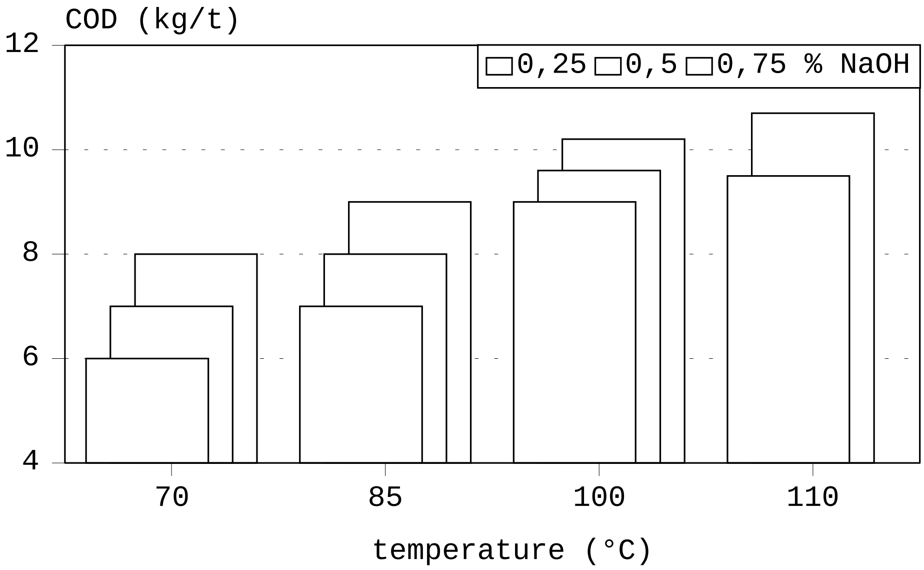


Figure 7: Effect of increasing caustic soda charges and temperature on COD

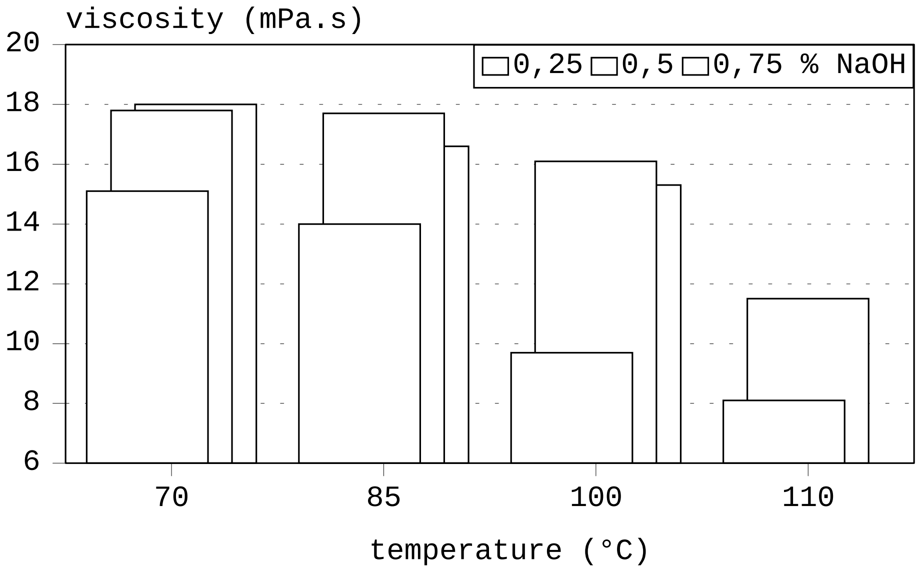


Figure 8: Effect of increasing caustic soda charges and temperature on viscosity

The higher intensity of the reaction at elevated temperature also has an effect on the viscosity of the pulp. Viscosity is highest at high alkalinity at moderate temperature (fig. 8). At low alkalinity the residual of hydrogen peroxide is higher and the slow decomposition of H_2O_2 yields a degradation of the pulp. At very high temperature the decomposition of hydrogen peroxide becomes pronounced and clearly visible as a severe drop of the viscosity. At higher caustic soda levels, the extraction effect eliminates the degraded compounds and the viscosity looks better. However, this higher viscosity has to be paid dearly, it means a higher COD load, which is a synonym for a lower yield.

In consequence, there is neither a wide range for the alkalinity, nor for the temperature increase. It is possible to push the bleaching reaction hard and to increase the turnover of hydrogen peroxide with higher temperature. However, the side effects seem to be inevitable: a lower viscosity and a lower yield. If this is acceptable, high temperature bleaching with hydrogen peroxide is a possibility to lift the brightness ceiling and to lower the requirement for chlorine dioxide in ECF bleaching. The reported conditions for the practical application of a "hot and pressurized“ P stage [3] are more realistic, a temperature level of only 80°C does not sacrify the pulp quality. However, these conditions seem to be rather normal, the label "hot“ is an exaggeration.

- Moderate peroxide charges in a final P stage do not need a high reaction temperature -
- High peroxide charges need high temperature for consumption, a steep brightness increase results -
- however, brightness increase is accompanied by a steep drop of the viscosity and a higher COD load.

COD and yield

During bleaching organic compounds are solubilized. Basically any bleaching agent is applied only to initiate oxidation thus increasing the solubility of the residual lignin. Simultaneously cellulose and hemicelluloses are dissolved in an undesired side reaction. In addition extractives become water soluble. The amount of dissolved organic material in the effluent can be correlated to a decrease of the yield. Measuring yield of pulping and bleaching is very complicated on mill scale and not easy on laboratory scale either. Several experiments have to be made in parallel in order to guarantee the reproducability and avoid differences in the chemicals demand because of drying steps for consistency analysis. Thus a precise gravimetrical procedure is difficult.

The organic compounds in the typical effluent of a pulp mill are nearly totally oxidized with potassium dichromate under the conditions of the COD test [16]. This allows the calculation of the oxygen demand for a known compound. It allows as well the calculation of the amount of organic material in an effluent, if the structure ($C_xH_yO_z$) of the organic compound is known. In consequence the analysis of the COD of a bleaching stage effluent can be a useful tool to evaluate the yield loss in bleaching. The prerequisites are some knowledge on the composition of the cellulose and lignin derivatives in the effluent.

For cellulose the formula $(C_{12}\ H_{20}\ O_{10})_n$ was used for the calculation. For 1 kg of cellulose about 1.185 kg of oxygen are required for complete oxidation. Thus 1 kg of COD is equivalent to 840 g of cellulose. Any cleavage of the cellulose chain in the bleaching process produces molecules with a lower molecular weight and a better solubility. The oxidation of the aldehyde group to a carbohydrate acid (uronic acid) additionally increases the solubility. The number of oxygen atoms needed to yield a better solubility is rather small. Therefore for a good estimate of the yield loss of carbohydrates in bleaching, the formula COD to cellulose = 1:1 can be applied. The oxidation of 10 kg of dissolved cellulose (per ton of pulp) in an effluent requires between 10 kg and 11 kg of oxygen, respectively is equivalent to a loss of 1% in yield. This ratio would apply for example for the products set free from cellulose by the peeling reaction at high temperature and high alkalinity. Severe oxidation of the cellulose would result in a lower ratio, i. e. less than 10 kg of oxygen would be needed in the COD test to oxidize 10 kg of dissolved cellulose.

The calculation for lignin is a bit more complicated. The residual of lignin is continuously modified and oxidized during the bleaching process. In consequence, the amount of oxygen in the formula is increasing with ongoing delignification. Kraft lignin has a chemical composition of approximately $(C_9\ H_{9,7}\ O_{3,3})_n$ [17]. This would result in an oxygen demand of 1.850 kg per kg lignin. Therefore 1 kg of COD is equivalent to 540 g of kraft lignin and the oxidation of 1 kg lignin would require up to 1,85 kg COD. An estimate of the increase of the oxygen content of the lignin can be calculated from the typical amounts of residual lignin and the amount of oxygen added with the bleaching agents.

It does certainly not help to just use OXE units, because the calculation with OXE [18] does neither consider decomposition reactions of the bleaching chemicals, nor the incomplete consumption of chemicals. Oxygen is always applied in excess. Ozone does not react with all available electrons, in the absence of hydrogen peroxide, the primarily formed ozonids are not oxidized completely, basically only four of the six oxidation equivalents do react with the pulp [19]. Thus any calculation has to be based on an estimation. However, figures for the composition of kraft lignin after a CE treatment are available [20]. In the begining of a bleaching sequence the molecular weight of the lignin extracted is rather high. In the final bleaching stages a more thorougly oxidized lignin is produced. Very likely the oxygen content of the residual lignin is increased from the low level in kraft lignin to about $(C_9\ H_{9,7}\ O_5)_n$ and may reach even higher levels in final bleaching. In consequence the demand for oxygen (as COD) becomes smaller and the ratio for COD to lignin will decrease during bleaching from the ratio 1: 1,8 (1 kg lignin needs 1,8 kg oxygen) to a ratio as low as 1:1.

Oxidized extractives, lignans and tannins are also present in the effluent. Their amount can be significant, especially with hardwood pulps [21]. However, extractives or related compounds are chemically rather close relatives to lignin and can be be treated in the calculation similarly.

Thus 10 kg to 11 kg COD/t pulp as dissolved cellulose and about 10 kg to 15 kg COD/t pulp as dissolved oxidized lignin are equivalent to about 1% loss in yield (10 kg/t). To evaluate the yield of a bleaching process this formula can be used for a rough calculation:

about 11 kg COD/t pulp are equivalent to a loss of 1% in yield.

A severe oxidation of either cellulose or lignin will shift the **COD to yield ratio to a level below 10 to 1**.

This calculation allows to compare the results of conventional conditions and more drastic conditions in peroxide bleaching. Hot (PO) conditions produce significantly more COD, this was shown in paragraphs 4 and 5 and was previously demonstrated [13] but not discussed.

For the ECF sequences in table 3 the difference of the COD load between the normal and hot sequence was about 11 kg to 12 kg. This corresponds to a yield loss of approximately 1%. The implementation of such a bleaching stage thus has a significant impact on the effluent treatment cost and certainly on the overall production costs. With a pulp price of 500 US$/t a yield loss of 1% is equivalent to a loss in production valid about 5 US$ for each ton of pulp. A pulp mill of average size running with such a sequence would easily every year loose pulp equivalent to a value of more than a million $US and would have to bear on top of this the costs for a higher steam demand and more effluent to treat. In consequence the potential savings in the costs for chemicals have to be compared to possible losses in yield. In the above case a replacement of the final D stage with a final P stage at moderate conditions is significantly more advantagous, it saves chemicals without sacificing yield.

Conclusions

- ✹ Delignification is improved with high peroxide charges at high temperature at the cost of a lower yield.
- ✹ In ECF bleaching moderate conditions in a hydrogen peroxide stage allow a substitution of chlorine dioxide and a cost decrease.
- ✹ COD can be used to calulate the yield loss in a bleaching stage.

Experimental

Peroxide and chlorine dioxide stages were run in sealed plastic bags at 10% consistency with a variation of time and temperature. All pulp samples were preheated (unless described differently) to the bleaching temperature and all the chemicals were added at once and mixed thoroughly with the pulp.
Pressurized peroxide stages resp. Eop stages were conducted in a laboratory scale stainless steel high shear mixer [22] at 10% consistency with variation of time and temperature, typically with an oxygen pressure of 0,3 MPa.
Brightness, etc. was measured according to the TAPPI standards. COD was determined according to the Zellcheming Merkblatt X/2/76. For the description of the bleaching stages the CPPA rules were applied.

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