# _Towards Effluent-Free TCF-Bleaching of Eucalyptus Prehydrolysis Kraft Pulp_

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# ABSTRACT:

Based on Lenzing's experience in new bleaching technologies, TCF bleaching of eucalyptus prehydrolysis kraft pulps for the production of dissolving grades with high reactivity, defined intrinsic viscosity and high alpha-cellulose has been developed.

Prebleaching conditions have shown to be of crucial importance for the overall selectivity, therefore main emphasis was directed towards optimization of the prebleaching stages. Evaluation of laboratory experiments resulted in close correlations between the conditions of TCF-bleaching and important quality parameters, such as alpha-cellulose content, intrinsic viscosity and brightness, which is a prerequisite for the production of dissolving grades with defined and constant quality.

In a set of experiments bleaching stages with different amounts of fresh water addition to a closed cycle have been simulated. The effect of carry-overs of different origin on the overall bleaching efficiency and selectivity will be described in detail.

# 1. INTRODUCTION:

The development and application of new bleaching technologies has a long tradition in Lenzing. After extensive investigations the sequence was changed from C-E-H-H to PE-H-P in 1979 for the production of beech sulfite dissolving pulp. Five years later a medium consistency oxygen bleaching stage was installed to reduce a significant amout of hydrogen peroxide in the first delignifying step. Due to the Environmental Authority's demand for the total elimination of AOX emissions research work had to be started in order to find a way replacing hypochlorite by a non-chlorine bleaching step. Ozone bleaching turned out to be the best non-chlorine alternative to hypochlorite bleaching. The development of the medium consistency ozone bleaching technology was carried out successfully in a big pilot scale unit (100 t/d) after a very short period of lab experiments (1). In the meantime TCF-bleaching including medium consistency ozone delignification is in full scale operation for more than one and a half years. Since the first presentation of Lenzing's new medium consistency ozone bleaching technology 1991 at the *Raleigh Workshop on Emerging Pulping and Chlorine-Free Bleaching Technologies* the development of ozone delignification as a part of TCF and ECF sequences has been very rapid. Eight pulp mills will be using ozone in full scale operation by end of this year.

However a lot of challenge remains in developing fairly selective TCF-bleaching sequences. Cellulose degradation takes place in any ozone containing bleaching sequence which is reflected in a substantial decrease of intrinsic viscosity. As any other non-chlorine containing sequences the application of ozone on high alpha-cellulose dissolving pulps requires a profound investigation of each bleaching stage. Because of the low hemicellulose content of these pulps oxidants severely attack the cellulose molecules during bleaching thus reducing viscosity and alpha-cellulose content to unacceptably low levels.

Dissolving pulps containing more than 94% alpha-cellulose are predominantly produced by the prehydrolysis kraft process [PHK] (figure 1). This cooking process (PHK) has many advantages compared to the common acid sulfite process, such as low sensitivity to wood species, moderate waste water pollution and superior product characteristics. Unfortunately bleachability is rather poor and therefore bleaching of prehydrolysis kraft pulps is still carried out conventionally. Despite the dramatic decrease in world's dissolving woodpulp production within the last four years (from 4,2 to 3,5 Mio t) there are clear indications that there will be an increasing demand of high alpha-cellulose pulps in the future.

Figure 1: Relationship between alpha-cellulose and intrinsic viscosity of dissolving
pulps. Single points represent analyzed values of the most important market
pulps available.
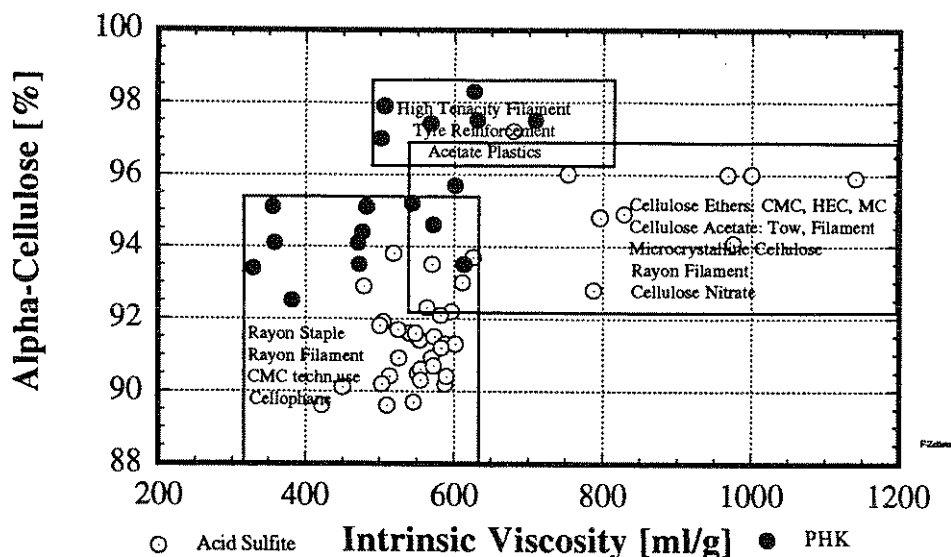


Also for these highly purified pulps TCF-bleaching will become a reality. Based on Lenzing´s experience in new bleaching concepts, TCF bleaching of eucalyptus prehydrolysis kraft pulps containing more than 96% alpha cellulose has been developed. Main emphasis has been directed towards the development of the prebleaching stages and measures to control pulp viscosity. By optimization of reaction conditions in the final bleaching sequence (Z-P) very promising product quality has been obtained.

In this study the performance of each single bleaching stage as well as the dependency within the stages was investigated. Moreover, the effect of carry-overs of different origin on overall bleaching efficiency and selectivity was examined.

## 2. EXPERIMENTAL

### Brownstock Samples

Samples have been supplied by VAI (pilot plant production) and Riocell (mill scale production). The samples from VAI were produced from eucalptus urograndis according to a new prehydrolysis displacement process (Visbatch). Prehydrolysis and cooking in the Riocell mill are performed in a continuous Kamyr digester. Wood species were both a blend of eucalyptus grandis with acacia and pure acacia. The acacia pulp was oxygen prebleached. Typical pulp properties are outlined in table 1.

Table 1: Characterization of unbleached pulps:

| ORIGIN | WOOD | Kappa Number | Intrinsic Viscosity ml/g | Alpha Cellulose % |
|---|---|---|---|---|
| VAI | E. urograndis | 8 - 12 | 1130 - 1250 | 96,0 - 97,0 |
| RIOCELL | E. grand.+acacia | 8,3 | 1243 | 96,0 |
| RIOCELL | acacia . | 3,1 | 934 | 95,2 |

## Oxygen Bleaching:

A MC-mixer/reactor was filled with a pulp suspension containing 200-250 g of dry pulp. The reactor was closed and evacuated before the prepared bleaching chemicals were added to the pulp suspension by means of a sluice and consistency was set to 10%. The oxygen gas was then introduced until the desired pressure was reached. The pulp suspension was heated to the preset reaction temperature by means of an indirect heating system. Only a short mixing time at fluidization conditions was required. Temperature and pressure were kept constant throughout the total bleaching reaction.

## Medium Consistency Ozone Bleaching:

The same mixer/reactor as described above was used. The reactor was filled with an acidified (pH 2) pulp suspension to leave a defined free gas volume. The temperature was set to 50°C. Once the reactor has been evacuated, compressed gas containing ozone was introduced until the desired pressure was reached. The specific amount of ozone was controlled by varying pressure and ozone concentration. Mixing time was 5 to 10 sec at fluidizing conditions. After stopping the mixer the pressure was kept up for a certain time. Typical ozone consumption values varied between 92 and 97%.

## Peroxide Bleaching:

Peroxide bleaching was carried out in PE-flasks plunged into an agitated water bath. The final bleached pulp was then acidified with diluted sulfuric acid before analytical characterization.

## Acid Washing, Chelation:

In all experiments metal surfaces have been strictly avoided.

Chlorination: 25°C, 2% a.Cl, 60 min, $pH_e=1,6$; chlorine dioxide: 70°C, 2% a.Cl., 60 min, $pH_e=3,3$;

Acidic treatments: a) $H_2SO_4$: 70°C, 30 min, $pH_e=1,9$. b) Citric acid: 70°, 30 min; $pH_e=1,8$. c) Acid peroxide: 70°C; 1% $H_2O_2$, 180 min, $pH_e=1,8$. Final pulp washing with water acidified to final pH.

Chelation: Dosage of EDTA, TIRON [4,5-dihydroxy-1,3-benzenedisulfonic acid] and DTPA 0,2%; 70°C, 60 min, $pH_e=5,1-5,5$.

Alkaline extraction after chlorination: 1,5% NaOH, 60°C, 10 min.

<u>Analytical Characterization:</u>

Kappa number was determined according to Tappi T 236 os-76, brightness and intrinsic viscosity were tested according to SCAN-C 11:75 and SCAN-CM 15:88, alpha cellulose and R 18 according to ZM IV/29/51 and ZM IV/39/67, DCM-extractives according to ZM IV/43/67, ash content according to DIN 54 370, copper number according to ZM IV/8/70, the filterability according to a modified „Treiber"method published in *das Papier, 20; No. 3, 125, (1966)*, carbohydrates by means of HPLC after hydrolysis to the monomers. Molecular weight distribution by GPC after direct solution in LiCl/DMAc with calibration by a set of polystyrene standards. DOC (dissolved organic carbon) was measured by means of an ASTRO UV-reactor, COD according to Austrian standards.
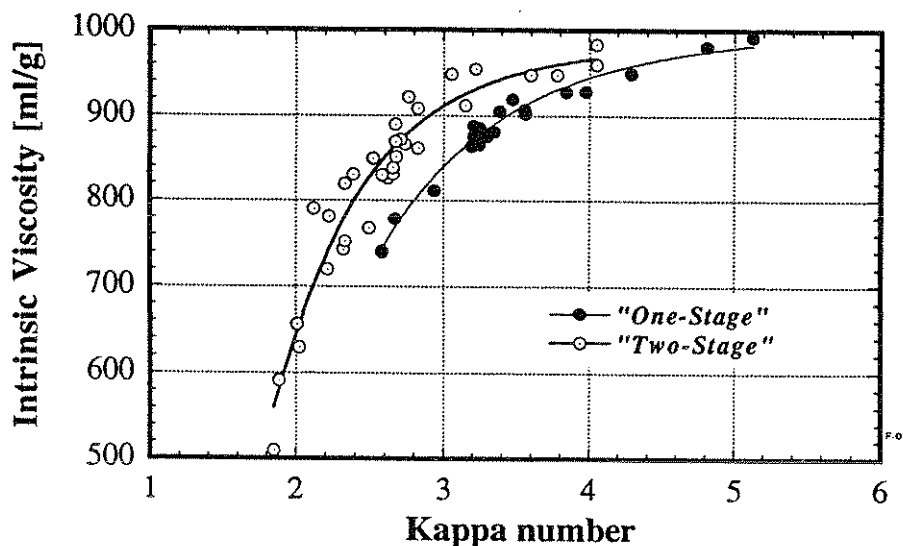
# 3. RESULTS

## 3.1.Oxygen Delignification

The purpose of oxygen delignification of dissolving pulps is to remove most part of the lignin and to level out the variations of the lignin content of the unbleached pulps before entering the ozone stage.

Although brownstock lignin content is already very low delignification proceeds much more efficient compared to paper grade pulps. Unfortunately cellulose degradation is also more severe due to the very low content of hemicellulose, lignin and extractives. In order to elaborate the most appropriate bleaching conditions the ratio between rate of delignification and rate of carbohydrate degradation, which determines the selectivity of oxygen bleaching, has to be considered. The experiments were startet with the concept of a one-stage oxygen delignification treatment. Applying temperatures between 98 and 115°C, alkali charges between 15 and 30 kg/bdt, retention times between 10 and 120 min and an initial oxygen pressure of 0,7 MPa the extent of delignification varied between 45 and 73%. A significant drop in viscosity was observed when increasing the lignin removal rate above 60%. Assuming kappa numbers above 10 for the unbleached pulps, this would mean a rather high ozone demand in the subsequent step. So an alternative concept with a two-stage delignification treatment was investigated. Lab and mill experience clearly indicate a better delignification selectivity of a two-stage oxygen-alkali treatment (2,3,4). The degradation of carbohydrates under oxygen bleaching conditions occurs mainly by random hydrolysis. This oxidative random hydrolysis is highly dependent on both the temperature and the alkali concentration (5). The same high rate of

delignification can be obtained without excessive cellulose degradation if a low alkali charge is applied in each stage. Preliminary experiments showed that a 10-20 min retention time would be enough for the first stage. The reaction time of the second-stage was variied from 30-90 min, with an optimum value around 60 min. In the first stage 50-80% of the total amount of alkali charge (15-50 kg/bdt) was applied. The experiments were carried out at temperature levels between 98 and 130°C with no change from the first to the second stage. Figure 2 shows the results of one- and two-stage oxygen bleaching lab trials of a kappa number 9-, viscosity 1200-eucalyptus-PHK-pulp.

Figure 2:Comparison of the selectivity of one- and two-stage oxygen delignification. Eucalyptus-PHK, kappa number 9, intrinsic viscosity 1200 ml/g.



The results show that - contrary to sulphite pulps - oxygen delignification of PHK-pulps causes viscosity degradation already at rather mild conditions. A rather constant and linear decline of viscosity can be observed as long as kappa number is above 3,5 in case of a one-stage and 2,9 in case of a two-stage oxygen-alkali treatment, which corresponds to an improvement of delignification efficiency from 61 to 68%. Figure 2 clearly reveals the advantage in selectivity of the two-stage concept at an extent of delignification higher than 55%. Most of the two-stage experiments were carried out at reaction conditions in order to achieve kappa number reductions of about 70%, which turned out to be highly reproducible in terms of kappa number and viscosity. If the same total amount of alkali is applied, the extent of delignification can be increased significantly by a two-stage oxygen-alkali treatment (figure 3). Due to a higher and more constant pH-level the kappa number decrease is clearly more pronounced for reaction times above 30 min (figure 4).

Figure 3: Course of kappa number for one- and two-stage oxygen delignification: NaOH-charge and temperature are equal.
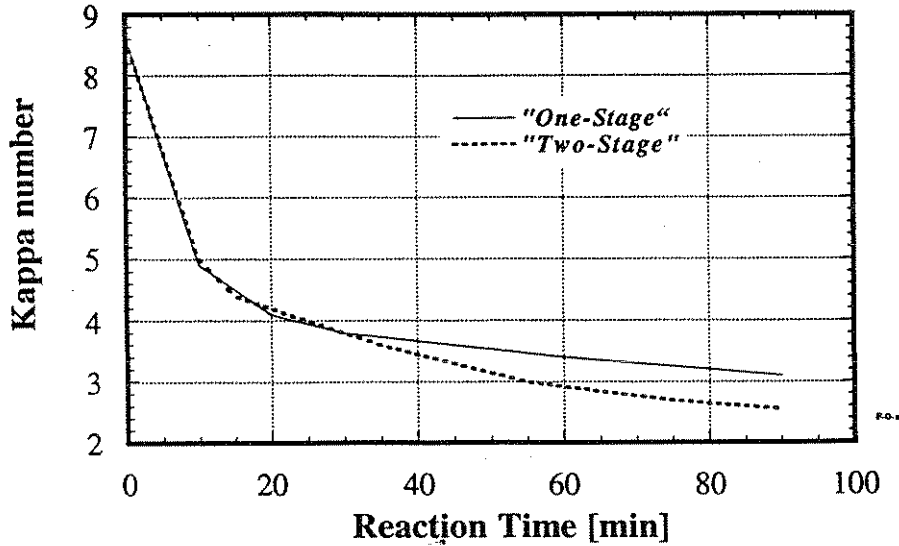


Figure 4: pH-profile during one- and two-stage oxygen delignification. Delignification results correspond to those shown in figure 3.
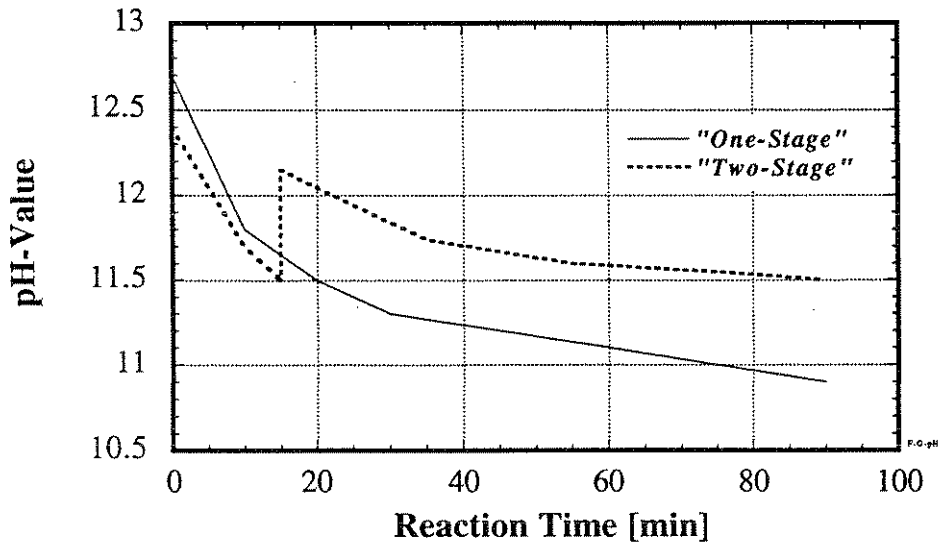


Figure 5 illustrates the relationship between kappa number and brightness for one- and two-stage oxygen bleached pulps. At a given kappa number the brightness of pulps bleached according to the one-stage concept is lower than that of two-stage oxygen-alkali treated pulps. Comparable brightness-kappa number relationships can only be achieved by more drastic conditions. Consequently, the higher brightness gain at lower kappa numbers may be due partly to the higher formation rate of hydrogen peroxide. All the experiments mentioned so far were carried out without

interstage washing. The influence of interstage washing was investigated in a limited set of experiments.

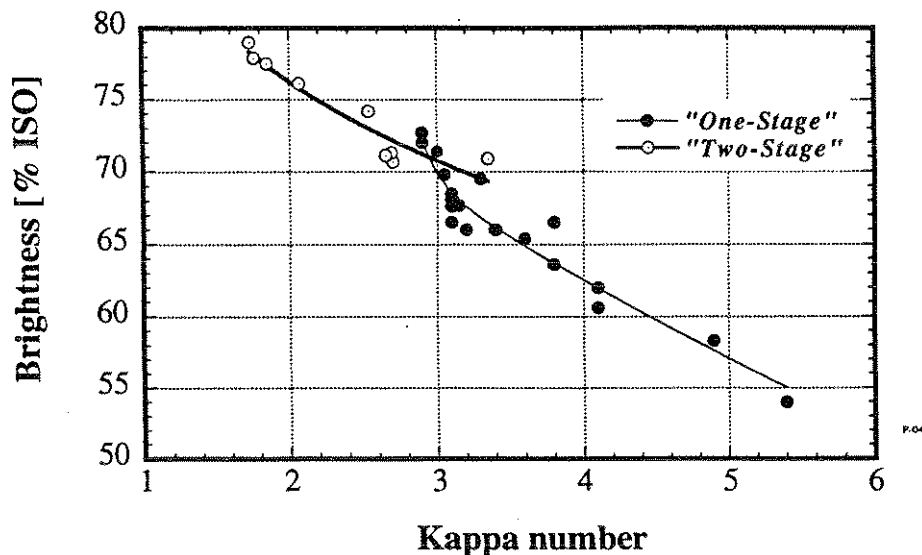Figure 5: Relationship between brightness and kappa number of one- and two-stage oxygen delignification.



Table 2 includes a summary of the results.

Table 2: Comparison of two-stage-oxygen delignifiation with and without interstage washing.

| PARAMETERS | UNIT | Without Washing | With Washing |
|---|---|---|---|
| Temperature | °C | 110 | 110 |
| ΣNaOH-Charge | kg/bdt | 40 | 40 |
| Σreaction time | min | 90 | 90 |
| Kappa-Brownstock | | 8,6 | 8,6 |
| Kappa-OO | | 2,7 | 2,5 |
| Viscosity-Brownstock | ml/g | 1131 | 1131 |
| Viscosity-OO | ml/g | 780 | 790 |

The table indicates that an efficient interstage washing slightly improves both the extent and the selectivity of delignification, which is contradictory to the results recently published by Parsard et al (6). A further advantage of interstage washing is the possibility of reducing the temperature and adding peroxide during the second bleaching stage. Anyhow, for most applications the shown benefits of interstage washing would not justify the high additional investment costs. Based on our results

we can conclude that two-stage oxygen delignification can be recommended as a very efficient and selective prebleaching treatment for PHK-pulps.

## 3.2. Removal of Transition Metals

It is well established that trace levels of transition metals have a profound negative impact on ozone and peroxide bleaching of kraft pulps. The presence of transition metals, particularly Co, Fe, Mn and Cu ions, results in both excessive ozone and hydrogen peroxide consumption by self-decay and in degradation of carbohydrates apparently caused by free radical reactions (7-11). To use ozone and hydrogen peroxide effectively during the subsequent bleaching stages transition metals must be removed or at least deactivated. Not only the bleaching process but also the product *dissolving pulp* itself requires a very low content of transition metals. It was decided to implement a separate (and open) washing stage between oxygen and ozone delignification. Transition metal ions can be removed either by chelating agents such as EDTA, DTPA and HEDTA at pH-levels between 5 and 6 or by acidic pretreatment followed by washing. In order to avoid additional contact with metal surfaces, the influence of different washing treatments was examined by means of an unbleached PHK-sample. The pulp sample is characterized in table 3.

Table 3: Characterization of unbleached eucalyptus/acacia-PHK-sample:

| PARAMETERS | UNIT | VALUE |
|---|---|---|
| Kappa number | | 8,2 |
| Intrinsic viscosity | ml/g | 1243 |
| Iron | ppm | 14,5 |
| Manganese | ppm | 7,2 |
| Copper | ppm | 0,4 |

In the first set of experiments the influence of both acids such as citric acid and sulfuric acid and of oxidants in an acidic environment such a acid peroxide, chlorine, chlorine dioxide and ozone has been investigated (reaction conditions are summarized in the experimental section). The concentration of copper ions is far below the level considered to be catalytically active (1-10 ppm, 12). Therefore the copper content was not analyzed after the washing treatments. The manganese ions can be removed quantitatively (<0,3 ppm) by any of the applied treatment. However, the removal of iron is not very efficient as can be seen from figure 6. Despite the very low pH (<1,8), citric acid and acid peroxide show a poor iron removal efficiency (34 and 37%). It is

interesting to note that treatments with ozone, chlorine, chlorine dioxide and sulfuric acid were quite comparable in their iron removal efficiency (55-59%).

Figure 6:   Iron removal efficiency by acidic and oxidative acidic treatments
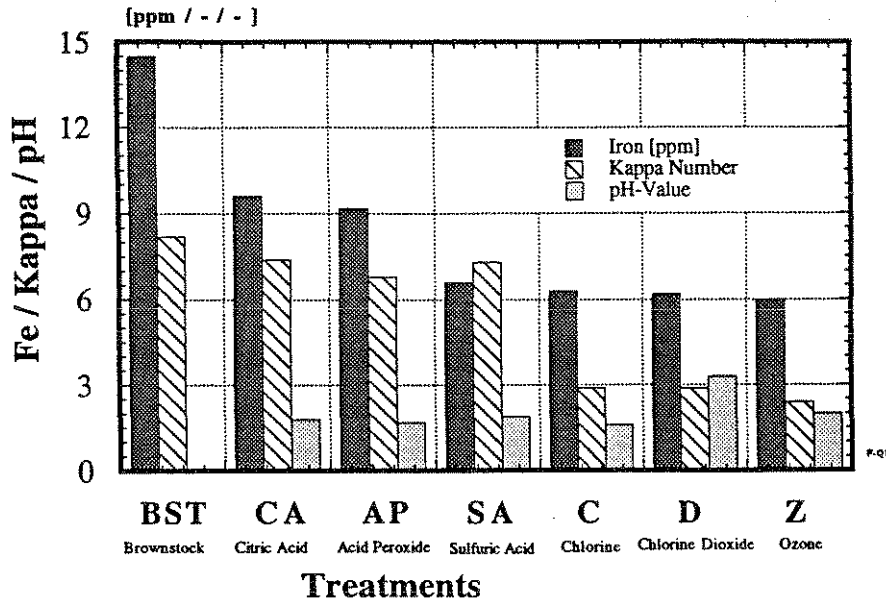


The simultaneous kappa number reduction by means of the oxidative treatments has obviously no benefit for the iron removal. The results of pretreatments with the complexing agents EDTA, DTPA and TIRON concerning the changes in iron content and kappa number are illustrated in figure 7.

Figure 7:   Iron removal efficiency by treatment with chelating agents
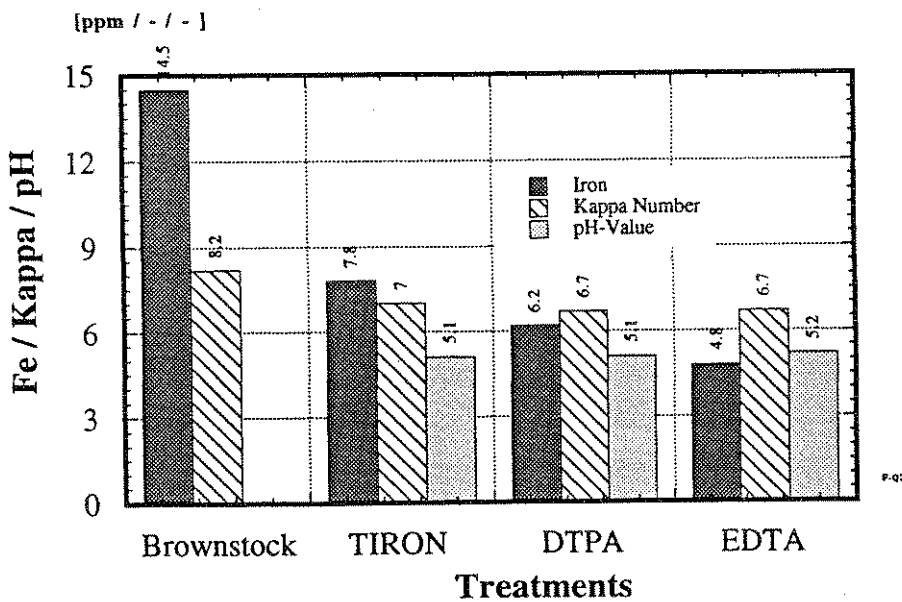


The EDTA-treatment turned out to be most effective for iron removal (68%). Despite a very high pK ($pK_{Tiron}$ = 47,2; $pK_{EDTA}$ = 25,1), TIRON was least efficient of all

tested chelating agents. Increasing the ETDA-dosage from 2 to 20 kg/bdt showed no noticeable improvement (figure 8).

Figure 8:   Influence of EDTA-dosage on iron removal rate.
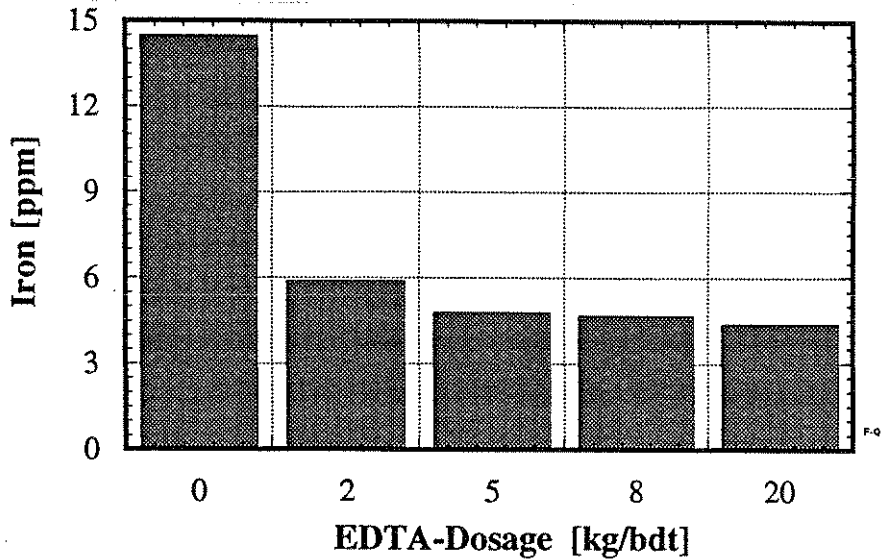


Sequential treatment of the pulp with either chlorine and alkali extraction or ozone and EDTA improve iron removal compared to either treatment alone but the effect of these treatments is not additive when applied in sequence (figure 9).

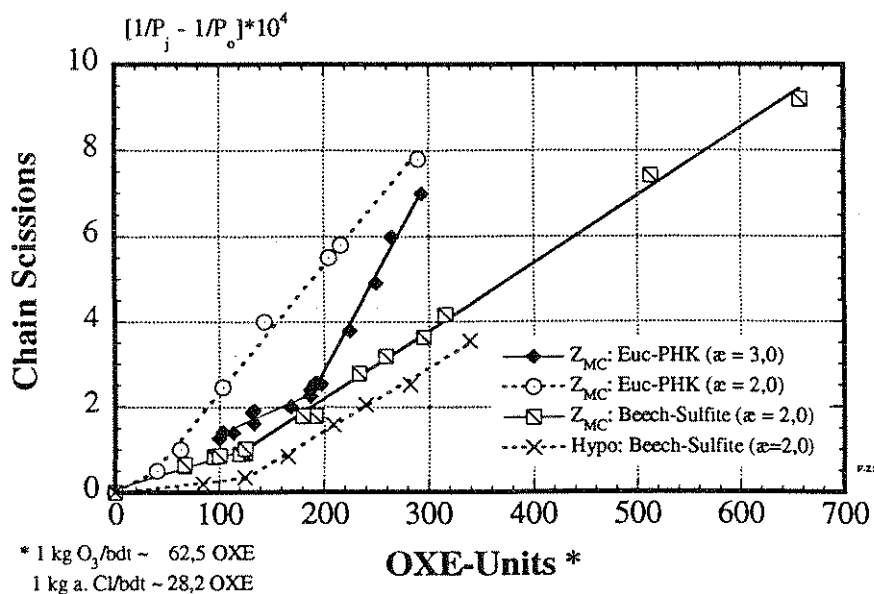Figure 9:  Influence of sequential treatments on iron removal rate.
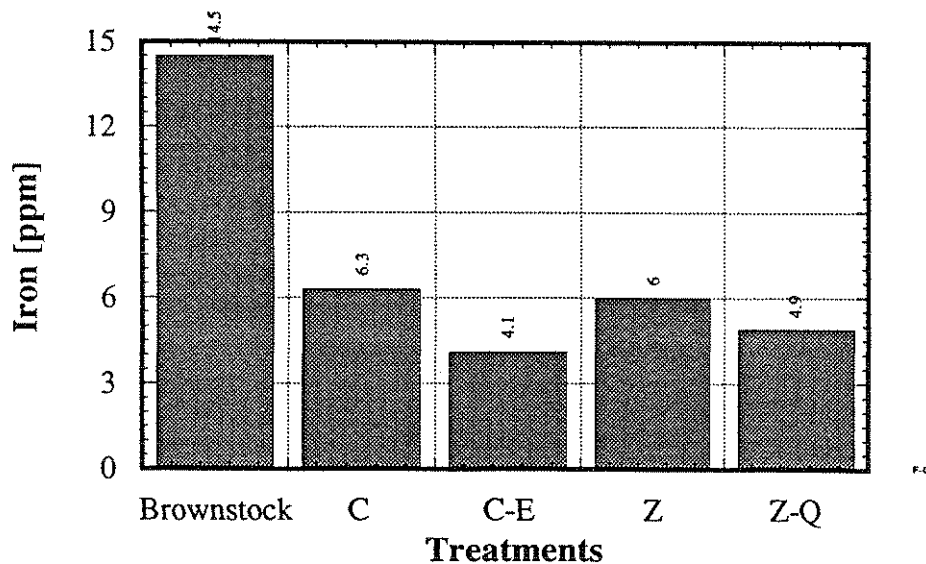


Iron in pulps from other sources than wood (soil, digester) is even more difficult to remove by any of the treatments described above. In order to reach the low concentration of iron and other transition metals required for dissolving grades any contamination must be avoided.

Work done by Colodette in connection with peroxide bleaching of mechanical pulp revealed that strongly attached iron may be attributed to the conversion of the colloidal amorphous iron (III) to crystalline iron (III) oxide which is insoluble to acidic treatment and not available for chelation (13). Opposite to our experiences, Colodette assumes that the iron originally present in the wood is strongly attached. This may be due to the fact that his experiments were carried out with wood meal.

## 3.3. Final Bleaching and Pulp Characterization

Final bleaching of oxygen preblached eucalyptus-PHK-pulps is carried out with a sequential treatment of ozone and peroxide which corresponds to the TCF-bleaching sequence developed for the Lenzing beech acid bisulfite dissolving pulp (1,14). The amount of ozone charged depends on the lignin content of the oxygen prebleached pulp, the brightness and viscosity target. As it is obvious that brightness and viscosity are interrelated it is necessary to determine a *first priority* for one of these two parameters. The linear relationship between chain scissions and ozone consumption reported by Godsay is a good indication of the possibility to use ozone to adjust viscosity in a controled way (15). In numerous experiments with beech sulphite dissolving pulps we found out that the action of ozone to viscosity is very similar to that of hypochlorite (16). Figure 10 reveals a clear relationship between the amount of both ozone and hypochlorit consumed - indicated as OXE-units - and the chain scissions.

Figure 10:  Carbohydrate degradation, indicated as number of chain scissions, in dependence on ozone and active chlorine consumption.



$[1/P_j - 1/P_o]*10^4$

Chain Scissions

— ◆ — $Z_{MC}$: Euc-PHK ($x$ = 3,0)
- - ○ - - $Z_{MC}$: Euc-PHK ($x$ = 2,0)
— ◻ — $Z_{MC}$: Beech-Sulfite ($x$ = 2,0)
- - ✕ - - Hypo: Beech-Sulfite ($x$=2,0)

* 1 kg $O_3$/bdt ~ 62,5 OXE
1 kg a. Cl/bdt ~ 28,2 OXE

**OXE-Units ***

This function should be reasonably proportional to the number of bonds broken in the carbohydrate molecules. The figure shows the subdivision into two periods, the initial one consuming ozone (or hypochlorite) with a very low effect on carbohydrate degradation, the following period causing a degradation proportional to the ozone (hypochlorite) consumption. The intercept with the abscissa and the slope of the curve are characteristic parameters for each pulp. They are dependent on the kappa number, the hemicellulose content, the carbonyl content and the accessibility of ordered regions. The experimental results show that, as the amount of residual lignin (before Z-stage) increases, the intercept increases and the slope remains constant or decreases. This suggests that the residual lignin of the pulp contains a *highly reactive* structure which reacts quickly with ozone, and a *less reactive* structure which reacts at a slower rate. The fact that the brightness of the pulp continues to increase substantially during the period in which the graph has the higher slope indicates that lignin is still present during that period, and thus confirms the ideas outlined above (17). With an increasing hemicellulose content of the pulp the slope decreases, whereas the intercept remains constant. The effect of ozone on the degradation of carbohydrates is much more pronounced using PHK-pulps as a substrate (figure 10). This is mainly due to the much higher alpha-cellulose content compared to the beech sulfite dissolving pulps (96% versus 91%). The results outlined in figure 10 demonstrate that ozone is suitable for adjusting viscosity provided that kappa number and viscosity of the oxygen prebleached pulp are within certain limits. Ozone is very effective in reducing the kappa number to very low levels which is an important issue for dissolving pulps (figure 11). As expected the course of brightness and kappa number are symmetrically as can be seen from figure 11.

Figure 11:   Course of kappa number and brightness versus ozone consumption.
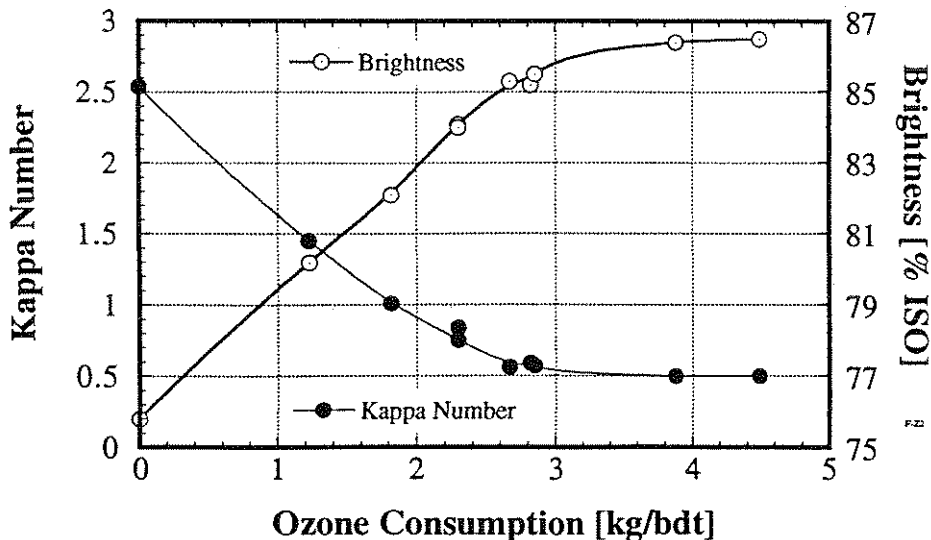
It is rather surprising that the influence of ozone is not very pronounced on the alpha-cellulose content (figure 12). The alpha-cellulose content remains nearly constant until an ozone consumption of 3 kg/bdt is reached. A further increase of ozone consumption induces a reduction of the alpha-cellulose content which is mainly due to the drop in viscosity.

Figure 12: Alpha-cellulose content versus ozone consumption:
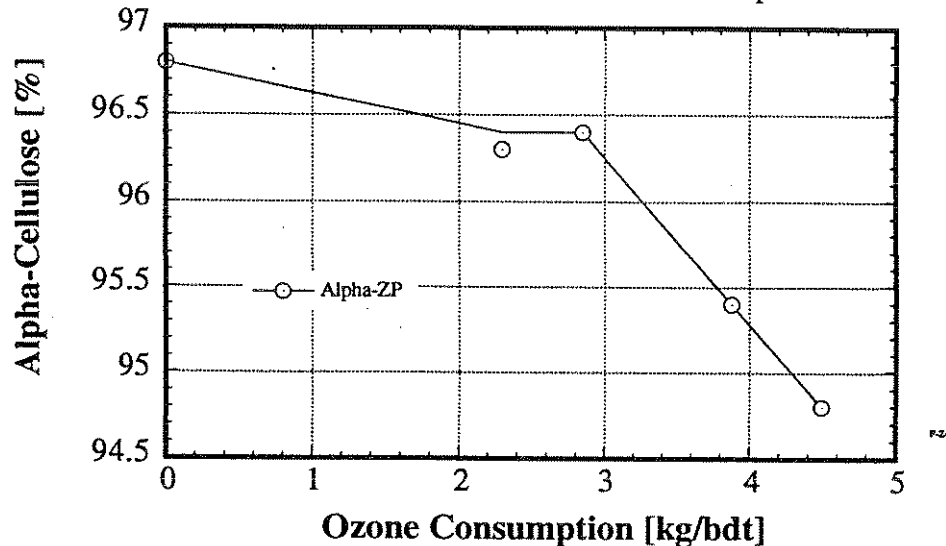


The ozone stage is followed by an alkaline peroxide stage. The purpose of this final bleaching stage is to adjust the brightness target. The reaction conditions of this peroxide stage are rather moderate because of the high incoming brightness and the activation potential of the preceding ozone stage. For that reason the viscosity loss can be kept very low.

The course of the total TCF-bleaching sequence in terms of viscosity-brightness relationship is illustrated in figure 13.

Figure 13: Course of viscosity and brightness during OZP-bleaching. Effect of different degrees of delignification after oxygen bleaching on overall selectivity.
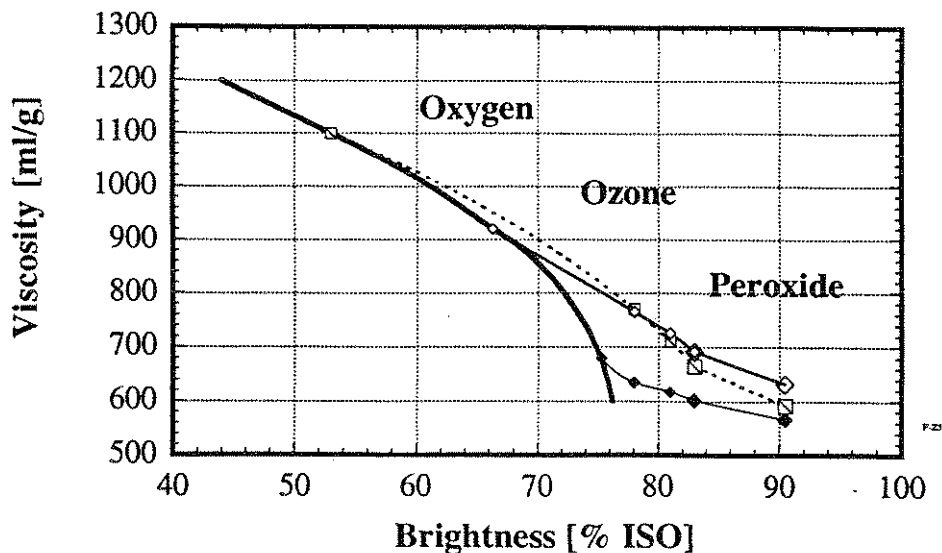
It is shown that the final viscosity at a given brightness level is highly dependent on the properties of the oxygen prebleached pulp. This figure clearly indicates that for optimum overall selectivity one has to find out carefully the optimum conditions in the oxygen delignification step.

The totally TCF-bleached eucalyptus-PHK pulp meets all quality requirements which are necessary for a dissolving pulp used for the production of high quality rayon staple and rayon filament. The lab-TCF-bleached pulp samples exceed the quality of conventionally bleached market pulps in terms of purity, *viscose-reactivity* and homogeneous molecular weight distribution. The most important quality parameters are compared in table 4.

Table 4: Characterization of conventionally bleached market pulps in comparison with lab-TCF-bleached pulp samples

| PARAMETERS | UNIT | Lab Sample | Market | Pulps |
|---|---|---|---|---|
| Wood | | eucalyptus urogr | eucalyptus | eucalyptus |
| Cooking Process | | PHK | PHK | SULFITE |
| Bleaching Process | | OZP | conventional | conventional |
| Brightness | % ISO | 90,5 | 90,6 | 92,5 |
| Intrinsic Viscosity | ml/g | 575 | 602 | 560 |
| Alpha-Cellulose | % | 96,3 | 95,5 | 92,6 |
| R-18 | % | 97,5 | 96,1 | 95,8 |
| Copper number | % | 0,68 | 0,76 | 1,24 |
| DCM-extract | % | 0,10 | 0,05 | 0,09 |
| Ash content | % | 0,04 | 0,07 | 0,07 |
| GPC: MW-PS | $*10^7$ | 2,94 | 2,68 | 2,86 |
| MN-PS | $*10^7$ | 0,33 | 0,29 | 0,19 |
| PDI | | 8,9 | 9,3 | 15,5 |
| Treiber-Reactivity | g | 423 | 235 | 415 |

Alkali resistance and *viscose-reactivity* according to Teiber of the TCF-bleached pulp sample are superior to that of the market pulps. Table 4 shows the polydispersity ratios obtained by GPC measurement of LiCl/DMAc solutions. The ozone bleached pulp sample shows even a lower polydispersity ratio than the hypochlorite treated samples which cannot be attributed to ozone bleaching but to more severe prehydrolysis conditions applied. Figure 14 illustrates the narrow molecular weight distribution of the lab TCF-bleached pulp sample.

Figure 14: Molecular weight distribution of lab OZP-bleached pulp compared with conventionally bleached PHK- and sulfite market pulps.
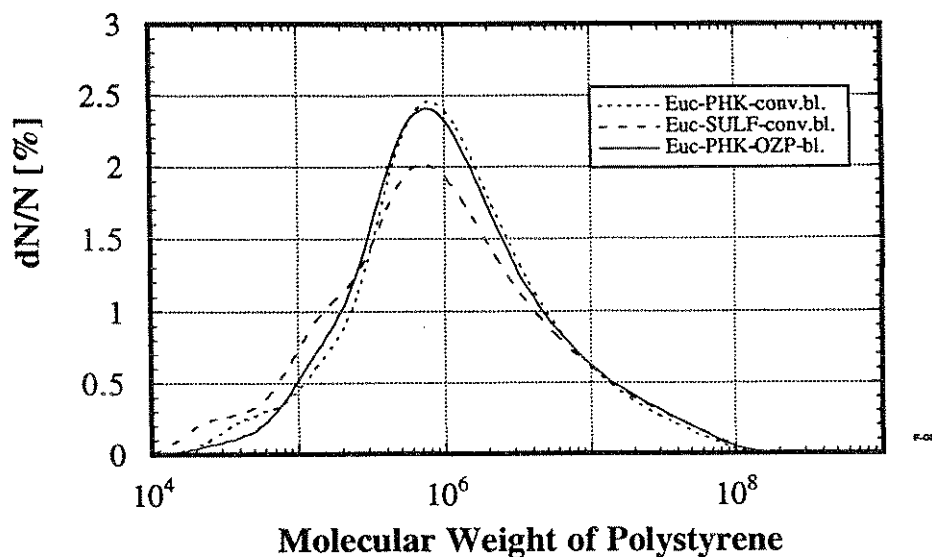


# 3.4. Effect of Organic Carry-over on the Final Bleaching Results

The final target of TCF-bleaching will be the closed mill system. In such a case filtrates have to be recycled and their loads will influence the efficiency of different bleaching stages, especially the ozone stage. Due to the high reactivity of ozone, any dissolved organic material entering the ozone stage is a potential reaction partner of ozone. It was the objective of our investigations to evaluate the influence of organic carry-over of different origin on ozone and final peroxide bleaching of a PHK pulp. In the laboratory tests filtrates from oxygen, ozone and peroxide bleaching were added with different loads (up to 14,4 kg COD/bdt) to an oxygen prebleached acacia-PHK pulp (kappa number 3,1; intrinsic viscosity 934 ml/g). In the next step the pulp was acidified and consistency was adjusted to 9 %. Medium consistency ozone bleaching was carried out at two different ozone consumption levels, 2,0 and 3,7 kg/bdt, respectively. The ozone bleached pulp was thoroughly washed and subjected to standard alkaline peroxide bleaching. The results are illustrated in terms of viscosity and brightness of the final bleached pulps in figure 15. As expected the dissolved organic material of the previous oxygen stage has a great impact on the final brightness. But, as indicated in figure 16, the selectivity of both ozone and peroxide bleaching is not affected by organic carry-over from oxygen and ozone stage. At an ozone consumption level of 3,7 kg/bdt a load of 14,4 kg COD/bdt leads to a brightness reduction from 89,7 to 85,1% ISO.

Figure 15: Viscosity-brightness relation of final bleached pulps. Influence of carry-overs of different origin on final pulp quality.
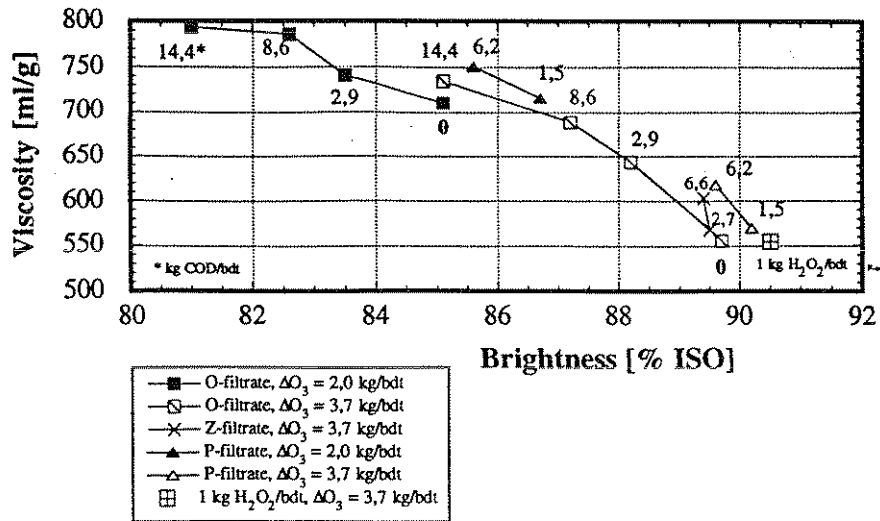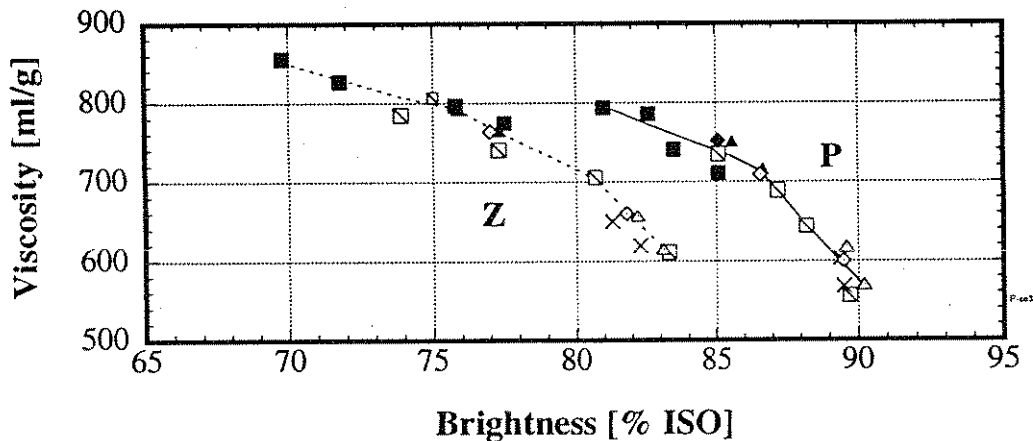


Figure 16: Selectivity of ozone and peroxide bleached pulps. Influence of carry-overs on selectivity.



The net influence on brightness is equal at the lower ozone consumption level. In agreement with the findings of Szopinski and Stromberg there is no significant effect of filtrate recirculated from the ozone stage itself on the ozone consumption and on the final quality of the PHK pulp (18). Organic carry-over from the P-stage even improves brightness and viscosity at the lower and to some extent also at the higher ozone consumption level. This advantage in selectivity compared to the well washed pulp can only be recognized after peroxide bleaching. Kappa number reduction and brightness are still slightly lower after ozone bleaching. Similar experiences were reported by Szopinski and Stromberg in case of the filtrate from the Ep-stage (18). Although reycling of the P-filtrate to the ozone stage improves final pulp quality, an increase in organic load (from 1,5 to 6,2 kg COD/bdt) leads to a brightness reduction

without altering selectivity. Therefore it can be concluded that the effect on selectivity is not due to the dissolved organic matter but probably to the residual peroxide which was present in a rather constant concentration of approximately 1 kg/bdt. The effect of hydrogen peroxide on ozone bleaching and on the final pulp quality was investigated in a further lab experiment where 1 kg $H_2O_2$/bdt was added to the well washed pulp before ozone bleaching. The results fully confirm the assumption that a small amount of hydrogen peroxide during ozonization improves the selectivity of Z-P-bleaching (figure 15). One reason for that - as has been pointet out by Gratzl - could be the reaction between hydrogen peroxide with hydroxyl radicals to form less harmful hydroperoxyl radicals (19). The impact of filtrate recycle on ozone consumption is thus primarily dependent on the organic carry-over of the oxygen delignification stage. The amount of extra ozone consumption per kg COD from oxygen bleaching for a given kappa number and brightness target after ozone and peroxide bleaching increases with the increasing extent of delignification in the Z-stage (figure 17). For a final brightness target of 90% ISO, an extra ozone cosumption of 0,20-0,22 kg per kg COD has to be considered. The effect of COD-load from the P-stage on extra ozone consumption is - disregarding the effect of residual hydrogen peroxide - indeed very small.

Figure 17: Specific extra ozone consumption per kg COD versus kappa number after the Z-stage.
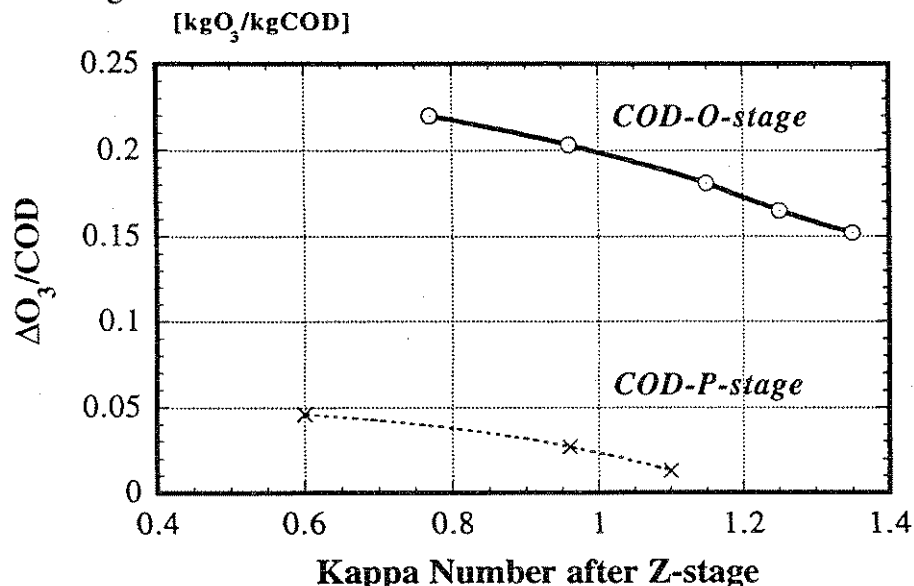


Recirculation of filtrates in a A-Z-P-sequence has been simulated by a computer model in order to calculate the accumulation of virgin and total organic material before the ozone stage. Two different cases were simulated representing two different levels of fresh water usage. For the *open* system, represented in figure 18, a specific

amount of fresh water of 19,3 $m^3$/bdt was considered. The water consumption in the case of the *closed* bleach plant model was 8,8 $m^3$/bdt (figure 19).

Figure 18: Simplified flow scheme of *open* bleach plant model:
E-factor for all filters 2,2; vat consistency 1,2%; discharge consistency 12%; dilution factor for O- and P-filters 1,5, for A-filter 2,0.
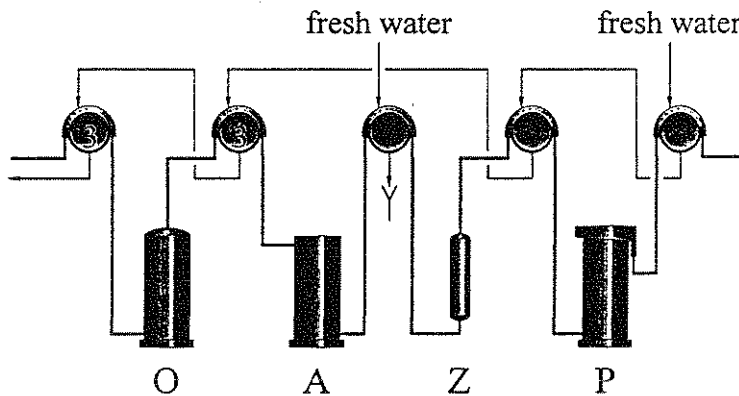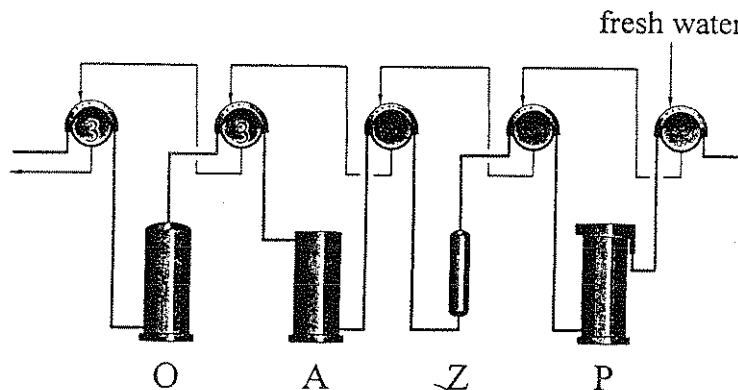
## Open Bleach Plant Model



Figure 19: Simplified flow scheme of *closed* bleach plant model:
E-factor for all filters 2,2; vat consistency 1,2%; discharge consistency 12%; dilution factor for O- and P-filters 1,5, for A-filter 2,0.

## Closed Bleach Plant Model



The build up of organic material before Z-stage is illustrated in figure 20 (see also reference 20). The total COD-load increases considerably when reducing the specific amount of fresh water . At the same time the COD-load from oxygen bleaching (virgin organic material) increases at a much lower rate. The effect of the simultaneous addition of carry-overs of different origin according to the two calculated cases (*open* and *closed*) on the overall bleaching efficiency was investigated in a few lab experiments (figure 21). Figure 21 shows that the influence

of the organic carry-overs of the *open* system is almost negligible. Closing the water-cycle has a clear impact on final brightness (-3% ISO), but almost exclusively due to the COD-load from oxygen bleaching.

Figure 20: Build up of total COD and COD from oxygen delignification before Z-stage for different amounts of fresh water addition.
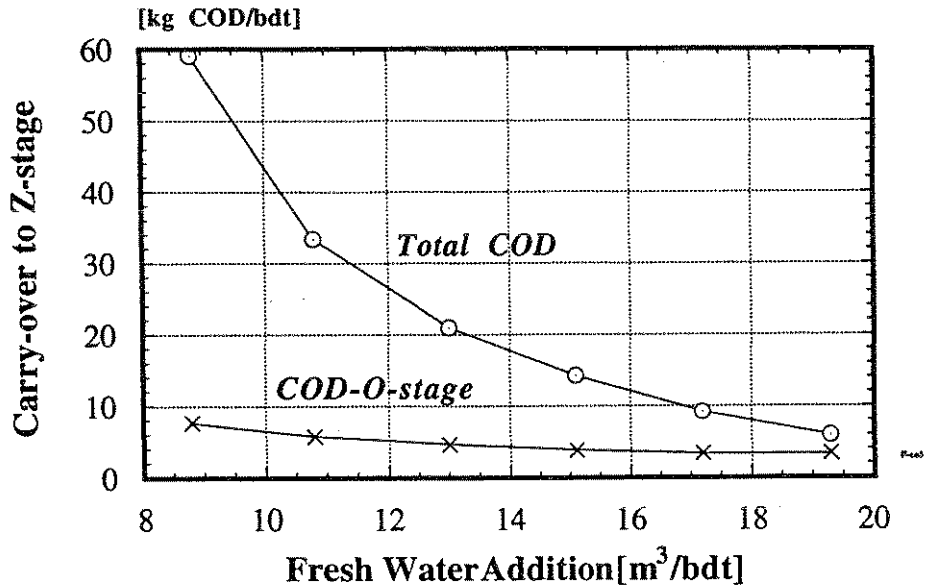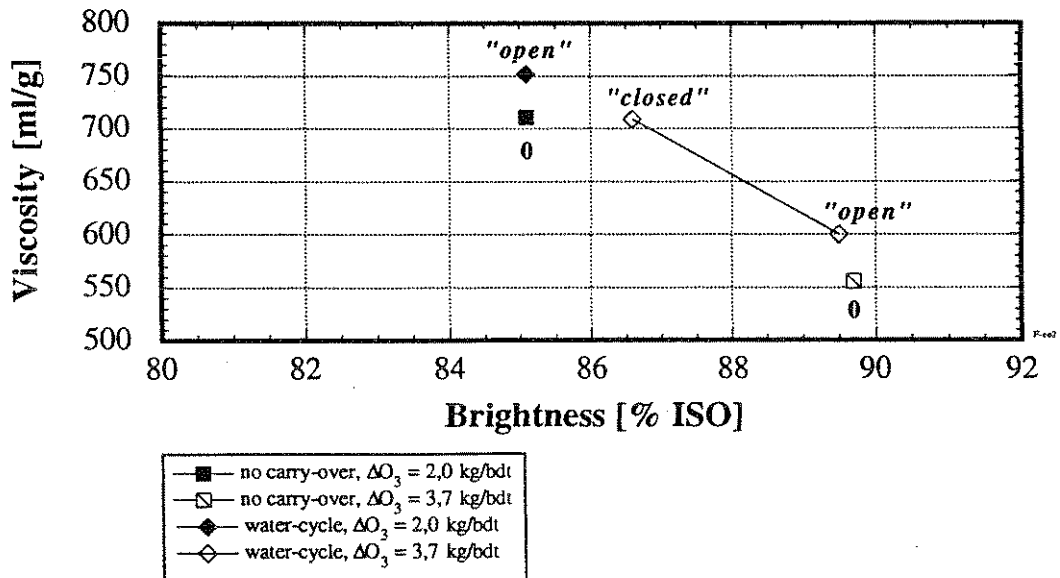
**[kg COD/bdt]**

Figure 21: Influence of *open* and *closed* bleach plant on final product quality.

For a given brightness target ozone consumption increases with decreasing amounts of fresh water usage according to figure 22. As the extra ozone is consumed predominately by the carry-over coming from oxygen bleaching a very efficient washing after O-stage is a prerequisite for a *closed* water cycle in the bleach plant.

Based on the results of this lab study it can be assumed that it should be possible to close the bleach plant, considering a certain increase in ozone consumption.

Figure 22: Ozone consumption for a final brightness of 90% ISO in dependence on fresh water adition.
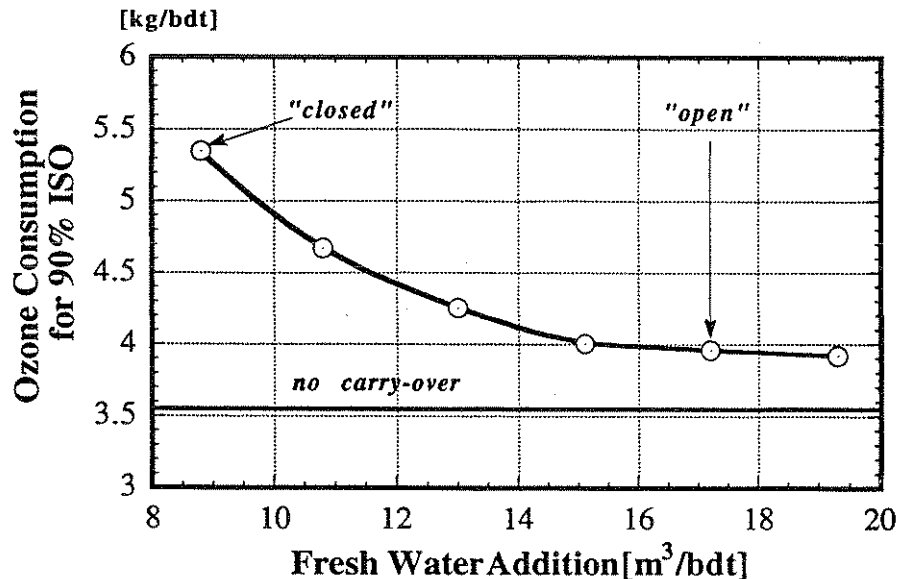
This conclusion is, however, valid only for the accumulation of dissolved organic material. The build up of transition metals as a consequence of closing the water cycle could be detrimental to ozone and peroxide bleaching. The influence of transition metals on overall bleaching efficiency and selectivity will be the subject of further investigations.

# 4. CONCLUSIONS

The study confirmed that eucalyptus-PHK dissolving pulps with alpha-cellulose contents higher than 96%, low polydispersity ratios, brightness above 90% ISO and high viscose reactivity can be produced by TCF-bleaching according to an OZP-sequence.

Selectivity and efficiency of oxygen delignification can be improved by using a two-stage concept without interstage washing. Compared to a conventional one-stage system delignification can be extended which in return reduces the specific ozone charge.

Conventional chlorine and hypochlorite bleaching has no advantage over treatments with acids or chelating agents concerning the efficiency of iron and mangenese removal. More than 60% of the iron present in the unbleached pulp can be removed by means of an EDTA treatment. The removal efficiency can further be improved by sequential treatments with acids and chelating agents.

Ozone bleaching is suitable for both adjusting viscosity and delignifying to low kappa number. The alpha cellulose content is almost not effected by ozone bleaching which is demonstrated by a narrow and uniform molecular weight distribution. TCF-bleached dissolving pulp meets all quality requirements which are necessary for the production of high quality rayon staple and rayon filament.

The simulation of a closed water-cycle shows that the impact on final brightness is mainly due to the build up of organic carry-over from oxygen delignification which can be compensated by additional ozone consumption. It is very important to note that the selectivity of ozone and peroxide bleaching is not effected by organic carry-over from oxygen and ozone stage. Selectivity is clearly improved by adding hydrogen peroxide to ozone bleaching. As far as organic carry-over is concerned a totally closed bleach plant seems to be possible provided that washing after O-stage is very efficient.

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